

Bretherick's  
Handbook of  
**Reactive  
Chemical  
Hazards**

Sixth Edition

Volume 2

AN INDEXED GUIDE TO PUBLISHED DATA

---

Bretherick's  
Handbook of  
**Reactive  
Chemical  
Hazards**

Sixth Edition — Volume 2

---

*Edited by*  
**P G Urben**  
**Akzo-Nobel**

*Compiler*  
**M J Pitt**  
**Department of Chemical Engineering**  
**University of Leeds**

**B**UTTERWORTH  
**H**EINEMANN

OXFORD AUCKLAND BOSTON JOHANNESBURG MELBOURNE NEW DELHI

Butterworth-Heinemann Ltd  
Linacre House, Jordan Hill, Oxford OX2 8DP

 A member of the Reed Elsevier plc group

First published 1975  
Second edition 1979  
Reprinted 1979, 1981, 1984  
Third edition 1985  
Reprinted 1987, 1989  
Fourth edition 1990  
Fifth edition 1995  
Sixth edition 1999  
© Butterworth-Heinemann 1999

All rights reserved. No part of this publication may be reproduced in any material form (including photocopying or storing in any medium by electronic means and whether or not transiently or incidentally to some other use of this publication) without the written permission of the copyright holder except in accordance with the provisions of the Copyright, Designs and Patents Act 1988 or under the terms of a licence issued by the Copyright Licensing Agency Ltd, 90 Tottenham Court Road, London, England W1P 9HE. Applications for the copyright owners written permission to reproduce any part of this publication should be addressed to the Publishers.

**British Library Cataloguing in Publication Data**

A record for this title is available from the British Library

**Library of Congress Cataloguing in Publication Data**

A record for this title is available from the Library of Congress

ISBN 0 7506 3605 X

Typeset by Laser Words, Madras, India  
Printed and bound in Great Britain by Bath Press

# Introduction

**THIS SHOULD BE READ THROUGH CAREFULLY  
TO GAIN FULL BENEFIT FROM WHAT FOLLOWS**

## **Aims of the Handbook**

This compilation has been prepared and revised to give access to a wide and up-to-date selection of documented information to research students, practising chemists, safety officers and others concerned with the safe handling and use of reactive chemicals. This will allow ready assessment of the likely potential for reaction hazards which may be associated with an existing or proposed chemical compound or reaction system.

A secondary, longer-term purpose is to present the information in away which will, as far as possible, bring out the causes of, and interrelationships between, apparently disconnected facts and incidents. This is designed to encourage an increased awareness of potential chemical reactivity hazards in school, college and university teaching laboratories, and to help to dispel the relative ignorance of such matters which is still in evidence in this important area of safety training during the formative years of technical education.

Others involved in a more general way with the storage, handling, packing, transport and distribution of chemicals, or emergencies related thereto, are likely to find information of relevance to their activities.

## **Scope and source coverage**

This Handbook includes all information which had become available to the editor by January 1999 on the reactivity hazards of individual elements or compounds, either alone or in combination. Appropriate source references are included to give access to more expansive information than that compressed into the necessarily abbreviated text entries.

A wide variety of possible sources of published information has been scanned to ensure maximum coverage. Primary sources have largely been restricted to journals known to favour or specialise in publication of safety matters, and the textbook series specialising in synthetic and preparative procedures.

Secondary sources have been a fairly wide variety of both specialised and general textbooks and encyclopaedic collections (notably those of Mellor, Sidgwick, Pascal and Bailar in the inorganic area, Houben-Weyl in the organic and

organometallic areas, and Kirk-Othmer in the industrial area). Section 50 of *Chemical Abstracts*, the CAS selection *Chemical Hazards, Health, & Safety*, the *Universities' Safety Association Safety News*, the CIA CISHC *Chemical Safety Summary*, (publication of which ceased in 1986 after 56 years), and the IChE *Loss Prevention Bulletin* have been rich sources, together with the more recent RSC *Laboratory Hazards Bulletin* and *Chemical Hazards in Industry*. Additionally, various safety manuals, compilations, summaries, data sheets and case histories have been used, and fuller details of all the sources used are set out in Appendix 1. References in the text to textbooks are characterised by absence of the author's initials after the surname.

More recently, some reports have been picked from the Internet, when two of the three following conditions obtained: the editor finds the report credible; it represents a hazard not already present in the handbook; or the source is authoritative. Information on toxic hazards has been specifically excluded because it is available elsewhere in many well-ordered and readily usable forms.

However, it should be remembered that many of the compounds included in this Handbook show high reactivity of one sort or another toward other materials, so may in general terms be expected to be reactive even in brief contact with animal organisms or tissue (including yours), with possible toxic effects, either acute or chronic. Also, no attempt has been made to include details of all flammable or combustible materials capable of burning explosively when mixed with air and ignited, nor of any incidents related to this most frequent cause of accidents, such information again being available elsewhere.

However, to focus attention on the potential hazards always associated with the use of flammable and especially highly flammable substances, some 560 gases and liquids with flash points below 25°C and/or autoignition temperature below 225°C have been included in the text, their names prefixed with a dagger. The numerical values of the fire hazard-related properties of flashpoint, autoignition temperature and explosive (flammability) limits in air where known are given in the Five Data Table. Those elements or compounds which ignite on exposure to air are included in the text, but not in the Table.

## General arrangement

The information presented on reactive hazards is of two main types, specific or general, and these types of information have been arranged differently in their respective separate volumes 1 and 2.

FOR CROSS REFERENCES IN CAPITALS, PAGE NUMBERS REFER TO VOLUME 2.

Specific information on instability of individual chemical compounds, and on hazardous interactions of elements and/or compounds, is contained in the main formula-based Volume 1 of the Handbook. For an example of an unstable compound,

*see* Ethyl perchlorate

For an example of a hazardous interaction between 2 compounds,

*see* Nitric acid: Acetone

or 2 separate examples involving the same compound,

*see* Nitric acid: Acetone, or: Ethanol  
and one involving 3 compounds,

*see* Hydrogen peroxide: Nitric acid, Thiourea

General information relating to classes or groups of elements or compounds possessing similar structural or hazardous characteristics is contained in the smaller alphabetically based Volume 2.

*See* ACYL NITRATES

PYROPHORIC METALS

References in the text to these general classes or groups of materials is always in small capitals to differentiate them from references to specific chemicals, the names of which are given in normal roman typeface.

Some individual materials of variable composition (substances) and materials which cannot conveniently be formulated and placed in Volume 1 are also included in this general section.

*See* BLEACHING POWDER, CELLULOSE NITRATE

Both theoretical and practical hazard topics, some indirectly related to the main theme of this book, are also included.

*See* DISPOSAL, EXPLOSIBILITY

GAS CYLINDERS, OXYGEN ENRICHMENT

Several topics which bring together incidents involving a common physical cause or effect but different types of chemicals are now included in Volume 2.

*See* CATALYTIC IMPURITY INCIDENTS

GAS EVOLUTION INCIDENTS

## **Specific chemical entries (Volume 1)**

A single unstable compound of known composition is placed in the main first volume and is located on the basis of its empirical molecular formula expressed in the Hill system used by *Chemical Abstracts* (C and H if present, then all other element symbols alphabetically). The use of this indexing basis permits a compound to be located if its structure can be drawn, irrespective of whether a valid name is known for it. A representation of the structure of each compound is given on the third bold title line while the name of the compound appears as the first bold title line. References to the information source are given, followed by a statement of the observed hazard, with any relevant explanation. Cross-reference to similar compounds, often in a group entry, completes the entry. *See* Trifluoroacetyl nitrite.

Where two or more elements or compounds are involved in a reactive hazard, and an intermediate or product of reaction is identifiable as being responsible for the hazard, both reacting substances are normally cross-referred to the identified product. The well-known reaction of ammonia and iodine to give explosive nitrogen triiodide-ammonia is an example of this type. The two entries

Ammonia: Halogens

Iodine: Ammonia

are referred back to the main entry under the identified material

Nitrogen triiodide-ammonia

No attempt has been made, however, to list all combinations of reactants which can lead to the formation of a particular main entry compound.

In a multi-reactant system where no identification of an unstable product was possible, one of the reactants had to be selected as primary reactant to prepare and index the main entry, with the other material(s) as secondary reactant(s). No strictly logical basis of choice for this is obvious.

However, it emerged during the compilation phase that most two component reaction hazard systems of this type involve a fairly obvious oxidant material as one of the reactants. Where this situation was recognised, the oxidant has normally been selected as primary (indexing) reactant, with the other as secondary reactant, following the colon.

*See* Potassium permanganate: Acetic acid, etc.

In the markedly fewer cases where an obvious reductant has been involved as one reactant, that was normally selected as primary reactant.

*See* Lithium tetrahydroaluminate: 3,5-Dibromocyclopentene

In the relatively few cases where neither (or none) of the reactants can be recognised as an oxidant or reductant, the choice was made which appeared to give the more informative main entry text.

*See* Chloroform: Acetone, etc.

Where some hazard has been noted during the preparation of a specific compound, but without it being possible to identify a specific cause, an entry for that compound states 'Preparative hazard', and back-refers to the reactants involved in the preparation.

*See* Sulfur dioxide

Occasionally, departures from these considerations have been made where such action appeared advantageous in bringing out a relationship between formally unrelated compounds or hazards. In all multi-component cases, however, the secondary reactants (except air and water) appear as formula entries back-referred to the main entry text, so that the latter is accessible from either primary or secondary reactants.

*See* Dimethyl sulfoxide: Acyl halides (main entry)

Acetyl chloride: Dimethyl sulfoxide (back reference)

## Grouping of Reactants

There are advantages to be gained in grouping together elements or compounds showing similar structure or reactivity, because this tends to bring out the relationships between structure and activity more clearly than separate treatment. This course has been adopted widely for primary reactants (see next heading), and for secondary reactants where one primary reactant has been involved separately with a large number of secondary materials. Where possible, the latter have been collected together under a suitable general group title indicative of the composition or characteristics of those materials.

*See* Chlorine: Hydrocarbons

Hydrogen peroxide: Metals, Metal oxides, Metal salts

Hydrogen sulfide: Oxidants

This arrangement means, however, that some practice will be necessary on the user's part in deciding into what group an individual secondary reactant falls before the longer-term advantages of the groupings become apparent. The formal group titles listed in Volume 2, Appendix 3, and classified in Appendix 4, will be of use in this connection. However, it should be noted that sometimes informal group titles are used which do not appear in these Appendices.

## **General group entries (Volume 2)**

In some cases literature references relating to well-defined groups of hazardous compounds or to hazard topics have been found, and these are given, with a condensed version of relevant information at the beginning of the topic or group entry, under a suitable bold title, the latter being arranged in alphabetical order in Volume 2.

Cross references to related group or sub-group entries are also included, with a group list of the names and serial (not page) numbers of the chemicals appearing in Volume 1 which lie within the structural or functional scope of the group entry title. Compounds which are closely similar to, but not in strict conformity with, the group definition are indicated by a prefixed asterisk.

The group entries thus serve as sub-indexes for each structurally based group of hazardous compounds. Conversely, each individual compound entry is back-referred to the group entry, and thence to all its strict structural analogues and related congeners included in Volume 1 of this Handbook. Note that these group lists of chemicals are now in alphabetical (not formula) order, and give the serial-number (not page number) for the chemical.

These features should be useful in attempts to estimate the stability or reactivity of a compound or reaction system which does not appear in this Handbook. The effects on stability or reactivity of changes in the molecular structure to which the destabilising or reactive group(s) is attached are in some cases discussed in the group entry. Otherwise such information may be gained from comparison of the information available from the individual compound entries listed collectively (now in alphabetical order, with serial number) in the group entry.

Care is, however, necessary in extrapolating from the described properties of compounds to others in which the user of this Handbook may be interested. Due allowance must be made for changes in elemental reactivity up or down the columns of the Periodic Table, and for the effects of variation in chain length, branching and point of group-attachment in organic systems. Purity of materials, possible catalytic effects (positive or negative) of impurities, and scale of operations may all have a direct bearing upon a particular reaction rate. These and other related matters are dealt with in more detail in the following Introductory Chapter.

## **Nomenclature**

With the direct encouragement and assistance of the Publishers, an attempt has been made to use chemical names which conform to recent recommendations of IUPAC. While this has not been an essential part of the compilation, because



each title name has the corresponding structural and molecular formula adjacent, it seems none the less desirable to minimise possible confusion by adopting the unambiguous system of nomenclature presented in the IUPAC publications.

Where the IUPAC name for a compound is very different from a previously used recent trivial name, the latter is included as a synonym in parentheses (and in single quotes where no longer an acceptable name). Generally, retained trivial names have not been used as main entry titles, but they have been used occasionally in the entry texts. Rarely, on the grounds of brevity, names not conforming strictly to IUPAC principles but recommended for chemicals used in industry in BS 2474: 1983 have been used. The prefix mixo-, to represent the mixtures of isomers sometimes used as industrial materials, is a case in point.

Some of the rigidly systematic names selected by the Association for Science Education for their nomenclature list in 1985 from the IUPAC possibilities, and some of the systematic indexing names used by *Chemical Abstracts* since 1972, are given as synonyms in the Index of Chemical Names (Appendix 4). This should assist those coming into industry and research with a command of those nomenclature systems but who may be unfamiliar with the current variety of names used for chemicals. The inclusion where possible of the CAS Registry Number for each title compound should now simplify the clarification of any chemical name or synonym problems, by reference to the Registry Handbook or other CAS source.

In connection with the group titles adopted for the alphabetically ordered Volume 2, it has been necessary in some cases to devise groupnames (particularly in the inorganic field) to indicate in a very general way the chemical structures involved in various classes, groups or sub-groups of compounds.

For this purpose, all elements have been considered either as METALS or NON-METALS, and of the latter, HALOGENS, HYDROGEN, NITROGEN, OXYGEN, and SULFUR were selected as specially important. Group names have then been coined from suitable combinations of these, such as the simple

METAL OXIDES, NON-METAL SULFIDES,  
N-HALOGEN COMPOUNDS, NON-METAL HYBRIDES,  
METAL NON-METALLIDES, COMPLEX HYBRIDES

or the more complex

METAL OXOHALOGENATES  
AMMINECHROMIUM PEROXOCOMPLEXES  
OXOSALTS OF NITROGENOUS BASES  
METALOXONON-METALLATES

Organic group entries are fairly conventional, such as

HALOALKENES  
NITROARL COMPOUNDS  
DIAZONIUM SALTS

Where necessary, such group names are explained in the appropriate group entry, of which a full listing is given in Volume 2, Appendix 3, and a classified listing in Appendix 4.

## Cross reference system

The cross-reference system adopted in this Handbook plays a large part in providing maximum access to, and use of, the rather heterogeneous collection of information herein. The significance of the five types of cross-reference which have been used is as follows.

*See* . . . refers to a directly related item.

*See also* . . . refers to an indirectly related item.

*See other* . . . refers to listed strict analogues of the compound etc.

*See related* . . . refers to listed related compounds (congeners) or groups not strictly analogous structurally.

*See entry* . . . points to a, or the relevant, reference in Volume 2.

## Information content of individual entries

A conscious effort has been made throughout this compilation to exclude all fringe information not directly relevant to the involvement of chemical reactivity in the various incidents or observations, with just enough detail present to allow the reader to judge the relevance or otherwise of the quoted reference(s) to his or her particular reactivity problems or interests.

It must be stressed that this book can do no more than to serve as a guide to much more detailed information available via the quoted references. It cannot relieve the student, the chemist and their supervisors of their moral and now legal obligation to themselves and to their co-workers, to equip themselves with the fullest possible information from the technical literature resources which are widely available, *before* attempting any experimental work with materials known, or suspected, to be hazardous or potentially so. It could be impossible for you *after* the event.

THE ABSENCE OF A MATERIAL OR A COMBINATION OF MATERIALS FROM THIS HANDBOOK CANNOT BE TAKEN TO IMPLY THAT NO HAZARD EXISTS. LOOK THEN FOR ANALOGOUS MATERIALS USING THE GROUP ENTRY SYSTEM AND THE INDEXES THERETO.

One aspect which, although it is excluded from most entry texts, is nevertheless of vital importance, is that of the potential for damage, injury or death associated with the various materials and reaction systems dealt with in this Handbook.

Though some of the incidents have involved little or no damage (*see* CAN OF BEANS), others have involved personal injuries, often of unexpected severity (*See* SODIUM PRESS), and material damage is often immense. For example, the incident given under Perchloric acid: Cellulose derivatives, (reference 1) involved damage to 116 buildings and a loss approaching \$ 3M at 1947 values. The death-toll associated with reactive chemical hazards has ranged from 1 or 2 (*see* Tetrafluoroethylene: Iodine pentafluoride) to some 600 with 2000 injured in the incident at Oppau in 1921 (*see* Ammonium nitrate, reference 4), and now to several thousand

with more than 100,000 injured by methyl isocyanate fumes at Bhopal in 1984 (reference 7).

This sometimes vast potential for destruction again emphasises the need to gain the maximum of detailed knowledge *before* starting to use an unfamiliar chemical or reaction system.

# Reactive Chemical Hazards

CROSS REFERENCES IN CAPITALS REFER TO PAGE NUMBERS IN VOLUME 2.

This introductory chapter seeks to present an overview of the complex subject of reactive chemical hazards, drawing attention to the underlying principles and to some practical aspects of minimising such hazards. It also serves in some measure to correlate some of the topic entries in the alphabetically arranged Volume 2 of the Handbook.

## **Basics**

All chemical reactions implicitly involve energy changes (energy of activation + energy of reaction), for these are the driving force. The majority of reactions liberate energy as heat (occasionally as light or sound) and are termed exothermic. In a minority of reactions, energy is absorbed into the products, when both the reaction and its products are described as endothermic.

All reactive hazards involve the release of energy in quantities or at rates too high to be absorbed by the immediate environment of the reacting system, and material damage results. The source of the energy may be an exothermic multi-component reaction, or the exothermic decomposition of a single unstable (often endothermic) compound.

All measures to minimise the possibility of occurrence of reactive chemical hazards are therefore directed at controlling the extent and rate of release of energy in a reacting system. In an industrial context, such measures are central to modern chemical engineering practice. Some of the factors which contribute to the possibility of excessive energy release, and appropriate means for their control, are now outlined briefly, with references to examples in the text.

## **Kinetic Factors**

The rate of an exothermic chemical reaction determines the rate of energy release. so factors which affect reaction kinetics are important in relation to possible reaction hazards. The effects of proportions and concentrations of reactants upon reaction rate are governed by the Law of Mass Action, and there are many examples where changes in proportion and/or concentration of reagents have transformed an

established uneventful procedure into a violent incident. For examples of the effect of increase in proportion,

*see* 2-Chloronitrobenzene: Ammonia

Sodium 4-nitrophenoxide

For the effect of increase in concentration upon reaction velocity,

*see* Dimethyl sulfate: Ammonia

Nitrobenzene: Alkali (reference 2)

The effects of catalysts (which effectively reduce the energy of activation), either intentional or unsuspected, is also relevant in this context. Increase in the concentration of a catalyst (normally used at 1–2%) may have a dramatic effect on reaction velocity.

*See* Trifluoromethanesulfonic acid: Acyl chlorides, etc.

2-Nitroanisole: Hydrogen

HYDROGEN CATALYSTS

The presence of an unsuspected contaminant or catalytic impurity may affect the velocity or change the course of reaction. For several examples,

*See* CATALYTIC IMPURITY INCIDENTS

In the same context, but in opposite sense, the presence of inhibitors (negative catalysts, increasing energy of activation) may seriously interfere with the smooth progress of a reaction. An inhibitor may initiate an induction period which can lead to problems in establishing and controlling a desired reaction. For further details and examples,

*See* INDUCTION PERIOD INCIDENTS

Undoubtedly the most important factor affecting reaction rates is that of temperature. It follows from the Arrhenius equation that the rate of reaction will increase exponentially with temperature. Practically, it is found that an increase of 10°C in reaction temperature often doubles or trebles the reaction velocity.

Because most reactions are exothermic, they will tend to accelerate as reaction proceeds unless the available cooling capacity is sufficient to prevent rise in temperature. Note that the exponential temperature effect accelerating the reaction will exceed the (usually) linear effect of falling reactant concentration in decelerating the reaction. When the exotherm is large and cooling capacity is inadequate, the resulting accelerating reaction may proceed to the point of loss of control (runaway), and decomposition, fire or explosion may ensue.

The great majority of incidents described in the text may be attributed to this primary cause of thermal runaway reactions. The scale of the damage produced is related directly to the size, and more particularly to the rate, of energy release.

*See* RUNAWAY REACTIONS

Reactions at high pressure may be exceptionally hazardous owing to the enhanced kinetic energy content of the system.

*See* HIGH-PRESSURE REACTION TECHNIQUES

Although detailed consideration of explosions is outside the scope of this Handbook, three levels of intensity of explosion (i.e. rates of fast energy release) can be discerned and roughly equated to the material damage potential.

Deflagration involves combustion of a material, usually in presence of air. In a normal liquid pool fire, combustion in an open situation will normally proceed

without explosion. Mixtures of gases or vapours with air within the explosive limits which are subsequently ignited will burn at normal flame velocity (a few m/s) to produce a 'soft' explosion, with minor material damage, often limited to scorching by the moving flame front. Injuries to personnel may well be more severe.

If the mixture (or a dust cloud) is confined, even if only by surface irregularities or local partial obstructions, significant pressure effects can occur. Fuel-air mixtures near to stoichiometric composition and closely confined will develop pressures of several bar within milliseconds, and material damage will be severe. Unconfined vapour explosions of large dimensions may involve higher flame velocities and significant pressure effects, as shown in the Flixborough disaster.

*See* DUST EXPLOSION INCIDENTS

PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

VAPOUR CLOUD EXPLOSIONS

Detonation is an extreme form of explosion where the propagation velocity becomes supersonic in gaseous, liquid or solid states. The temperatures and particularly pressures associated with detonation are higher by orders of magnitude than in deflagration. Energy release occurs in a few microseconds and the resulting shattering effects are characteristic of detonation. Deflagration may accelerate to detonation if the burning material and geometry of confinement are appropriate (endothermic compounds, long narrow vessels or pipelines).

*See* Acetylene (reference 9)

ENDOTHERMIC COMPOUNDS

EXPLOSIONS

UNIT PROCESS INCIDENTS

Factors of importance in preventing such thermal runaway reactions are mainly related to the control of reaction velocity and temperature within suitable limits. These may involve such considerations as adequate heating and particularly cooling capacity in both liquid and vapour phases of a reaction system; proportions of reactants and rates of addition (allowing for an induction period); use of solvents as diluents and to reduce viscosity of the reaction medium; adequate agitation and mixing in the reactor; control of reaction or distillation pressure; use of an inert atmosphere.

*See* AGITATION INCIDENTS

In some cases it is important not to overcool a reaction system, so that the energy of activation is maintained.

*See* Acetylene: Halogens (reference 1)

## Adiabatic Systems

Because process heating is expensive, lagging is invariably applied to heated process vessels to minimise heat loss, particularly during long-term hot storage. Such adiabatic or near-adiabatic systems are potentially hazardous if materials of limited thermal stability, or which possess self-heating capability, are used in them. Insufficiently stabilised bulk-stored monomers come into the latter category.

*See* 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent

POLYMERISATION INCIDENTS

SELF-HEATING AND IGNITION INCIDENTS  
THERMAL STABILITY OF REACTION MIXTURES  
VIOLENT POLYMERISATION

## **Reactivity vs. Composition and Structure**

The ability to predict reactivity and stability of chemical compounds from their composition and structure is as yet limited, so the ability accurately to foresee potential hazards during preparation, handling and processing of chemicals and their mixtures is also restricted. Although some considerable progress has been made in the use of computer programs to predict hazards, the best available approach for many practical purposes appears to be an initial appraisal based on analogy with, or extrapolation from, data for existing compounds and processes. This preliminary assessment should be supplemented with calorimetric instrumental examination, then bench-scale testing procedures for thermal stability applied to realistic reaction mixtures and processing conditions. A wide range of equipment and techniques is now available for this purpose.

*See* ACCELERATING RATE CALORIMETRY

ASSESSMENT OF REACTIVE CHEMICAL HAZARDS  
COMPUTATION OF REACTIVE CHEMICAL HAZARDS  
DIFFERENTIAL SCANNING CALORIMETRY  
DIFFERENTIAL THERMAL ANALYSIS  
MAXIMUM REACTION HEAT  
REACTION SAFETY CALORIMETRY

It has long been recognised that instability in single compounds, or high reactivity in combinations of different materials, is often associated with particular groupings of atoms or other features of molecular structure, such as high proportions or local concentrations of oxygen or nitrogen. Full details of such features associated with explosive instability are collected under the heading EXPLOSIBILITY.

An approximate indication of likely instability in a compound may be gained from inspection of the empirical molecular formula to establish stoichiometry.

*See* HIGH-NITROGEN COMPOUNDS

OXYGEN BALANCE

Endothermic compounds, formed as the energy-rich products of endothermic reactions, are thermodynamically unstable and may be liable to energetic decomposition with low energy of activation.

*See* ENDOTHERMIC COMPOUNDS

## **Reaction Mixtures**

So far as reactivity between different compounds is concerned, some subdivision can be made on the basis of the chemical types involved. Oxidants (electron sinks) are undoubtedly the most common chemical type to be involved in hazardous incidents, the other components functioning as fuels or other electron sources. Air (21% oxygen) is the most widely dispersed oxidant, and air-reactivity may lead to either short- or long-term hazards.

Where reactivity of a compound is very high, oxidation may proceed so fast in air that ignition occurs.

*See* PYROPHORIC MATERIALS

Slow reaction with air may lead to the longer-term hazard of peroxide formation.

*See* AUTOXIDATION

PEROXIDATION INCIDENTS

PEROXIDATION IN SOLVENTS

PEROXIDISABLE COMPOUNDS

Oxidants more concentrated than air are of greater hazard potential, and the extent of involvement of the common oxidants

Perchloric acid

Chlorine

Nitric acid

Hydrogen peroxide

Sulfuric acid

METAL CHLORATES

may be judged from the large number of incidents in the text involving each of them, as well as other OXIDANTS.

At the practical level, experimental oxidation reactions should be conducted to maintain in the reacting system a minimum oxygen balance consistent with other processing requirements. This may involve adding the oxidant slowly with appropriate mixing and cooling to the other reaction materials to maintain the minimum effective concentration of oxidant for the particular reaction. It will be essential to determine by a suitable diagnostic procedure that the desired reaction has become established, to prevent build-up of unused oxidant and a possible approach to the oxygen balance point.

*See* OXYGEN BALANCE

Reducants (rich electron sources) in conjunction with reducible materials (electron acceptors) feature rather less frequently than oxidants in hazardous incidents.

*See* REDUCANTS

Interaction of potent oxidants and reducants is invariably highly energetic and of high hazard potential.

*See* Dibenzoyl peroxide: Lithium tetrahydroaluminate

Hydrazine: Oxidants

REDOX REACTIONS

ROCKET PROPELLANTS

Similar considerations apply to those compounds which contain both oxidising and reducing functions in the same molecular structure.

*See* REDOX COMPOUNDS

Water is, after air, one of the most common reagents likely to come into contact with reactive materials, and several classes of compounds will react violently, particularly with restricted amounts of water.

*See* WATER-REACTIVE COMPOUNDS

Most of the above has been written with deliberate processing conditions in mind, but it must be remembered that the same considerations will apply, and



perhaps to a greater degree, under the uncontrolled reaction conditions prevailing when accidental contact of reactive chemicals occurs in storage or transit.

Adequate planning is therefore necessary in storage arrangements to segregate oxidants from fuels and reductants, and fuels and combustible materials from compressed gases and water-reactive compounds. This will minimise the possibility of accidental contact and violent reaction arising from faulty containers or handling operations, and will prevent intractable problems in the event of fire in the storage areas.

*See* SAFE STORAGE OF CHEMICALS

Unexpected sources of ignition may lead to ignition of flammable materials during chemical processing or handling operations.

*See* FRICTIONAL IGNITION OF GASES

IGNITION SOURCES

SELF-HEATING AND IGNITION INCIDENTS

STATIC INITIATION INCIDENTS

## **Protective Measures**

The need to provide protective measures will be directly related to the level of potential hazards which may be assessed from the procedures outlined above. Measures concerned with reaction control are frequently mentioned in the following text, but details of techniques and equipment for personal protection, though usually excluded from the scope of this work, are obviously of great importance.

Careful attention to such detail is necessary as a second line of defence against the effects of reactive hazards. The level of protection considered necessary may range from the essential and absolute minimum of effective eye protection, via the safety screen, fume cupboard or enclosed reactor, up to the ultimate of a remotely controlled and blast-resistant isolation cell (usually for high-pressure operations). In the absence of facilities appropriate to the assessed level of hazard, operations must be deferred until such facilities are available.

# Volume 2

## Class, Group and Topic

(Entries arranged in alphabetical order)

### EXPLANATORY NOTES

The entries in this volume are of two principal types, each accounting for about half of the total of 650 entries. The first type of entry gives general information on the hazardous behaviour of some recognisably discrete classes or groups of the almost 5000 individual compounds for which details are given in Volume 1, or of groups for which there may not be individual entries. Where possible, a general structural formula ranged right on the title line indicates the typical structure(s) of the members of each class of group of compounds. In these formulae, the following general symbols are used in addition to the usual symbols for the elements.

Ar = AROMATIC nucleus

E = NON-METALLIC element

M = METALLIC element

R = organic RESIDUE

X = HALOGEN

Z = non-halogen ANION species

Information on the derivation of the class and group names is given in the Introduction.

The second type of entry concerns reactive hazard topics, techniques or incidents which have a common theme or pattern of behaviour involving compounds of several different groups, so that no common structural feature exists for the compounds involved.

Substances not easily described as individual compounds of known empirical formula also appear in Volume II, constituting a third class of entries, which are essentially similar to a Volume I entry in nature.

The *ca.* 300 group-lists of compounds in the first type of entry serve as an index to analogues and homologues of a compound falling within the scope of the structural or behavioural group. Those compounds (congeners) of generally similar, but not identical structure to the majority in the group-lists are prefixed \*. Flammable analogues are prefixed + to remind of the fire hazard. For flammable congeners,

the dagger prefix has taken precedence over the asterisk for the same reason. The order in the group-lists is alphabetic, rather than being order of empirical formulae as in the main text of Volume 1.

There is a full index to the the Volume 2 entry titles in Appendix 3. Appendix 4 contains the same entries classified on the basis of similarity in type of information content, as indicated by the bold sub-titles. This Appendix should be useful in locating reaction hazard information of a more general nature.

Details of corrections of typographical or factual errors, or of further items for inclusion in the text, will be welcomed, and a page which can be photocopied for this purpose will be found at the back of the book.

### ACCELERATING RATE CALORIMETRY (ARC)

1. Townsend, D. I. *et al.*, *Thermochim. Acta*, 1980, **37**, 1–30
2. Townsend, D. I., *Runaway Reactions*, 1981, Paper 3Q, 1–14
3. Coates, C. F., *Chem. & Ind.*, 1984, 212–216
4. Gibson, N., *Chem. & Ind.*, 1984, 209–212
5. *Explosion at the Dow Chemical Factory, King's Lynn, 27th June 1976*, London, HSE, 1977
6. Cardillo, P. *et al.*, *J. Haz. Mat.*, 1984, **9**, 221–234

Of the instrumental methods currently available for detailed small scale predictive investigation of hazardous and potentially hazardous reactions, the accelerating rate calorimeter appears to be the most sophisticated, sensitive, accurate and wide ranging in application. In essence the ARC maintains a sample in adiabatic condition once an exothermic reaction is detected, and then measures the consequent increases in temperature and pressure inside the sample holder in relation to elapsed time. The sample (1–5 g) is contained in a small spherical metal bomb, usable up to 500°C and 170 bar, within an insulated oven inside a massive steel containment vessel. The sample is heated on a stepped heat-wait-search programme until an exotherm is detected, when adiabatic conditions are then automatically established. The results can be processed to yield data relevant either to process control or reaction mechanism considerations. Fuller details of the theoretical background, construction and instrumentation, operation and capabilities of the technique have been published [1], and the theory behind the development of methods of estimating time to maximum rate of decomposition (TMR) from ARC results is discussed [2]. The place of ARC as part of a comprehensive hazard evaluation system in a chemical manufacturing context has been discussed [3]. The use of much simpler (and less expensive) Dewar flask methods for identifying potentially hazardous decompositions in reaction masses and powders has been compared and contrasted with ARC methods [4]. The part played by ARC in the investigation of the industrial explosions at King's Lynn (3,5-dinitro-2-toluamide) [5], and at Seveso (2,4,5-trichlorophenol) [6] shows the potential of the technique.

*See* ADIABATIC CALORIMETRY, CALORIMETRY, CHEMICAL STABILITY/REACTIVITY ASSESSMENT

### ACCIDENTAL DECONTAMINATION

Kletz, T. A., *J. Loss Prev. Proc. Ind.*, 1989, **2**, 117

In a brief review of chemical accidents caused by accidental contamination of process materials, attention is drawn to the much less frequent opposite effect of accidental decontamination (or purification) as a cause of accidents. Some examples of the effects arising from accidental loss or inactivation of stabilisers or antioxidants from reactive materials are given.

*See* CATALYTIC IMPURITY INCIDENTS

### ACCIDENT DATABASES

*Database*, Rugby, Institution of Chemical Engineers  
*MARS(Major Accident Reporting System) Database*

Several organisations have lately established electronic databases, recording details of industrial chemical accidents. These should enable the user to learn from others mistakes and also establish a fixed version of accidents, which hitherto have changed in the retelling, and the more important have often been retold. The two above are examples of a wider trend. All tend to reflect the pre-occupations of their compilers, which are generally not so much the precise chemical causes of the mishap, but its effects.

## ACETYLENIC COMPOUNDS



1. Davidsohn, W. E. *et al.*, *Chem. Rev.*, 1967, **67**, 74
2. Mushii, R. Ya. *et al.*, *Chem. Abs.*, 1967, **67**, 92449
3. Dutton, G. G. S., *Chem. Age*, 1947, **56**(1436), 11–13

The presence of the endothermic triply-bonded acetylene (ethyne) group confers explosive instability on a wide range of acetylenic compounds (notably when halogen is also present) and derivatives of metals (and especially of heavy metals) [1]. Explosive properties of butadiyne, buten-3-yne, hexatriyne, propyne and propadiene have been reviewed, with 74 references [2]. The tendency of higher acetylenes to explosive decomposition may be reduced by dilution with methanol [3]. The class includes the separately treated groups:

ACETYLENIC PEROXIDES  
ALKYNES  
COMPLEX ACETYLIDES  
ETHOXYETHYNYL ALCOHOLS  
HALOACETYLENE DERIVATIVES  
METAL ACETYLIDES

and the individually indexed compounds:

Acetylenedicarboxaldehyde, 1403  
Acetylenedicarboxylic acid, 1405  
Azido-2-butyne, 1473  
3-Azidopropyne, 1114  
Benzyloxyacetylene, 3133  
Bis(cyclopentadienyl)hexafluoro-2-butynechromium, 3636  
Bis(dibutylborino)acetylene, 3775  
Bis(dipropylborino)acetylene, 3670  
Butoxyacetylene, 2428  
2-Butyne-1,4-diol, 1526  
2-Butyne-1-thiol, 1546  
3-Butyn-1-yl 4-toluenesulfonate, 3399  
N-Chloro-3-aminopropyne, 1129  
1-Chloro-3-phenylpent-1-en-4-yn-3-ol, 3402  
\* 3-Cyanopropyne, 1416  
1,2-Di(3-buten-1-ynyl)cyclobutane, 3509  
Dibutyl-3-methyl-3-buten-1-ynylborane, 3618  
Diethyl acetylenedicarboxylate, 2987

1-Diethylamino-1-buten-3-yne, 3020  
*cis*-3,4-Diethynylcyclobut-3-ene-1,2-diol, 2921  
 2,4-Diethynyl-5-methylphenol, 3393  
 2,4-Diethynylphenol, 3244  
 1,10-Di(methanesulfonyloxy)deca-4,6-diyne, 3543  
 Dimethyl acetylenedicarboxylate, 2943  
 (Dimethylamino)acetylene, 1564  
 3,3-Dimethyl-1-nitro-1-butyne, 2395  
 Diphenylethyne, 3634  
 Di(1-propynyl) ether, 2326  
 Di(2-propynyl) ether, 2327  
 † Ethoxyacetylene, 1521  
 4-Ethoxy-2-methyl-3-butyn-2-ol, 2844  
 1-Ethoxy-2-propyne, 1909  
 2-Ethynylfuran, 2212  
 Ethynyl vinyl selenide, 1449  
 2-Heptyn-1-ol, 2841  
 4,5-Hexadien-2-yn-1-ol, 2328  
 2,4-Hexadiyne-1,6-dioic acid, 2094  
 2,5-Hexadiyn-1-ol, 2329  
 1,5-Hexadiyn-3-one, 2213  
 2,4-Hexadiynylene chloroformate, 2890  
 2,4-Hexadiynylene chlorosulfite, 2162  
 Lithium ethynediolate, 0993  
 † Methoxyacetylene, 1146  
 3-Methoxypropyne, 1523  
 † 2-Methyl-3-butyn-2-ol, 1910  
 2-Methyl-3,5,7-octatriyn-2-ol, 3135  
 3-Methyl-2-penten-4-yn-1-ol, 2384  
 1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene, 3760  
 † Methyl propiolate, 1442  
 2-Nitrophenylpropionic acid, 3113  
 2-Nonen-4,6,8-triyn-1-al, 3112  
 Octacarbondioxide pentamer, 3904  
 Octacarbondioxide tetramer, 3884  
 Octatetrayne-1,8-dicarboxylic acid, 3235  
 Oligo(octacarbondioxide), 3108  
 1,3-Pentadiyne, 1825  
 2-Penten-4-yn-3-ol, 1879  
 Phenoxyacetylene, 2920  
 Phenyl, phenylethynyliodonium perchlorate, 3635  
 Poly(2,4-hexadiyne-1,6-yne carbonate), 2669  
 Potassium acetylene-1,2-dioxide, 4934  
 Potassium ethynediolate, 0990  
 Potassium hydrogen acetylenedicarboxylate, 1382  
 Propiolaldehyde, 1085

Propiolic acid, 1086  
Propioloyl chloride, 1065  
3-Propynethiol, 1152  
3-Propynol, 1147  
5-(Prop-2-ynyloxy)-1,2,3,4-thiazotriazole, 1420  
2-Propynyl vinyl sulfide, 1883  
Sodium ethynediolate, 1023  
1,2:5,6:11,12:15,16-Tetrabenzocycloocta-1,5,11,15-tetraene-  
3,7,9,13,17,19-hexayne, 3888  
Tetracyclo[20.2.0.0<sup>6,9</sup>.0<sup>4,17</sup>]tetracos-1(22),6(9),14(17)-triene-  
2,4,10,12,18, 20-hexayne-7,8,15,16,23,24-hexone, 3858  
1,3,5-Triethynylbenzene, 3443  
\* Triethynylphosphine, 2124

See also PEROXIDISABLE COMPOUNDS

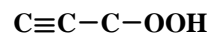
#### Metals

*Chemical Intermediates*, 1972 Catalogue, 158, Tamaqua (Pa.), Air Products and Chemicals Inc., 1972

Acetylenic compounds with replaceable acetylenically bound hydrogen atoms must be kept out of contact with copper, silver, magnesium, mercury or alloys containing them, to avoid formation of explosive metal acetylides.

See METAL ACETYLIDES

#### ACETYLENIC PEROXIDES



1. Milas, N. A. *et al.*, *Chem. Eng. News*, 1959, **37**(37), 66
  2. Milas, N. A. *et al.*, *J. Amer. Chem. Soc.*, 1952, **75**, 1472; 1953, **76**, 5970
- The importance of strict temperature control [1] to prevent explosion during the preparation [2] of acetylenic peroxides is stressed. Use of inert solvent to prevent undue increase in viscosity which leads to poor temperature control is recommended [1].

Individually indexed compounds are:

- 2-(4-Bromophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3709  
2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3711

See other PEROXIDES

#### ACID ANHYDRIDES



The several members of this reactive group involved in hazardous incidents are:

- Acetic anhydride, 1534  
Benzeneseleninic anhydride, 3495  
Benzenesulfonic anhydride, 3498  
\* Chromium trioxide, 4242  
Dichloromaleic anhydride, 1359  
\* Dinitrogen pentoxide, 4748  
Disulfur heptaoxide, 4870

- \* Disulfuryl dichloride, 4103
- \* Disulfuryl difluoride, 4326
- \* Methaneboronic anhydride–pyridine complex, 0427
- \* Peroxypropionyl nitrate, 1187
- \* Peroxypropionyl perchlorate, 1167
- Phthalic anhydride, 2899
- \* Pivaloyloxydiethylborane, 3198
- † Propadiene-1,3-dione, 1349
- Succinic anhydride, 1443
- Sulfur trioxide, 4849
- \* Sulfur trioxide–dimethylformamide, 4850
- Tetraphosphorus decaoxide, 4872
- Trifluoroacetic anhydride, 1366
- Trifluoroacetyl trifluoromethanesulfonate, 1057

### ACRYLIC MONOMERS



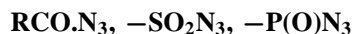
Schulze, S. *et al.*, *Chem. Eng. Technol.*, 1998, **21**, 829

Most of these monomers are inclined to violent polymerisation unless stabilised. Stabilisation usually involves oxygen as well as the nominal stabiliser. A kinetic study of the process for acrylic and methacrylic acids is reported.

See VIOLENT POLYMERISATION

See also POLYMERISATION INCIDENTS

### ACYL AZIDES



1. Smith, P. A. S., *Org. React.*, 1946, **3**, 373–375
2. Houben-Weyl, 1952, Vol. 8, 680
3. Lieber, E. *et al.*, *Chem. Rev.*, 1965, **65**, 377
4. Balabanov, G. P. *et al.*, *Chem. Abs.*, 1969, **70**, 59427
5. Renfrow, W. B. *et al.*, *J. Org. Chem.*, 1975, **40**, 1526
6. Anon., *Sichere Chemiarb.*, 1984, **36**, 143–144
7. Hazen, G. G. *et al.*, *Synth. Comm.*, 1981, **11**(12), 947
8. Tuma, L. D. *Thermochim. Acta.*, 1994, 243(2) 161

Azides of low molecular weight (more than 25% nitrogen content) should not be isolated from solution, as the concentrated material is likely to be dangerously explosive [1]. The concentration of such solutions (prepared below 10°C) should be <10% [2]. Carbonyl azides are explosive compounds, some exceptionally so, and suitable handling precautions are necessary [3]. The sensitivity to friction, heat and impact of benzenesulfonyl azide, its 4-chloro-, methyl-, methoxy-, methoxycarbonylamino-, and nitro-derivatives, and 1,3-benzenedisulfonyl diazide were studied [4]. Benzenesulfonyl azide and 2-toluenesulfonyl azide may be smoothly thermolysed in benzene [5]. In this Curtius procedure for rearrangement with loss of nitrogen to isocyanates, it is important to ensure (by IR examination) that the products of such rearrangements are substantially free of residual acyl azide before attempting distillation of the material. Failure to make this check led to a



violent explosion of 70 g of an unspecified crude isocyanate when the distillation flask was immersed in a preheated oil-bath [6]. Further mishaps have provoked further studies: Tests for safety as reagents for azo transfer were conducted on five arylsulfonyl azides. It was concluded that toluenesulfonyl azide (with the lowest molecular weight) was the least safe, of shock sensitivity and power variously compared with TNT and tetryl (and elsewhere with nitroglycerine). [Such power seems thermodynamically implausible, it is assigned only 80 kcal/mole, 1.7 kJ/g.] The safest was 4-dodecylbenzenesulfonyl azide (with the highest m.w.). Thermally most stable was 4-carboxybenzenesulfonylazide, but its decomposition rate was highest once started, it was marginally shock sensitive [7]. Another safety study of sulfonyl azides, including detonation, also preferred dodecylbenzenesulfonyl azide [8]. Individually indexed compounds are:

- Acetyl azide, 0771
- N*-Azidocarbonylazepine, 2728
- Azidocarbonyl fluoride, 0339
- \* Azidocarbonylguanidine, 0820
- 4-Azidocarbonyl-1,2,3-thiadiazole, 1069
- Azidodithioformic acid, 0386
- Benzene-1,3-bis(sulfonyl azide), 2210
- Benzenesulfinyl azide, 2273
- Benzenesulfonyl azide, 2274
- Benzoyl azide, 2698
- 4,4'-Biphenylene-bis-sulfonylazide, 3468
- cis*-1,2-Bis(azidocarbonyl)cyclobutane, 2323
- 1,2-Bis(azidocarbonyl)cyclopropane, 1835
- Bis(azidothiocarbonyl) disulfide, 1016
- 4-Bromobenzoyl azide, 2644
- N*-Butylamidofuryl azide, 1693
- tert*-Butyl azidoformate, 1936
- Carbonic diazide, 0550
- Carboxybenzenesulfonyl azide, 2699
- 4-Chlorobenzenesulfonyl azide, 2152
- 4-Chlorobenzoyl azide, 2654
- N*-(2-Chloroethyl)-*N*-nitrosocarbamoyl azide, 1131
- Cyanodiazooacetyl azide, 1346
- Cyanohydranoacetyl azide, 1083
- 1,2-Diazidocarbonylhydrazine, 0720
- Diazoacetyl azide, 0679
- Disulfuryl diazide, 4780
- Ethyl azidoformate, 1193
- Fluorothiophosphoryl diazide, 4308
- 2-Furoyl azide, 1821
- Glutaryl diazide, 1874
- 4-Methylaminobenzene-1,3-bis(sulfonyl azide), 2785
- 4-Nitrobenzenesulfinyl azide, 2204
- Palladium(II) azidodithioformate, 1015

- Phenylphosphonic azide chloride, 2233
  - Phenylphosphonic diazide, 2284
  - 3-Phenylpropionyl azide, 3144
  - Phenylthiophosphonic diazide, 2285
  - Phthaloyl diazide, 2898
  - Pivaloyl azide, 1935
  - Potassium azidodisulfate, 4655
  - Potassium azidosulfate, 4653
  - 6-Quinolinecarbonyl azide, 3243
  - \* Silver azidodithioformate, 0303
  - Sodium azidosulfate, 4759
  - Succinoyl diazide, 1438
  - Sulfamoyl azide, 4472
  - Sulfinyl azide, 4778
  - Sulfuryl azide chloride, 4031
  - Sulfuryl diazide, 4779
  - \* Thallium(I) azidodithiocarbonate, 0543
  - 4-Toluenesulfinyl azide, 2780
  - 4-Toluenesulfonyl azide, 2781
  - Trifluoroacetyl azide, 0627
  - N*-(Trifluoromethylsulfinyl)trifluoromethylimidodisulfinyl azide, 0640
  - Trifluoromethylsulfonyl azide, 0348
  - 1,3,5-Tris(4-azidosulfonylphenyl)-1,3,5-triazinetriene, 3818
- See also 2-AZIDOCARBONYL COMPOUNDS, CUBANES, SULFINYL AZIDES*

## ACYL CHLORIDES

## RCO.Cl

Aromatic hydrocarbons, Trifluoromethanesulfonic acid  
*See* Trifluoromethanesulfonic acid: Acyl chlorides, etc.

## ACYL HALIDES

## RCO.X, -SO.X, -SO<sub>2</sub>X

This group tends to react violently with protic organic solvents, water, and the aprotic solvents, dimethylformamide and dimethyl sulfoxide. Their facile reaction with ethers is also potentially hazardous.  
*See* Propionyl chloride: Diisopropyl ether

Individually indexed compounds are:

- Acetyl bromide, 0728
- † Acetyl chloride, 0735
- † Acryloyl chloride, 1093
- Azidocarbonyl fluoride, 0339
- Benzenesulfinyl chloride, 2234
- Benzenesulfonyl chloride, 2235
- Benzoyl chloride, 2675
- \* Benzyl chloroformate, 2931

- tert*-Butyl chloroperoxyformate, 1926
- † Butyryl chloride, 1555
- \* Carbonyl dichloride, 0329
- \* Carbonyl difluoride, 0343
- \* Chlorine fluorosulfate, 3975
- (Chlorocarbonyl)imidodisulfur difluoride, 0318
- N*-(Chlorocarbonyloxy)trimethylurea, 1924
- \* Chlorosulfonyl isocyanate, 0324
- Chlorosulfuric acid, 3997
- \* Chromyl fluorosulfate, 4225
- Cyanoacetyl chloride, 1075
- Cyanoformyl chloride, 0600
- 4,4-Diferrocenylpentanoyl chloride, 3859
- 2,2-Dinitro-2-fluoroethoxycarbonyl chloride, 1072
- Disulfuryl dichloride, 4103
- Disulfuryl difluoride, 4326
- † Ethyl chloroformate, 1164
- Ethyl oxalyl chloride, 1456
- N*-Ethyl-*N*-propylcarbamoyl chloride, 2468
- \* Fluorine fluorosulfate, 4324
- Furoyl chloride, 1818
- 2,4-Hexadiynylene chloroformate, 2890
- 2,4-Hexadiynylene chlorosulfite, 2162
- † Isobutyryl chloride, 1558
- Isophthaloyl chloride, 2888
- † Isopropyl chloroformate, 1560
- Methanesulfinyl chloride, 0435
- Methoxyacetyl chloride, 1165
- 4-Methoxybenzoyl chloride, 2930
- † Methyl chloroformate, 0599
- Oleoyl chloride, 3772
- Oxalyl dibromide, 0583
- Oxalyl dichloride, 0605
- \* Oxopropanedinitrile, 1341
- Pentafluoropropionyl fluoride, 1054
- Peroxodisulfuryl difluoride, 4328
- \* Phenylphosphonyl dichloride, 2245
- † Pivaloyl chloride, 1925
- Propioloyl chloride, 1065
- † Propionyl chloride, 1163
- Sebacoyl chloride, 3341
- Sulfinyl chloride, 4096
- Sulfonyl chloride, 4099
- Sulfur oxide-(*N*-fluorosulfonyl)imide, 4305
- Sulfuryl azide chloride, 4031
- Terephthaloyl chloride, 2880

- \* 2,4,6-Trichloro-1,3,5-triazine, 1038
- Trifluoroacryloyl fluoride, 1049
- Trifluoromethanesulphenyl chloride, 0322
- Trifluoromethanesulfinyl fluoride, 0354

### **O-ACYLHYDROXAMIC ACIDS**

### **HOC(R)=NOCOR'**

Houben Weyl 10/4, 1968, 232

Warning is given against dry distillation of the alkali salts as an isocyanate preparation. The decomposition is often explosive

See other N-O COMPOUNDS

### **ACYL HYPOHALITES**

### **RCO.OX**

1. Tari, I. *et al.*, *Inorg. Chem.*, 1979, **18**, 3205–3208

2. Skell, P. S. *et al.*, *J. Amer. Chem. Soc.*, 1983, **105**, 4000, 4007

Sodium salts of fluoroacids react with chlorine fluoride at  $-112$  to  $-78^{\circ}\text{C}$  to give explosively unstable fluoroacyl hypochlorites. Trifluoroacetyl hypochlorite and its pentafluoropropionyl, heptafluorobutyryl, difluoroacetyl and chlorodifluoroacetyl analogues explode without fail if the partial pressure exceeds 27–67 mbar. Hexafluoroglutaryl dihypochlorite explodes above  $-10^{\circ}\text{C}$  [1]. Of the 4 compounds prepared, acetyl, propionyl, isobutyryl and pivaloyl hypobromites, the 2 latter appeared stable indefinitely at  $-41^{\circ}\text{C}$  in the dark, while the 2 former exploded unpredictably as isolated solids [2].

See Acetyl hypobromite, Propionyl hypobromite

Individually indexed compounds are:

- Acetyl hypobromite, 0729
- Acetyl hypofluorite, 0751
- Caesium fluoroxysulfate, 4256
- Chlorodifluoroacetyl hypochlorite, 0603
- Difluoroacetyl hypochlorite, 0653
- Fluorine fluorosulfate, 4324
- Heptafluorobutyryl hypochlorite, 1352
- Heptafluorobutyryl hypofluorite, 1369
- Hexafluoroglutaryl dihypochlorite, 1806
- Pentafluoropropionyl hypochlorite, 1034
- Pentafluoropropionyl hypofluorite, 1056
- Propionyl hypobromite, 1154
- Rubidium fluoroxysulfate, 4309
- Trifluoroacetyl hypochlorite, 0594
- Trifluoroacetyl hypofluorite, 0633

### **ACYL NITRATES**

### **RCO.ONO<sub>2</sub>**

A thermally unstable group of compounds, tending to violent decomposition or explosion on heating. Individually indexed compounds are:

Acetyl nitrate, 0765  
Benzoyl nitrate, 2689  
Butyryl nitrate, 1573  
3-Nitrobenzoyl nitrate, 2664  
\* Peroxyacetyl nitrate, 0766  
\* Peroxypropionyl nitrate, 1187  
See Nitric acid: Phthalic anhydride, etc., 4436

## ACYL NITRITES

RCO.ON:O

1. Ferrario, E., *Gazz. Chim. Ital.* [2], 1901, **40**, 98–99
2. Francesconi, L. *et al.*, *Gazz. Chim. Ital.* [1], 1895, **34**, 442

The stabilities of propionyl nitrite and butyryl nitrite are greater than that of acetyl nitrite, butyryl nitrite being the least explosive of these homologues [1]. Benzyl nitrite is also unstable [2]. Individual compounds are:

Acetyl nitrite, 0762  
Heptafluorobutyryl nitrite, 1368  
Propionyl nitrite, 1185  
Trifluoroacetyl nitrite, 0626  
See Sodium nitrite: Phthalic acid, etc., 4720

## ADHESIVE LABELS

Tolson, P. *et al.*, *J. Electrostat.*, 1993, **30**, 149  
A heavy duty lead-acid battery exploded when an operator peeled an adhesive label from it. Investigation showed that this could generate >8 kV potential. Discharge through the hydrogen/oxygen headspace consequent upon recharging batteries caused the explosion. The editor has remarked very vivid discharges when opening Chemical Society self-adhesive envelopes.  
See STATIC INITIATION INCIDENTS

## ADIABATIC CALORIMETRY

1. Hub, L., *Runaway Reactions*, 1981, Paper 3/K, 1–11
2. Hakl, J., *Runaway Reactions*, 1981, Paper 3/L, 1–11
3. Brogli, F. *et al.*, *Runaway Reactions*, 1981, Paper 3/M, 1–10
4. Townsend, D. I., *Runaway Reactions*, 1981, Paper 3/Q, 1–14
5. Cardillo, P. *et al.*, *J. Haz. Mat.*, 1984, **9**, 224

The Sikarex safety calorimeter system and its application to determine the course of adiabatic self-heating processes, starting temperatures for self-heating reactions, time to explosion, kinetic data, and simulation of real processes, are discussed with examples [1]. The Sedex (sensitive detection of exothermic processes) calorimeter uses a special oven to heat a variety of containers with sophisticated control and detection equipment, which permits several samples to be examined simultaneously [2]. The bench-scale heat-flow calorimeter is designed to provide data specifically oriented towards processing safety requirements, and a new computerised design

has become available [3]. The accelerating rate calorimeter is the most sophisticated and sensitive of the techniques, and it is claimed that very close parallels with large-scale process operations can be simulated [4].

*See* ACCELERATING RATE CALORIMETRY, ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY, HEAT FLOW CALORIMETRY

## AGITATION INCIDENTS

Weir, D. E., *Plant/Oper. Progr.*, 1986, **5**, 142–147

The relationship of agitation problems (failure, incomplete mixing, shear energy input) with thermal runaway reactions and ways of avoiding these, are discussed.

Several of the runaway reactions or violent incidents in the main text were caused by ineffective agitation or by the complete absence of agitation, particularly in reactions between 2 phases of widely differing densities. Individual cases involved are:

2-Chloronitrobenzene, 2141

Chromyl chloride, 4054

Diethyl 4-nitrophenyl thionophosphate, 3328

Ethylmagnesium iodide, 0859

Hydrogen peroxide, : Iron(II) sulfate, 2-Methylpyridine, Sulfuric acid, 4477

Lead(IV) oxide, : Carbon black, Chlorinated paraffin, Manganese(IV) oxide, 4834

Lithium tetrahydroaluminate, : Fluoroamides, 0075

4-Methyl-2-nitrophenol, 2767

Nitric acid, : *tert*-Butyl-*m*-xylene, Sulfuric acid, 4436

Nitric acid, : 2-Formylamino-1-phenyl-1,3-propanediol, 4436

Nitric acid, : Hydrocarbons, 4436

Nitric acid, : Nitrobenzene, Sulfuric acid, 4436

Nitric acid, : 1-Nitronaphthalene, Sulfuric acid, 4436

2-Nitrotoluene, : Alkali, 2763

Phosphorus tribromide, : Phenylpropanol, 0293

Potassium hydroxide, : Water, 4428

Sodium carbonate, 0552

Sodium dichromate, : Sulfuric acid, Trinitrotoluene, 4250

Sodium hydrogen carbonate, : Carbon, Water, 0390

Sulfinyl chloride, : Tetrahydrofuran, 4096

Sulfuric acid, : 2-Aminoethanol, 4479

Sulfuric acid, : 4-Methylpyridine, 4479

Tetrachlorosilane, : Ethanol, Water, 4173

*See related* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## AIR

1. Anon., *Site Safe News*, 1991, Summer, (HSE, Bootle, UK)
2. Allan, M., *CHAS Notes*, 1991, **IX**(5), 2
3. Sagan, C. *et al.*, *Nature*, 1993, **365**(6448), 720

A dangerous oxidant by virtue of its oxygen content, responsible for almost all fires, dust and vapour-cloud explosions, and for many other incidents. When heated to decomposition, air produces fumes of highly toxic nitrogen oxides. Air is frequently encountered compressed in combustible containers (tyres) which can explode with fatal results. Sometimes combustion seems to be the cause of the burst, this may be attributed to excessive heating and prior decomposition reactions generating a gaseous fuel [1]. Another fuel source causing a similar burst was an emergency inflator powered by liquid propane/butane [2].

The editor has been told that air can be explosive in its own right in a eucalyptus wood on a hot day, and, having smelt one, does not find this absolutely incredible. Explosive air is sometimes also found in caves and mines when decaying vegetable matter is present.

From a theoretical and thermodynamic standpoint, air should be considered a poison to carbon-based life [3]. Handle with due caution.

*See also* BATS, DIESEL ENGINES

## ALDEHYDES

## RCO.H

1. Editor's comments, 1995
2. Britton, L. B. *Process Saf. Progr.*, 1998, **17**(2), 138

These materials are very easily autoxidised and often have a low autoignition temperature. It is reported that many of the less volatile liquid aldehydes will eventually inflame if left exposed to air on an absorbent surface. The mechanism is undoubtedly similar to that giving rise to easy ignition in the air-oxidation of acetaldehyde and propionaldehyde; initial formation of a peroxy-acid which catalyses the further oxidation[1]. Autoignition temperatures of lower aldehydes are much reduced by pressure, but appear to depend little on oxygen content. The effect is worst in the presence of free liquid, in which initial oxidation appears to occur, possibly catalysed by iron, followed by ignition of the vapour phase [2]. An acetaldehyde/rust mix exploded at room temperature on increasing the air pressure to 7 bar.

*See* Acetaldehyde

Individually indexed compounds are:

- † Acetaldehyde, 0828
  - 4-Acetoxy-3-methoxybenzaldehyde, 3290
  - 4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3266
- † Acrylaldehyde, 1145
  - 4-Azidobenzaldehyde, 2697
- † Benzaldehyde, 2731
- † Butyraldehyde, 1607
- \* Chloroacetaldehyde oxime, 0787
  - 2-Chloro-6-nitrobenzaldehyde, 2650
  - 4-Chloro-3-nitrobenzaldehyde, 2651
  - 5-Chloro-2-nitrobenzaldehyde, 2652
- Cinnamaldehyde, 3134

- † Crotonaldehyde, 1516
- † 2-Ethylhexanal, 3050
- † Formaldehyde, 0416
- 2-Furaldehyde, 1836
- 4-Hydroxy-3-methoxybenzaldehyde, 2958
- 3-Hydroxy-4-nitrobenzaldehyde, 2690
- 4-Hydroxy-3-nitrobenzaldehyde, 2691
- 2-Indanecarboxaldehyde, 3288
- † Isobutyraldehyde, 1611
- † Isovaleraldehyde, 1958
- † Methacrylaldehyde, 1522
- 4-Methoxybenzaldehyde, 2956
- 3-Methoxy-2-nitrobenzaldehyde, 2937
- \* 2-Nitroacetaldehyde oxime, 0809
- 2-Nitroacetaldehyde
- 3-Nitrobenzaldehyde, 2687
- 4-Nitrobenzaldehyde, 2688
- Paraformaldehyde, 0417
- $\alpha$ -Pentylcinnamaldehyde, 3663
- Propionaldehyde, 1224
- Tridecanal, 3619
- † Valeraldehyde, 1966

*See also* PEROXIDISABLE COMPOUNDS, INSULATION, PAPER TOWELS

#### ALKALI-METAL ALLOYS

1. Mumford, C., *Chem. Brit.*, 1978, **14**, 170
2. Ingham, P. L., *Chem. Brit.*, 1978, **14**, 326
3. Bretherick, L., *Chem. Brit.*, 1978, **14**, 426
4. Sloan, S. A., *Chem. Brit.*, 1978, **14**, 597

In response to a statement [1] that alloys of 2 alkali-metals (Li–Na, K–Na) can be prepared in small amounts by beating the solid components together, without heating in the latter case, it was emphasised that the real hazard arises not from reaction of the surface coating of potassium superoxide with potassium, but with residues of oil or organic matter on the potassium which will explode under impaction with the superoxide [2]– [4].

*See* Potassium (*Slow oxidation*) *also* ALKALI METALS, below

#### ALKALI-METAL DERIVATIVES OF HYDROCARBONS

RM, ArM

1. Sidgwick, 1950, 68, 75
2. Leleu, *Cahiers*, 1977(88), 370

Alkali-metal derivatives of aliphatic or aromatic hydrocarbons, such as methyl-lithium, ethylsodium or phenylpotassium, are the most reactive towards moisture and air, immediately igniting in the latter. Derivatives of benzyl compounds, such as benzylsodium, are of slightly lower activity, usually but not always igniting in



air. Derivatives of hydrocarbons with definitely acidic hydrogen atoms (acetylene, phenylacetylene, cyclopentadiene, fluorene), though readily oxidised, are usually relatively stable in ambient air. Sodium phenylacetylde if moist with ether, ignites; derivatives of triphenylmethane also when dry [1]. Biphenyl-, naphthyl-, anthryl- and phenanthryl-sodium may all ignite in air when finely divided, and all react violently with water [2].

Specific compounds may be found in the groups:

*See also* ALKYL METALS, ARYL METALS, ORGANOMETALLICS

## ALKALI METALS

1. *Handling and Uses of the Alkali Metals* (Advances in Chemistry Series No. 19), Washington, ACS, 1957
2. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633–636
3. *Alkali Metal Dispersions*, Fatt, I. *et al.*, London, Van Nostrand, 1961
4. John, G. D., *School Sci. Rev.*, 1980, **62**(219), 279–286

The collected papers of a symposium at Dallas, April 1956, cover all aspects of the handling, use and hazards of lithium, sodium, potassium, their alloys, oxides and hydrides, in 19 chapters [1]. Interaction of all 5 alkali metals with water under various circumstances has been discussed comparatively [2]. In a monograph covering properties, preparation, handling and applications of the enhanced reactivity of metals dispersed finely in hydrocarbon diluents, the hazardous nature of potassium dispersions, and especially of rubidium and caesium dispersions is stressed [3]. Alkaline-earth metal dispersions are of relatively low hazard. Safety practices for small-scale storage, handling, heating and reactions of lithium potassium and sodium with water are reviewed [4].

*See* Potassium (reference 6)

## ALKANETHIOLS

## RSH

Ethylene oxide

*See* Ethylene oxide: Alkanethiols

Nitric acid

*See* Nitric acid: Alkanethiols

Individually indexed compounds are:

- † Butanethiol, 1712
- † 2-Butanethiol, 1713
- Dodecanethiol, 3567
- † Ethanethiol, 0933
- † Methanethiol, 0489
- † 2-Methylbutane-2-thiol, 2023
- † 3-Methylbutanethiol, 2024
- † 2-Methylpropanethiol, 1715
- † 2-Methyl-2-propanethiol, 1716

- † Pentanethiol, 2025
- † Propanethiol, 1289
- † 2-Propanethiol, 1290

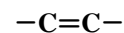
**ALKENE BIS(SULFONIUM PERCHLORATES)**       $R_2S^+ - C=C - S + R_2 \cdot 2ClO_4$

Shine, H. J. *et al.*, *J. Org. Chem.*, 1979, **44**, 915–917

The perchlorate salts of the bis-adducts of thianthrene (X = S) or phenoxathiin (X = O) with substituted acetylenes explode on heating.

See Thianthrenium perchlorate See other NON-METAL PERCHLORATES

**ALKENES**



Oxides of nitrogen

Simmons, H. E. *et al.*, *Chem. Eng. News*, 1995, **73**(32), 4

Several nitrogen oxides; dinitrogen trioxide, dinitrogen tetroxide and dinitrogen pentoxide; can readily add to alkenes; the resultant nitronitroso-dinitro- and nitronitrato-alkanes will be explosive if of low molecular weight and impurities make them more so. The tendency of nitroso compounds to exist as insoluble dimers, which precipitate and thus concentrate, makes dinitrogen trioxide a more hazardous contaminant than its higher homologues.

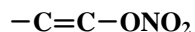
See Nitrogen oxide: Dienes, Oxygen

See 2-Chloro-1,3-butadiene: Preparative hazard

- † 1-Butene, 1577
- † *cis*-2-Butene, 1578
- † *trans*-2-Butene, 1623
- \* Δ 3-Carene, 3336
- † Cyclobutene, 1483
- cis*-Cyclododecene, 3351
- † Cycloheptene, 2837
- † Cyclohexene, 2406
- † Cyclopentene, 1891
- \* 2-Deuterobicyclo[2.2.1]hept-2-ene, 2811
- † 2,6-Dimethyl-3-heptene, 3190
- \* 1,1-Diphenylethylene
- \* *trans*-1,2-Diphenylethylene
- † Ethylene, 0781
- † 1-Heptene, 2851
- † 2-Heptene, 2852
- † 3-Heptene, 2853
- † 1-Hexene, 2459
- † 2-Hexene, 2460
- † 4-Methylcyclohexene, 2839
- † 2-Methyl-1-pentene, 2462
- † 4-Methyl-1-pentene, 2463

- † *cis*-4-Methyl-2-pentene, 2464
- † *trans*-4-Methyl-2-pentene, 2465
- † 2-Methylpropene, 1582
- † 1-Octene, 3040
- † 2-Octene, 3041
- \* 2-Pinene, 3339
- † Propene
- \* 1-Pyrrolidinylcyclohexene, 3350
- \* Styrene, 2945
- † 2,3,3-Trimethylbutene, 2855
- † 2,3,4-Trimethyl-1-pentene, 3042
- † 2,3,4-Trimethyl-2-pentene, 3044
- † 2,4,4-Trimethyl-1-pentene, 3043
- † 2,4,4-Trimethyl-2-pentene, 3045
- † 3,4,4-Trimethyl-2-pentene, 3046
- † Vinylcyclohexane, 3026

#### ALKENYL NITRATES

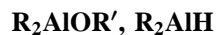


Tetrafluorohydrazine

*See* Tetrafluorohydrazine: Alkenyl nitrates

*See related* ALKYL NITRATES

#### ALKYLALUMINIUM ALKOXIDES AND HYDRIDES



Although substitution of a hydrogen atom or an alkoxy group for one alkyl group in a trialkylaluminium tends to increase stability and reduce reactivity and the tendency to ignition, these compounds are still of high potential hazard, the hydrides being used industrially as powerful reductants.

*See* ALKYLALUMINIUM DERIVATIVES (references 1,3,6)

Ethers

Wissink, H. G., *Chem. Eng. News*, 1997, **75**(9), 6

Dialkylaluminium hydrides can cleave lower ethers to generate gaseous products (hydrocarbons and/or hydrogen), which may pressurise and burst containers if solutions in ethers be stored.

Individually indexed compounds of this relatively small sub-group of commercially available compounds are:

- Diethylaluminium hydride, 1719
- Diethylethoxyaluminium, 2554
- Diisobutylaluminium hydride, 3082
- Dimethylaluminium hydride, 0936
- Dipropylaluminium hydride, 2552
- \* 4-Ethoxybutyldiethylaluminium, 3372
- Ethoxydiisobutylaluminium, 3373

Tetramethyldialuminium dihydride, 1778  
\* Triethoxydialuminium tribromide, 2555

## ALKYLALUMINIUM DERIVATIVES

1. Mirviss, S. B. *et al.*, *Ind. Eng. Chem.*, 1961, **53**(1), 53A –56A
2. Heck, W. B. *et al.*, *Ind. Eng. Chem.*, 1962, **54**(12), 35–38
3. Kirk-Othmer, 1963, Vol. 2, 38, 40
4. Houben-Weyl, 1970, Vol. 13.4, 19
5. 'Aluminium Alkyls', Brochure PB 3500/1 New 568, New York, Ethyl Corp., 1968
6. 'Aluminium Alkyls', New York, Texas Alkyls, 1971
7. Knap, J. E. *et al.*, *Ind. Eng. Chem.*, 1957, **49**, 875
8. Thomas, W. H., *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**(1), 120–122
9. Van Vliet, M. R. P. *et al.*, *Organometallics*, 1987, **6**, 1652–1654

This main class of ALKYLALUMINIUM DERIVATIVES is divided for structural convenience into the 3 groups: TRIALKYLALUMINIUMS; ALKYLALUMINIUM ALKOXIDES AND HYDRIDES; and ALKYLALUMINIUM HALIDES.

Individual compounds are indexed under their appropriate group titles, but since most of the available compounds are liquids with similar hazardous properties, these will be described collectively here. These aspects of the class have been extensively reviewed and documented [1,2,3,4,5,6,7,8].

Compounds with alkyl groups of C<sub>4</sub> and below all ignite immediately on exposure to air, unless diluted with a hydrocarbon solvent to 10–20% concentration [6]. Even these solutions may ignite on prolonged exposure to air, owing to exothermic autoxidation, which becomes rapid if solutions are spilled (high surface:volume ratio) [2,6]. Compounds with C<sub>5</sub>–C<sub>14</sub>alkyl groups (safe at 20–30% conc.) smoke in air but do not burn unless ignited externally or if the air is very moist. Contact with air enriched with oxygen above the normal 21% content will cause explosive oxidation to occur.

Fires involving alkylaluminium compounds are difficult to control and must be treated appropriately to particular circumstances [1,5,6], usually with dry-powder extinguishers. Halocarbon fire extinguishants (carbon tetrachloride, chlorobromomethane, etc.), water or water-based foam must not be applied to alkylaluminium fires. Carbon dioxide is ineffective unless dilute solutions are involved [5,6]. Suitable handling and disposal procedures have been detailed for both laboratory [1,2,5,6,7] and manufacturing [5,6] scales of operation.

See TRIALKYLALUMINIUMS

See ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

See ALKYLALUMINIUM HALIDES

### Alcohols

Alkylaluminium derivatives up to C<sub>4</sub> react explosively with methanol or ethanol, and triethylaluminium also with 2-propanol.

### Halocarbons

With the exception of chlorobenzene and 1,2-dichloroethane, halocarbon solvents are unsuitable diluents, as carbon tetrachloride and chloroform may react violently with alkylaluminium derivatives. The hazards of individually mixing 7 alkylaluminiums with 7 chlorinated solvents have been assessed comparatively. Most of a series of cyclic coordination complexes between triethylaluminium and  $\alpha$ -iminoketones decomposed violently when dissolved in halogenated solvents.

### Oxidants

In view of the generally powerfully reducing properties of alkylaluminium derivatives, deliberate contact with known oxidants must be under careful control with appropriate precautions.

### Water

Interaction of alkylaluminium derivatives up to C<sub>9</sub> chain length with liquid water is explosive and violent shock effects have been noted [4].

*See other* ALKYL METAL HALIDES, ALKYL METAL HYDRIDES, ALKYL METALS

## ALKYLALUMINIUM HALIDES

## RAIX<sub>2</sub>, R<sub>2</sub>AlX, R<sub>3</sub>Al·AlX<sub>3</sub>

Three main structural sub-groups can be recognised: alkylaluminium dihalides, dialkylaluminium halides, and trialkyldialuminium trihalides (equimolar complexes of a trialkylaluminium and an aluminium trihalide). While this is generally a very reactive group of compounds, similar in reactivity to trialkylaluminium compounds, increase in size of the alkyl groups present and in the degree of halogen substitution tends to reduce pyrophoricity.

*See* ALKYLALUMINIUM DERIVATIVES (references 1,2)

Individually indexed compounds of this group many of which are commercially available in bulk are:

- Diethylaluminium bromide, 1670
- Diethylaluminium chloride, 1671
- Diisobutylaluminium chloride, 3064
- Dimethylaluminium bromide, 0882
- Dimethylaluminium chloride, 0883
- Ethylaluminium bromide iodide, 0841
- Ethylaluminium dibromide, 0842
- Ethylaluminium dichloride, 0843
- Ethylaluminium diiodide, 0844
- \* Hexaethyltrialuminium trithiocyanate, 3695
- Methylaluminium diiodide, 0423
- Triethyldialuminium trichloride, 2556
- Trimethyldialuminium trichloride, 2556

*See other* ALKYL METAL HALIDES

**ALKYLBORANES****RBH<sub>2</sub>, R<sub>2</sub>BH, R<sub>3</sub>B**

1. Sidgwick, 1950, 371
2. Mirviss, S. B. *et al.*, *Ind. Eng. Chem.*, 1961, **53**(1), 53A
3. Brown, H. C. *et al.*, *Tetrahedron*, 1986, **42**, 5523–5530

Trimethylborane and triethylborane ignite in air, and tributylborane ignites in a thinly diffused layer, as when poured on cloth [1]. Generally, the pyrophoric tendency of trialkylboranes decreases with increasing branching on the 2- and 3-carbon atoms of the alkyl substituent(s) [2]. Reaction of a trialkylborane with oxygen under controlled, mild and safe conditions gives high yields of the corresponding alkanols [3].

Individually indexed compounds are:

- Bis(dibutylborino)acetylene, 3775
  - \* *N,N'*-Bis(diethylboryl)methylamine, 3223
  - Bis(dipropylborino)acetylene, 3670
  - Dibutyl-3-methyl-3-buten-1-ynylborane, 3618
  - † 1,2-Dimethylborane, 0961
  - † 1,1-Dimethyldiborane, 0960
  - Ethylpentaborane(9), 0973
  - \* Methylborylene, 0425
  - Methyldiborane, 0513
  - \* Perhydro-9*b*-boraphenalene, 3550
  - \* 1-Phenylboralane, 3317
  - \* Pivaloyloxydiethylborane, 3198
  - 'Tetraethyldiborane', 3098
  - Tetramethyldiborane, 1779
  - 'Tetrapropyldiborane', 3580
  - Tri-2-butylborane, 3570
  - miso*-Tributylborane, 3569
  - Triethylborane, 2559
  - Triethyldiborane, 2588
  - Trimethylborane, 1295
  - Trimethyldiborane, 1334
  - Tripropylborane, 3217
  - \* Tris(dimethylfluorosilylmethyl)borane, 3224
- See other* ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

**ALKYL CHLORITES****ROCl:O**

Chlorite esters, like chlorite salts, are explosively unstable.  
*See* Silver chlorite, Alone, or Iodoalkanes  
*See also* CHLORITE SALTS

**ALKYLHALOBORANES****RBX<sub>2</sub>, R<sub>2</sub>BX**

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

- \* Bis(difluoroboryl)methane, 0394
  - Bromodimethylborane, 0887
  - Butyldichloroborane, 1629
  - Chlorodibutylborane, 3065
  - Chlorodiethylborane, 1673
  - Chlorodipropylborane, 2534
  - Dibromomethylborane, 0426
  - Dichloroethylborane, 0845
  - \* Dichlorophenylborane, 2222
- See other* ALKYLNON-METAL HALIDES

### ALKYLHALOPHOSPHINES

### RPX<sub>2</sub>, R<sub>2</sub>PX

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

- \* 1,2-Bis(dichlorophosphino)ethane, 0797
  - Bis(trifluoromethyl)chlorophosphine, 0597
  - \* Bis(trifluoromethyl)cyanophosphine, 1053
  - tert*-Butyldifluorophosphine, 1646
  - Chlorodimethylphosphine, 0899
  - Di-*tert*-butylfluorophosphine, 3067
  - Dichloromethylphosphine, 0438
  - Difluorotrifluoromethylphosphine, 0361
  - Difluorotrifluoromethylphosphine oxide, 0360
  - Fluorobis(trifluoromethyl)phosphine, 0646
  - \* Fluorobis(trifluoromethyl)phosphine oxide, 0645
  - \* Tetrachlorotrifluoromethylphosphorane, 0333
- See other* ALKYLNON-METAL HALIDES

### ALKYLHALOSILANES

### RSiX<sub>3</sub>, RSiHX<sub>2</sub>, R<sub>2</sub>SiX<sub>2</sub>, R<sub>2</sub>SiHX, R<sub>3</sub>SiX

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

- † Chloromethylphenylsilane, 2810
  - † Chlorotrimethylsilane, 1304
  - † Cyanotrimethylsilane, 1665
  - † Dichlorodiethylsilane, 1683
  - † Dichlorodimethylsilane, 0902
  - † Dichloroethylsilane, 0903
  - † Dichloromethylsilane, 0470
  - † Dichloromethylvinylsilane, 1208
  - † Iodotrimethylsilane, 1306
  - † Methyltrichlorosilane, 0439
  - † Trichloroethylsilane, 0854
  - † Trichlorovinylsilane, 0746
  - \* Tris(dimethylfluorosilylmethyl)borane, 3224
- See other* ALKYLNON-METAL HALIDES

## ALKYL HYDROPEROXIDES

## ROOH

Swern, 1970, Vol. 1, 19; 1971, Vol. 2, 1, 29

Most alkylhydroperoxides are liquid, the explosivity of the lower members (possibly owing to presence of traces of the dialkyl peroxides) decreasing with increasing chain length.

### Transition metal complexes

Skibida, I. P., *Russ. Chem. Rev.*, 1975, 789–800

The kinetics and mechanism of decomposition of organic hydroperoxides in presence of transition metal complexes has been reviewed.

Individually indexed compounds are:

- \* 1-Acetoxy-6-oxo-cyclodecyl hydroperoxide, 3547
  - Allyl hydroperoxide, 1226
  - \* Barium methyl hydroperoxide, 0889
  - \* Bis(2-hydroperoxy-2-butyl) peroxide, 3078
  - \* Bis(2-hydroperoxy-4-methyl-2-pentyl) peroxide, 3566
  - 1,2- or 1,4-Bis(2-hydroperoxy-2-propyl)benzene, 3542
  - \*  $\alpha$ -(4-Bromophenylazo)benzyl hydroperoxide, 3606
  - \*  $\alpha$ -(4-Bromophenylazo)phenylethyl  $\alpha$ -hydroperoxide, 3648
  - \* 2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3156
  - tert*-Butyl hydroperoxide, 1698
  - 2-(4-Chlorophenyl)-1,1-dimethylethyl hydroperoxide, 3018
  - 2-Cyclohexenyl hydroperoxide, 2435
  - 1,1-Dichloroethyl hydroperoxide, 0794
  - 3,5-Dimethyl-3-hexyl hydroperoxide, 3075
  - Ethyl hydroperoxide, 0925
  - 1-Hydroperoxyphenylethane, 2985
  - Isopropyl hydroperoxide, 1283
  - Methyl hydroperoxide, 0486
  - \*  $\alpha$ -Phenylazobenzyl hydroperoxide, 3609
  - \*  $\alpha$ -Phenylazo-4-bromobenzyl hydroperoxide, 3607
  - \*  $\alpha$ -Phenylazo-4-fluorobenzyl hydroperoxide, 3608
  - 2-Phenyl-1,1-dimethylethyl hydroperoxide, 3332
  - 2-Phenyl-2-propyl hydroperoxide, 3166
  - 2-Tetrahydrofuryl hydroperoxide, 1624
  - \* 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide, 3312
- See also* ALLYLIC HYDROPEROXIDES,  $\alpha$ -PHENYLAZO HYDROPEROXIDES

## ALKYLIMINIOFORMATE CHLORIDES

'IMINOESTER HYDROCHLORIDES'  $\text{RC}(\text{:N}^+\text{H}_2)\text{OR}' \text{Cl}^-$

### Preparative hazard

*See* Hydrogen chloride: Alcohols, etc.



## ALKYLMETAL HALIDES

## RMX, RMX<sub>2</sub>, R<sub>2</sub>MX

This highly reactive group of organometallic compounds includes the groups:

ALKYLALUMINIUM HALIDES, GRIGNARD REAGENTS,  
TRIALKYLANTIMONY HALIDES

and the individually indexed compounds:

- \* Bis(chloromethyl)thallium chloride, 0796
- \* Chloroethylbismuthine, 0892
- \* Dichlorodi- $\mu$ -chlorobis(pentamethylcyclopentadienyl)dirhodium, 3806
- Diethylbismuth chloride, 1676
- Diethylgold bromide, 1672
- Dimethylantimony chloride, 0900
- Dimethylbismuth chloride, 0893
- Ethylmagnesium iodide, 0859
- Methylmagnesium iodide, 0446
- Methylzinc iodide, 0447

## ALKYLMETAL HYDRIDES

## R<sub>m</sub>MH<sub>n</sub>

This small group shows high reactivity or instability, individual compounds being:

Diethylgallium hydride, 1721  
Methylstibine, 0499

- \* Chloroethylbismuthine, 0892

## ALKYLMETALS

This reactive and usually pyrophoric class includes the groups

DIALKYL MAGNESIUMS, DIALKYLZINCS, DIPLUMBANES,  
TRIALKYLALUMINIUMS, TRIALKYLBISMUTHS

and the individually indexed compounds:

- \* Acetylenebis(triethyllead), 3672
- \* Acetylenebis(triethyltin), 3674
- Allyllithium, 1177
- \* Benzylsodium, 2787
- \* Bis(1-chloroethylthallium chloride) oxide, 1591
- \* Bis(dimethylamino)dimethylstannane, 2597
- \* Bis(dimethylstibinyl) oxide, 1761
- \* Bis(dimethylthallium)acetylide, 2519
- \* Bis(trifluoromethyl)cadmium-1,2-dimethoxyethane adduct, 0587
- \* Bis(trimethylsilylmethyl)magnesium, 3099
- 3-Buten-1-ynyltriethyllead, 3357
- \* 1-Butoxyethyl 3-trimethylplumbylpropionate, 3552
- Butyllithium, 1651
- tert*-Butyllithium, 1652
- Butylsodium, 1667
- \* 2-Chlorovinyltrimethyllead, 1989

- Cyclopentadienylgold(I), 1839
- Cyclopentadienylsodium, 1855
- $\mu$ -Cyclopentadienyltrimethyltitanium, 3038
- \* 1,2-Diaminoethanebis(trimethylgold), 3105
- \* Di-2-butenylcadmium, 3027
- Dibutylmagnesium, 3068
- \* Dibutylthallium isocyanate, 3193
- Dibutylzinc, 3080
- Diethylberyllium, 1675
- Diethylcadmium, 1677
- \* Diethyllead dinitrate, 1692
- Diethylmagnesium, 1687
- Diethyl telluride, 1717
- Diethylzinc, 1718
- Diisobutylzinc, 3081
- Diisopentylmercury, 3368
- Diisopentylzinc, 3371
- Diisopropylberyllium, 2535
- Dimethylberyllium, 0890
- \* Dimethylberyllium-1,2-dimethoxyethane, 0891
- Dimethylcadmium, 0894
- \* Di- $\mu$ -methylenebis(methylpentamethylcyclopentadienyl)dirhodium, 3855
- Dimethylmagnesium, 0908
- Dimethylmanganese, 0909
- Dimethylmercury, 0907
- Dimethyl(phenylethynyl)thallium, 3298
- Dimethyl-1-propynylthallium, 1938
- \* (Dimethylsilylmethyl)trimethyllead, 2605
- \* Dimethyltin dinitrate, 0914
- Dimethylzinc, 0935
- Dipropylmercury, 2537
- \* Divinylmagnesium, 1498
- \* Divinylzinc, 1547
- \* Dodecamethyltetraplatinum(IV) perchlorate, 3587
- \* 3-Ethoxycarbonyl-4,4,5,5-tetracyano-3-trimethylplumbyl-4,5-dihydro-3*H*-pyrazole, 3611
- \* Ethylenedicaesium, 0798
- Ethyllithium, 0862
- Ethylsodium, 0877
- $\mu,1,1'$ -Ferrocenediyldilithium, 3256
- \* Hexacyclohexyldilead, 3894
- Hexamethyldiplatinum, 2606
- \* Hexamethylerbium–hexamethylethylenediaminelithium complex, 2592
- Hexamethylrhenium, 2607
- Hexamethyltungsten, 2609
- \* Lithium hexamethylchromate(3–), 2590

- \* Lithium pentamethyltitanate–bis(2,2'-bipyridine), 2042
- \* Lithium tetramethylchromate(II), 1744
- \* Methylaluminiumbis(pentamethylcyclopentadienyltrimethyliridium), 3866
- \* Methylbismuth oxide, 0428
- 3-Methyl-3-buten-1-ynyltriethyllead, 3413
- Methylcopper, 0440
- Methylenedilithium, 0401
- Methylenemagnesium, 0402
- Methylithium, 0452
- Methylpotassium, 0448
- Methylsilver, 0421
- Methylsodium, 0463
- Octylsodium, 3053
- Pentamethyltantalum, 2046
- Potassium cyclopentadienide, 1846
- Propylcopper(I), 1251
- Propyllithium, 1253
- Propylsodium, 1269
- \* Tellurane-1,1-dioxide, 1980
- \* Tetraallyluranium, 3548
- Tetraethyllead, 3095
- Tetraethyltin, 3097
- Tetraisopropylchromium, 3577
- \* Tetramethylbis(trimethylsilanoxy)digold, 3382
- Tetramethyldigallane, 1748
- Tetramethyldistibane, 1769
- Tetramethyllead, 1767
- Tetramethylplatinum, 1768
- Tetramethyltellurium(IV), 1772
- † Tetramethyltin, 1771
- \* Tetravinyllead, 3016
- \* Triallylchromium, 3180
- Tributylgallium, 3572
- Tributylindium, 3573
- \* Tributyl(phenylethynyl)lead, 3811
- † Triethylaluminium, 2553
- Triethylantimony, 2574
- Triethylgallium, 2563
- Triethylindium, 2564
- Trimethylaluminium, 1291
- Trimethylantimony, 1320
- Trimethylbismuthine, 1298
- Trimethylgallium, 1305
- \* Trimethylgermylphosphine, 1332
- Trimethylindium, 1307

- \* Trimethylsilylmethyl lithium, 1722
- Trimethylthallium, 1321
- Tripropylantimony, 3221
- Tripropylindium, 3219
- \* Tripropyllead fulminate, 3363
- Tris(trimethylsilyl)aluminium etherate, 3620
- \* Tris(trimethylsilylmethyl)aluminium, 3584
- \* Tris(trimethylsilylmethyl)indium, 3585
- \* Trivinylantimony, 2405
- \* Trivinylbismuth, 2391
- \* Vinyl lithium, 0757

See also ARYLMETALS, METAL ACETYLIDES

See LITHIUM PERALKYLURANATES, TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES, ALKYLALUMINIUM DERIVATIVES

See ARYLMETALS

## ALKYL NITRATES

## RONO<sub>2</sub>

Alone, or Lewis acids

1. Boschan, R. *et al.*, *Chem. Rev.*, 1955, **55**, 505
2. Slavinskaya, R. A., *J. Gen. Chem. (USSR)*, 1957, **27**, 844
3. Boschan, R. *et al.*, *J. Org. Chem.*, 1960, **25**, 2012
4. Smith, 1966, Vol. 2, 458
5. Rüst, 1948, 284
6. Urbanski, 1965, Vol. 2, 128
7. Marker, C. D. *et al.*, *Synthesis*, 1977, 485–486
8. Olah, G. A. *et al.*, *Synthesis*, 1978, 452–453
9. Dougherty, V., *J. Haz. Mat.*, 1983, **7**, 247–258
10. Colclough, M. E. *et al.*, *Polym. Adv. Technol.*, 1994, **5**(9), 554

The group of potentially or actually explosive compounds has been reviewed [1]. Ethyl [1], isopropyl, butyl, benzyl and triphenylmethyl nitrates [3] in contact with sulfuric acid [2], tin(IV) chloride [2,3] or boron trifluoride [3] interact violently (after an induction period of up to several hours) with gas evolution. An autocatalytic mechanism was proposed. Although pure alkyl nitrates are stable in storage, traces of oxides of nitrogen sensitise them to decomposition, and may cause explosion on heating or storage at ambient temperature [4].

The most important applications of alkyl nitrates are based on their explosive properties. Methyl and ethyl nitrates are too volatile for widespread use; propyl nitrate has been used as a liquid monopropellant (as also has isopropyl nitrate). Ethylene dinitrate, glyceryl trinitrate and pentaerythritol tetranitrate are widely used as explosives, the two former liquids adsorbed on or blended with other compounds [1]. Poly(nitrate esters) such as poly(glycidyl nitrate) are being studied as energetic binders for explosives and propellants [10]. The nitrate esters of many polyhydroxy compounds (ethylene glycol, glycerol, 1-chloro-2,3-dihydroxypropane, erythritol, mannitol, sugars or cellulose) are all more or less shock-sensitive and will ignite or

explode on heating [5]. Glyceryl dinitrate is a slightly less sensitive and powerful explosive than the trinitrate, while the mononitrate explodes at 170°C in a sealed tube [6]. Use of dichloromethane as diluent provides a low-hazard procedure for preparing such esters [7], and in a new method of preparation, the esters are not isolated from solution in acetonitrile [8]. Methods of assessing the relative thermal stabilities of formulated propellant materials containing nitrate esters are reviewed, and a new test to measure isothermal time to auto-ignition is described, together with the Osawa method of predicting the half-life of the substances [9].

#### Transition metal derivatives

Lur'e, B. A. *et al.*, *Chem. Abs.*, 1981, **95**, 83199

The decomposition rates of several glycol nitrates and glyceryl trinitrate are greatly enhanced by the presence of transition metal oxides or chelates.

The decomposition rates of several glycol nitrates and glyceryl trinitrate are greatly enhanced by the presence of transition metal oxides or chelates.

2-*trans*-1-Azido-1,2-dihydroacenaphthyl nitrate, 3466

Benzyl nitrate, 2765

2,2-Bis[(nitrooxy)methyl]propane-1,3-diol dinitrate, 1901

\* Bis(2-nitratoethyl)nitric amide, 1602

Butyl nitrate, 1661

\* 1-Chloro-2,3-propylene dinitrate, 1160

2-Cyano-2-propyl nitrate, 1506

\* 2-Diethylammonioethyl nitrate nitrate, 2571

\* 2,3-Epoxypropyl nitrate

Ethylidene dinitrate, 0811

† Ethyl nitrate, 0870

Glyceryl trinitrate, 1196

† Isopropyl nitrate, 1266

Isosorbide dinitrate, 2380

Methyl nitrate, 0457

2,2'-Oxybis(ethyl nitrate), 1599

† Propyl nitrate, 1267

Triphenylmethyl nitrate, 3782

*See also* Lithium azide: Alkyl nitrates, etc., *also* NITRATING AGENTS (reference 3)

*See related* ALKENYL NITRATES

#### ALKYL NITRITES

#### RON:O

1. Sorbe, 1968, 146

2. Rüst, 1948, 285

3. Anon., private comm., 1985

Many alkyl nitrites are thermally unstable and may readily decompose or explode on heating [1]. Methyl nitrite explodes more violently than ethyl nitrite [2]. Lower alkyl nitrites have been known to decompose and burst the container, even in refrigerated storage [3]. Individually indexed compounds are:

† Butyl nitrite, 1658

† *tert*-Butyl nitrite, 1659

- Decyl nitrite, 3364
- † Ethyl nitrite, 0867
- † Isopentyl nitrite, 1996
- † Isopropyl nitrite, 1262
- † Methyl nitrite, 0455
- † Pentyl nitrite, 1998
- † Propyl nitrite, 1265

#### **ALKYLNON-METAL HALIDES**

**REX<sub>2</sub>, R<sub>2</sub>EX, R<sub>2</sub>EHX etc.**

This class of flammable, air-sensitive and usually pyrophoric compounds includes the groups:

*See also* ALKYLHALOBORANES, ALKYLHALOPHOSPHINES, ALKYLHALOSILANES

and the individually indexed compounds:

- \* Bis(trifluoromethyl)sulfur difluoride, 0648
- Chlorodimethylarsine, 0884
- \* Cyanodimethylarsine, 1199
- Dichloromethylarsine, 0424
- Dimethylfluoroarsine, 0885
- Dimethyliodoarsine, 0886
- Ethyliodomethylarsine, 1272
- Trifluoromethylsulfur trifluoride, 0363

#### **ALKYLNON-METAL HYDRIDES**

**REH<sub>2</sub>, R<sub>2</sub>EH, R<sub>2</sub>EH<sub>2</sub>, R<sub>3</sub>EH**

Several of the partially lower-alkylated derivatives of non-metal hydrides are pyrophoric in air. With other gaseous oxidants (halogens, etc.) the reaction may be explosive. The class includes the groups:

*See also* ALKYLBORANES, ALKYLPHOSPHINES, ALKYLSILANES

and the individually indexed compounds:

- Diethylarsine, 1720
- Dimethylarsine, 0937
- Ethylmethylarsine, 1293
- Methanetellurol, 0490
- † Methanethiol, 0489

*See* ALKANETHIOLS, ORGANIC BASES

*See also* the fully alkylated class ALKYLNON-METALS, below

#### **ALKYLNON-METALS**

**R<sub>n</sub>E**

Several of the fully lower-alkylated non-metals are pyrophoric in air, and with other gaseous oxidants (halogens, etc.), reaction may be explosive. The class includes the groups:

- ALKYLBORANES, ALKYLPHOSPHINES,
- ALKYLSILANES, SILYLHYDRAZINES

and the individually indexed compounds:

- \* Acetyldimethylarsine, 1628
- \* Allyldimethylarsine, 1983
- \* Bis(dimethylarsinyldiazomethyl)mercury, 2467
- \* Bis(dimethylarsinyl) oxide, 1737
- \* Bis(dimethylarsinyl) sulfide, 1738
- \* Bis(trifluoromethyl) disulfide, 0644
- Bis(trifluoromethyl) sulfide, 0643
- \* Dimethylphenylarsine, 2991
- \* Hexaphenylhexaarsane, 3891
- \* Lithium tetramethylborate, 1740
- Tetraethyldiarsane, 3087
- Tetramethyldiarsane, 1736
- Tribenzylarsine, 3822
- Triethylarsine, 2557
- Trimethylarsine, 1294

*See related* TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES

*See also* the partially alkylated class ALKYLNON-METAL HYDRIDES

#### ALKYL PERCHLORATES

#### ROClO<sub>3</sub>

1. Hofmann, K. A. *et al.*, *Ber.*, 1909, **42**, 4390
2. Meyer, J. *et al.*, *Z. Anorg. Chem.*, 1936, **228**, 341
3. Schumacher, 1960, 214
4. Burton, H. *et al.*, *Analyst*, 1955, **80**, 4
5. Hoffman, D. M., *J. Org. Chem.*, 1971, **36**, 1716
6. Zefirov, N. S. *et al.*, *J. Org. Chem.*, 1985, **50**, 1875

Methyl, ethyl and propyl perchlorates, readily formed from the alcohol and anhydrous perchloric acid, are highly explosive oils, sensitive to shock, heat and friction [1]. Many of the explosions which have occurred on contact of hydroxylic compounds with conc. perchloric acid or anhydrous metal perchlorates are attributable to the formation and decomposition of perchlorate esters [2,3,4]. Safe procedures for preparation of solutions of 14 *sec*-alkyl perchlorates are described. Heated evaporation of solvent caused explosions in all cases [5]. 1-Chloro-2-propyl, *trans*-2-chlorocyclohexyl, 1-chloro-2-propyl, 1,6-hexanediyl, hexyl, and 2-propyl perchlorates, prepared by a new method, are all explosive oils [6].

Relevant Individual entries are:

- \* 2-Azatricyclo[2.2.1.0<sup>2,6</sup>]hept-7-yl perchlorate, 2368
- Chlorine, : 2-Chloroalkyl aryl sulfides, Lithium perchlorate, 4020
- trans*-2-Chlorocyclohexyl perchlorate, 2420
- 3-Chloro-2-hydroxypropyl perchlorate, 1207
- 1-Chloro-2-propyl perchlorate, 1206
- Ethylene diperchlorate, 0795
- Ethyl perchlorate, 0852
- 1,6-Hexanediyl perchlorate, 2470

- Hexyl perchlorate, 2520
- 2(2-Hydroxyethoxy)ethyl perchlorate, 1643
- Magnesium perchlorate, : Trimethyl phosphite, 1315
- Methoxycarbonylmethyl perchlorate, 1166
- Methyl perchlorate, 0436
- \* Peroxyacetyl perchlorate, 0737
- Propyl perchlorate, 1249
- 2-Propyl perchlorate, 1250
- Trichloromethyl perchlorate, 0334
- Trifluoromethyl perchlorate, 0321

## ALKYLPHOSPHINES

## RPH<sub>2</sub>, R<sub>2</sub>PH, R<sub>3</sub>P

Many of the lower-alkyl substituted phosphines are pyrophoric; individually indexed compounds are:

- \* 1,2-Bis(*tert*-butylphosphino)ethane, 3378
- \* 1,2-Bis(di-*tert*-butylphosphino)ethane, 3776
- 1,2-Bis(diethylphosphino)ethane, 3379
- \* 1,2-Bis-(di-2-propylphosphino)ethane, 3673
- \* Bis(2-hydroxyethyl)methylphosphine, 2035
- \* Bis(trimethylphosphine)di(3,5-dibromo-2,6-dimethoxyphenyl)nickel, 3837
- \* Bis(trimethylphosphine)nickel(0)–acetylene complex, 3093
- \* Di[bis(trifluoromethyl)phosphido]mercury, 1375
- \* Diethyl ethanephosphonite, 2572
- Diethylmethylphosphine, 2036
- Diethylphosphine, 1734
- \* 2,6-Dimethyl-1,3-dioxo-2,6-diphosphacyclooctane, 2548
- Dimethylphenylphosphine, 3003
- \* Dimethylphenylphosphine oxide, 3002
- Dimethylphosphine, 0948
- \* Dimethyltrimethylsilylphosphine, 2045
- \* Diphenylphosphine, 3508
- 1,2-Diphosphinoethane, 0957
- \* Ethoxytriethyldiphosphinyl oxide, 3094
- Ethyldimethylphosphine, 1735
- Ethylenebis(dimethylphosphine), 2585
- Ethylphosphine, 0949
- \* 5-Methyl-1(1-methylethyl)-1,2,3-azadiphosphole, 2455
- Methylphosphine, 0498
- \* Phenylphosphine, 2360
- \* Potassium dinitrogentris(trimethylphosphine)cobaltate(1–), 3228
- \* 2-Tetrahydrofuranylidene(dimethylphenylphosphine-trimethylphosphine)-2,4,6-trimethylphenylnickel perchlorate, 3854
- \* 2-Tetrahydropyranylidene-bis(dimethylphenylphosphine)-3,4,6-trimethylphenyl-nickel perchlorate, 3877
- \* Tetrakis(diethylphosphino)silane, 3733



- Tetramethyldiphosphane, 1765
  - \* Tetramethyldiphosphane disulfide, 1766
  - † Tributylphosphine, 3575
  - Triethylphosphine, 2573
  - \* Triethylphosphinegold nitrate, 2558
  - \* Triethynylphosphine, 2124
  - Trifluoromethylphosphine, 0399
  - Triisopropylphosphine, 3220
  - Trimethylphosphine, 1319
  - 1-Trimethylsilyloxy-1-trimethylsilylphosphylidene-2,2-dimethylpropane, 3417
  - \* Triphenylphosphine, 3756
  - \* Tris(2,2-dimethylethyl)triphosphirane, 3576
  - \* Tris(2-propylthio)phosphine,
  - \* Tris(trifluoromethyl)phosphine, 1063
- See other* ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

## ALKYLSILANES

## $\text{RSiH}_3$ , $\text{R}_2\text{SiH}_2$ , $\text{R}_3\text{SiH}$ , $\text{R}_4\text{Si}$

- Griffiths, S. T. *et al.*, *Combust. Flame*, 1958, **2**, 244–252
- Measurements of the autoignition temperatures for several series of mono-, di-, tri- and tetra-alkylsilanes showed that the ease of oxidation decreases with increasing substitution. In this group of easily ignited or pyrophoric compounds, individually indexed compounds are:
- \* Benzylsilane, 2832
  - Bis(2-fluoro-2,2-dinitroethoxy)dimethylsilane, 2421
  - \* 1,2-Bis(triethylsilyl)hydrazine, 3583
  - \* 1,2-Bis(triethylsilyl)trimethylsilylhydrazine, 3696
  - \* *N,N'*-Bis(trimethylsilyl)aminoborane, 2612
  - \* *cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615
  - \* Bis(trimethylsilyl) chromate, 2591
  - \* Bis(trimethylsilyl)mercury, 2593
  - \* Bis(trimethylsilylmethyl)magnesium, 3099
  - † Bis(trimethylsilyl) oxide, 2601
  - \* 1,2-Bis(tripropylsilyl)hydrazine, 3777
  - \* *N-tert*-Butyl-*N*-trimethylsilylaminoborane, 2878
  - \* *N, N'*-Di-*tert*-butyl-*N, N'*-bis(trimethylsilyl)diaminophosphene, 3675
  - † Diethoxydimethylsilane, 2582
  - † Dimethylaminotrimethylsilane, 2043
  - \* (Dimethylsilylmethyl)trimethyllead, 2605
  - \* Dimethyltrimethylsilylphosphine, 2045
  - Formyl(triisopropyl)silane, 3370
  - Hexamethyldisilane, 2608
  - † Hexamethyldisilazane, 2610
  - Methylsilane, 0510
  - Propylsilane, 1331
  - \* Tetrakis(diethylphosphino)silane, 3733

- Tetrakis(trimethylsilyl)diaminodiphosphene, 3588
- \* Tetramethyldisiloxane, 1783
  - † Tetramethylsilane, 1770
  - \* 1,1,3,3-Tetramethylsiloxalane, 1774
  - \* Triethoxysilane, 2584
  - Triethylsilane, 2585
  - \* Triethylsilyl-1,2-bis(trimethylsilyl)hydrazine, 3586
  - \* Trimethylsilylmethylithium, 1722
  - \* *N*-Trimethylsilyl-*N*-trimethylsilyloxyacetamide, 3375
  - \* Tris(2-pylthio)silane, 3222
  - \* Tris(trimethylsilyl)aluminium, 3227
  - \* Tris(trimethylsilyl)aluminium etherate, 3620
  - \* *N, N, N'*-Tris(trimethylsilyl)diaminophosphine, 3232
  - \* Tris(trimethylsilylmethyl)aluminium, 3584
  - \* Tris(trimethylsilylmethyl)indium, 3585
  - \* Tris(trimethylsilyl)phosphine, 3229
  - Tris(trimethylsilyl)silane, 3231
- See other* ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

#### ALKYL TRIALKYLLEAD PEROXIDES

**ROOPbR'<sub>3</sub>**

Houben-Weyl, 1975, Vol. 13.3, 111

These unstable compounds may decompose very violently on heating.

*See other* ORGANOMINERAL PEROXIDES

#### ALKYNES

**R-C≡C-**

Oxides of Nitrogen

*See* Nitrogen oxide: Dienes, etc.

- † Acetylene, 0686
- † 1,3-Butadiyne, 1385
- \* 4,4'-(Butadiyne-1,4-diyl)bis(2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl), 3838
- † Buten-3-yne, 1423
- † 1-Butyne, 1481
- † 2-Butyne, 1482
- 1,7,13-Cyclooctadecatriene-3,5,9,11,15,17-hexayne, 3740
- 1,7,13,19-Cyclotetracosatetraene-3,5,9,11,15,17,21,23-octayne, 3843
- 1,4-Diethynylbenzene, 3241
- 11,12-Diethynyl-9,10-dihydro-9,10-ethenoanthracene, 3792
- 3,3-Dimethyl-1-butyne, 2408
- 1,8-Diphenyloctatetrayne, 3788
- Hepta-1,3,5-triyne, 2641
- 1-Heptene-4,6-diyne, 2707
- † 1-Heptyne, 2838
- 1,3-Hexadien-5-yne, 2290

- † 1,5-Hexadien-3-yne, 2291
- 1,5-Hexadiyne, 2292
- 2,4-Hexadiyne, 2293
- 1,3,5-Hexatriyne, 2074
- 3-Hexyne, 2415
- † 1-Hexyne, 2414
- † 2-Methyl-1-buten-3-yne, 1858
- † 3-Methyl-1-butyne, 1894
- 3-Nitrophenylacetylene, 2905
- \* 1,3,7-Octatrien-5-yne, 2944
- † 1-Octyne, 3022
- † 2-Octyne, 3023
- † 3-Octyne, 3024
- † 4-Octyne, 3025
- † 1-Pentyne, 1898
- † 2-Pentyne, 1899
- Phenylacetylene, 2912
- \* Poly(butadiyne), 1386
- † Propyne, 1125

*See other* ACETYLENIC COMPOUNDS

*See* ACYL AZIDES

*See also* ROTANES

## ALLOYS

### INTERMETALLIC COMPOUNDS

Individually indexed alloys or intermetallic compounds are:

- Aluminium amalgam, 0051
- Aluminium–copper–zinc alloy, 0050
- Aluminium–lanthanum–nickel alloy, 0080
- Aluminium–lithium alloy, 0052
- Aluminium–magnesium alloy, 0053
- Aluminium–nickel alloys, 0055
- Aluminium–titanium alloys, 0056
- Copper–zinc alloys, 4268
- Ferromanganese, 4389
- Ferrotitanium, 4391
- Lanthanum–nickel alloy, 4678
- Lead–tin alloys, 4883
- Lead–zirconium alloys, 4884
- Lithium–magnesium alloy, 4681
- Lithium–tin alloys, 4682
- Plutonium bismuthide, 0231
- Potassium antimonide, 4673
- Potassium–sodium alloy, 4646
- Silicon–zirconium alloys, 4910

- Silver–aluminium alloy, 0002
  - \* Silvered copper, 0003
  - Sodium–antimony alloy, 4797
  - Sodium germanide, 4418
  - Sodium–zinc alloy, 4798
  - Titanium–zirconium alloys, 4921
- See also* LANTHANIDE–TRANSITION METAL ALLOY HYDRIDES

## ALLYL COMPOUNDS



Several allyl compounds are notable for their high flammability and reactivity. There are group entries for:

*See also* ALLYLIC HYDROPEROXIDES, ALLYL TRIFLUOROMETHANESULFONATES

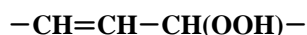
Individually indexed compounds are:

- † Allyl acetate, 1912
  - Allyl benzenesulfonate, 3155
- \* Allyldimethylarsine, 1983
- † Allyl formate, 1524
  - Allyl hydroperoxide, 1226
- \* Allyl isothiocyanate, 1471
  - Allyllithium, 1177
  - Allylmercury(II) iodide, 1173
  - 1-Allyloxy-2,3-epoxypropane, 2434
  - Allyl phosphorodichloridite, 1169
  - N*-Allylthiourea, 1600
  - Allyl 4-toluenesulfonate, 3315
- † Allyl vinyl ether, 1904
- † 3-Aminopropene, 1254
  - 3-Azidopropene, 1188
- † 1-Bromo-2-butene, 1548
- † 3-Bromo-1-propene, 1153
  - N*-Chloroallylamine, 1202
  - 1-Chloro-4-(2-nitrophenyl)-2-butene, 3270
- † 3-Chloropropene, 1158
- † 3-Cyanopropene, 1465
- † Diallylamine, 2450
- † Diallyl ether, 2431
  - Diallyl peroxydicarbonate, 2989
  - Diallyl phosphite, 2456
  - Diallyl sulfate, 2443
  - Diallyl sulfide, 2447
- \* Di-2-butenylcadmium, 3027
- † 3,3-Dimethoxypropene
  - 1-Heptene-4,6-diyne, 2707
- † 3-Iodopropene, 1174

- † 2-Propene-1-thiol, 1239
- † 2-Propen-1-ol, 1223
  - Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3505
  - Tetraallyl-2-tetrazene, 3545
- \* Tetraallyluranium, 3548
- \* Triallylchromium, 3180
  - 2,4,6-Triallyloxy-1,3,5-triazine, 3530
  - Triallyl phosphate, 3184
  - 3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2847

*See other* PEROXIDISABLE COMPOUNDS

### ALLYLIC HYDROPEROXIDES



Preparative hazard

Frimer, A. A., *J. Org. Chem.*, 1977, **42**, 3194–3196, footnote 7

A new method of preparation involves interaction of allylic halides in solvents with 98% hydrogen peroxide in presence of silver ion and base at ambient temperature under argon. The reactions must be run in the dark to prevent precipitation of metallic silver, which will catalyse decomposition of the hydroperoxide or excess hydrogen peroxide. In an experiment not run in the dark, the hydroperoxide from 3-chlorocyclohexene ignited spontaneously after isolation and concentration.

*See other* ALKYL HYDROPEROXIDES

### ALLYL TRIFLUOROMETHANESULFONATES



Alone, or Aprotic solvents

Vedejs, E. *et al.*, *J. Org. Chem.*, 1977, **42**, 3109–3113

Trifluoromethanesulfonate esters ('triflates') of allyl alcohol and its derivatives are very reactive and undiluted samples must be stored in vented containers at  $-78^\circ\text{C}$ . A chilled sample of allyl triflate in a sealed ampoule exploded on being allowed to warm to ambient temperature. The esters react violently with aprotic solvents such as DMF or DMSO. Individually indexed compounds are:

2-Chloro-2-propenyl trifluoromethanesulfonate, 1426

3-Methoxycarbonylpropen-2-yl trifluoromethanesulfonate, 2353

Prop-2-enyl trifluoromethanesulfonate, 1461

3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2847

*See other* ALLYL COMPOUNDS, SULFUR ESTERS

### AMINATION INCIDENTS

Gordon, M. D., *Adv. Instrum.*, 1988, **43**(1), 75–81

Kinetic simulation methods are used as advisory controls in potentially thermally hazardous batch amination reactions of nitroaromatic compounds. Time–temperature process data are fed as input to a kinetic simulation computer program which calculates conversions, heat release and pressure profiles. Results

are compared continuously on-line with measured batch data to detect any deviations from normal operating conditions.

Incidents involving reactions with either ammonia or organic amines (sometimes only in catalytic proportions) may be found under the entries:

Benzenediazonium-2-carboxylate, : Aniline, or Isocyanides, 2659

4-Chloroacetophenone, : Dimethylamine, 2929

1-Chloro-2,4-dinitrobenzene, : Ammonia, 2098

2-Chloronitrobenzene, : Ammonia, 2141

*See related* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## AMINE OXIDES

**RR'R''N → O**

Editor's comments

Several tertiary amine oxides are reported as exploding, usually on heating well above 100°C. Paradoxically, these tend to be the more stable members of the group, those which for conformational reasons cannot undergo the Cope rearrangement. As this class of compound is of growing importance, more incidents can be expected, possibly including violent decomposition of the alkylhydroxylamine products of the Cope reaction as well as the apparently radical branched chain, higher temperature decomposition which accounts for present reports. Early workers developed spot tests for amine oxides which later study has shown they do not perform but hydrogen peroxide does; since amine oxides tenaciously hold water as hydrates it must be suspected that they can also form hydrogen peroxides if made using excess hydrogen peroxide. These will be more dangerous than the amine oxide itself.

*See also* CRYSTALLINE HYDROGEN PEROXIDATES

*See other* N-O COMPOUNDS, N-OXIDES

## AMINIUM IODATES AND PERIODATES

**RN<sup>+</sup>H<sub>3</sub> IO<sub>3</sub><sup>-</sup>, RN<sup>+</sup>H<sub>3</sub>IO<sub>4</sub><sup>-</sup>**

Fogel'zang, A. E. *et al.*, *Chem. Abs.*, 1975, **83**, 8849

Combustion rates of the periodate salts of amines exceed those of the corresponding iodate salts.

*See* OXOSALTS OF NITROGENOUS BASES, PERCHLORATE SALTS OF NITROGENOUS BASES

## AMINIUM NITRATES

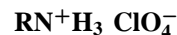
**RN<sup>+</sup>H<sub>3</sub> NO<sub>3</sub><sup>-</sup>**

1. Anon., *Chem. Hazards Ind.*, 1992, (Jul.) 1218

Many nitrate salts of amines are highly crystalline, which encourages their use to isolate amines; they are also often explosive, which does not. An industrial explosion consequent upon inadvertent isolation of such in part of a production plant, with subsequent overheating is reported [1].

Nitric Acid: Alkylamines

OXOSALTS OF NITROGENOUS BASES

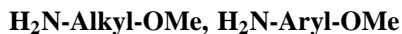
**AMINIUM PERCHLORATES**

Datta, R. L. *et al.*, *J. Chem. Soc.*, 1919, **115**, 1006–1010

Many perchlorate salts of amines explode in the range 215–310°C, and some on impact at ambient temperature. Individually indexed compounds are to be found in the group entries:

PERCHLORATE SALTS OF NITROGENOUS BASES

POLY(AMINIUM) PERCHLORATES

**AMINOMETHOXY COMPOUNDS**

Several members of this group show considerable energies of decomposition by DSC examination.

*See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Individually indexed compounds are:

- 2-Bromo-3,5-dimethoxyaniline, 2974
- 3-Chloro-4-methoxyaniline, 2795
- 3,5-Dimethoxyaniline, 2999
- 2-Methoxyaniline, 2816
- 3-Methoxyaniline, 2817
- 4-Methoxyaniline, 2818
- \* 2-Methoxyanilinium nitrate, 2829
- 3-Methoxybenzylamine, 2997
- † 2-Methoxyethylamine, 1312
- 2-Methoxy-5-nitroaniline, 2802
- 4-Methoxy-1,3-phenylenediamine, 2826
- \* 1-(4-Methoxyphenyl)-3-methyltriazene, 3000
- 3-Methoxypropylamine, 1730

*See other* ORGANIC BASES

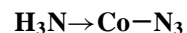
**AMMINECHROMIUM PEROXOCOMPLEXES**

This group of compounds, previously described as ‘amine perchromates’, is characterised by the presence of basic nitrogen and peroxy ligands within the same coordination sphere. This creates a high tendency towards explosive decomposition, which sometimes apparently occurs spontaneously. Individually indexed compounds are:

- Ammine-1,2-diaminoethanediperoxochromium(IV), 0968
- Aqua-1,2-diaminoethanediperoxochromium(IV), 0965
- Aqua-1,2-diaminopropanediperoxochromium(IV) dihydrate, 1336
- Bis(2-aminoethyl)aminediperoxochromium(IV), 1776
- 1,2-Diamino-2-methylpropaneoxodiperoxochromium(VI), 1746
- Dianilineoxodiperoxochromium(VI), 3523
- \* (Dimethyl ether)oxodiperoxochromium(VI), 0904
- \* Hexamethylenetetrammonium tetraperoxochromate(V)?, 3779
- Hydrogen cyanide, 0380

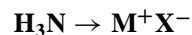
- Oxidiperoxodipyridinechromium(VI), 3274
- \* Oxodiperoxodi(pyridine *N*-oxide)molybdenum, 3279
  - \* Oxodiperoxodi(pyridine *N*-oxide)tungsten, 3283
  - Oxidiperoxodiquinolinechromium(VI), 3748
  - \* Oxodiperoxomolybdenum–hexamethylphosphoramide, 4718
  - Oxidiperoxopyridinechromium *N*-oxide, 1844
  - \* Oxodiperoxy(pyridine)(1,3-dimethyl-2,4,5,6-tetrahydro-2-*1H*)-pyrimidinone)molybdenum, 3410
  - \*  $\mu$ -Peroxobis[ammine(2,2',2''-triaminotriethylamine)cobalt(III)](4+) perchlorate, 3591
  - \* Potassium pentacyanodiperoxochromate(5–), 1810
  - Triamminediperoxochromium(IV), 4231
  - \* Triphenylphosphine oxide-oxodiperoxochromium(VI), 3752
- See PEROXOCHROMIUM COMPOUNDS  
See related AMMINEMETAL OXOSALTS

### AMMINEMETAL AZIDES



1. Joyner, T. B., *Chem. Abs.*, 1970, **72**, 113377
  2. Narang, K. K. *et al.*, *Synth. React. Inorg. Met.-Org. Chem.*, 1996, **26**(4), 573
- The explosive properties of a series of 5 amminecobalt(III) azides were examined in detail. Compounds were hexaamminecobalt triazide, pentaammineazidocobalt diazide, *cis*- and *trans*-tetraamminediazidocobalt azide, triamminecobalt triazide [1]. A variety of hydrazine complexed azides and chloroazides of divalent metals have been prepared. Those of iron, manganese and copper could not be isolated; cobalt, nickel, cadmium and zinc gave products stable at room temperature but more or less explosive on heating [2].
- See related METAL AZIDES, METAL AZIDE HALIDES

### AMMINEMETAL HALIDES



Author's comment.

Although free from the formally oxidising anions present in the two groups below, a few of these compounds show instability. These are:

*cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615

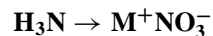
Pentaamminechlororuthenium chloride, 4137

*N,N,N',N'*-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) bromide, 3225

*N,N,N',N'*-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) iodide, 3226

See AMMINEMETAL OXOSALTS

### AMMINEMETAL NITRATES



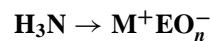
Author's comment.

Compounds in this group show explosive instability tending towards that of the perchlorate analogues in the entry following. Individual nitrates are:



- Bis(2-aminoethyl)aminesilver nitrate, 1773  
 Bis(1-methylbenzotriazole)cobalt(II) nitrate, 3652  
 Diamminenitratocobalt(II) nitrate, 4202  
 Diamminepalladium(II) nitrate, 4562  
 Hexaamminechromium(III) nitrate, 4234  
 \* Hexaamminecobalt(III) hexanitrocobaltate(3-), 4219  
 Hexaamminecobalt(III) nitrate, 4210  
 \* Hexahydroxylaminecobalt(III) nitrate, 4211  
 \* Hexaureachromium(III) nitrate, 2623  
 Pentaaminenitratocobalt(III) nitrate, 4207  
 Pentaaminenitrochromium(III) nitrate, 4233  
 Tetraamminecopper(II) nitrate, 4276  
 Tetraamminehydroxynitratoplatinum(IV) nitrate, 4594  
 Tetraaminenickel(II) nitrate, 4587  
 Tetraaminepalladium(II) nitrate, 4588  
 Tetraamineplatinum(II) nitrate, 4589  
 Triaminenitratoplatinum(II) nitrate, 4582  
 1,2,4-Triazolo[4,3-*a*]pyridine-silver nitrate, 2270  
 \* Triethylphosphinegold nitrate, 2558  
 Tris(2,3-diaminobutane)nickel(II) nitrate, 3589  
 Tris(1,2-diaminoethane)cobalt(III) nitrate, 2622  
 See AMMINEMETAL OXOSALTS (next below)

#### AMMINEMETAL OXOSALTS



1. Mellor, 1941, Vol. 2, 341–364, 404
2. Tomlinson, W. R. *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 375
3. Wendlandt, W. W. *et al.*, *Thermal Properties of Transition Metal Complexes*, Barking, Elsevier, 1967
4. Bretherick, L., *J. Chem. Educ.*, 1970, **47**, A204
5. Ray, P., *Chem. Rev.*, 1961, **61**, 313
6. Joyner, T. B., *Can. J. Chem.*, 1969, **47**, 2729–2730
7. Hoppesch, C. W. *et al.*, *ACS Div. Fuel Chem. Preprints*, 1963, **7**(3), 235–241
8. Friederich, W. *et al.*, *Chem. Abs.*, 1927, **21**, 1184
9. Anagnostopoulos, A. *et al.*, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2235–2238
10. Patil, K. C., *Thermochim. Acta*, 1976, **15**, 257–260
11. Springborg, J. *et al.*, *Inorg. Synth.*, 1978, **18**, 78
12. Shidlovskii, A. A. *et al.*, *Chem. Abs.*, 1979, **90**, 57447
13. Robinson, W. R., *J. Chem. Educ.*, 1985, **62**(11), 1001
14. Hasenpusch, W. J., *Prakt. Chem./Chem. Ztg.*, 1993, **335**(2), 193

Metal compounds containing both coordinated ammonia, hydrazine, hydroxylamine or similar nitrogenous donors, and coordinated or ionic perchlorate, chlorate, nitrate, nitrite, nitro, permanganate or other oxidising groups will decompose violently under various conditions of impact, friction or heat [1,2]. From tabulated data for 17 such compounds of Co and Cr, it is considered that oxygenated *N*-coordinated compounds, (particularly those which are oxygen balanced) cover

a wide range of explosive types; many may explode powerfully with little or no provocation, and should be considered extremely dangerous, as some are sensitive enough to propagate explosion under water. The same considerations may be expected to apply to amines of silver, gold, cadmium, lead and zinc which contain oxidising radicals [2]. The topic has been reviewed [3] and possible hazards in published student preparations were emphasised [4]. Some of the derivatives of metal biguanide and guanylurea complexes [5] are of this group.

Unexpected uniformities observed in the impact-sensitivities of a group of 22 aminocobalt oxosalts are related to kinetic factors during the initiation process [6]. A series of ammine derivatives of cadmium, cobalt, copper, mercury, nickel, platinum and zinc with (mainly) iodate anions was prepared and evaluated as explosives [7]. Earlier, ammine and hydrazine derivatives of cadmium, cobalt, copper and nickel with chlorate or perchlorate anions had been evaluated as detonators. Dihydrazinecopper(II) chlorate had exploded when dried at ambient temperature [8].

A series of pyrazole complexes which decompose explosively above 200°C is notable in that the anion is sulfate, rather than the more obvious oxidant species usually present. The compounds are manganese sulfate complexed with 4 mol of pyrazole or 3-methylpyrazole, and cadmium or zinc sulfates complexed with 4 and 3 mol of 3-methylpyrazole, respectively [9]. Around 100°C the hexaammine diperchlorates of copper and zinc decompose to the tetraammines, and those of cadmium, cobalt, manganese and nickel to the diammines. Around 220°C all these lower amines decompose explosively to the metal oxides (or the chloride for cadmium) [10]. The use of a soft polythene rod is recommended to reduce the possibility of explosions when handling perchlorate and similar salts on sintered filters [11]. Ignition temperatures and burning velocities of the hydrazine complexes of the picrates, styphnates or nitrates of cobalt, copper or nickel were 100°C lower, and an order of magnitude higher, respectively, than those of the corresponding ammine complexes [12]. A 3 g sample of the perchlorate salt of a polyaminerrhodium complex exploded with great violence in a rotary evaporator flask heated in a water bath [13]. A series of tetrammine metal(II) nitrates (Pt, Pd, Cu, Ni) were all found to be practically and legally classifiable as sensitive explosives. It was suggested that heavy metal contamination was responsible for the ammonium nitrate/sulphate explosion at Oppau [14].

Individually indexed compounds in this large group are:

- Ammonium hexanitrocobaltate(3-), 4206
- Aquafluorobis(1,10-phenanthroline)chromium(III) perchlorate, 3846
- \* Basic trihydrazinecadmium perchlorate, 3951
- (Benzenesulfonato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614
- \* 2,2'-Bipyridine *N,N'*-dioxide-dicarbonylrhodium(I) perchlorate, 3454
- 4,4'-Bipyridyl-bis(pentaammineruthenium(III) perchlorate), 3385
- 2,2'-Bipyridyldichloropalladium(IV) perchlorate, 3255
- Bis(2-aminoethyl)aminesilver nitrate, 1773
- N,N'*-Bis(3-aminopropyl)-1,4-diazacycloheptanenickel(II) perchlorate, 3415

- Bis(1,2-diaminoethane)diaquacobalt(III) perchlorate, 1793  
 Bis(1,2-diaminoethane)dichlorocobalt(III) chlorate, 1786  
 Bis(1,2-diaminoethane)dichlorocobalt(III) perchlorate, 1787  
*cis*-Bis(1,2-diaminoethane)dinitrocobalt(III) iodate, 1784  
 Bis(1,2-diaminoethane)dinitrocobalt(III) perchlorate, 1784  
 Bis(1,2-diaminoethane)hydroxooxorhenium(V) perchlorate, 1791  
 Bis(1,2-diaminopropane)-*cis*-dichlorochromium(III) perchlorate, 2613  
 Bis(diethylenetriamine)cobalt(III) perchlorate, 3106  
 \* 1,2-Bis(diphenylphosphino)ethanepalladium(II) perchlorate, 3864  
 Bis(hydrazine)diperchloratochromium(III) perchlorate, 4128  
 Bis(hydrazine)nickel perchlorate, 4069  
 \* Bis(hydrazine)tin(II) chloride, 4070  
 \* Bis(hydroxylamine)zinc chloride, 4067  
 \* Bis(2-methyl-1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3833  
 \* Bis(1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3791  
 \* Bis *O,N*[(*N'*-pent-2-en-2-oxy-4-ylidene)-*N,S*-dimethyldithiocarbazate]  
 copper(II)perchlorate, 3718  
 Bis(*O*-salicylidenaminopropylaziridine)iron(III) perchlorate, 3853  
 \* Bis(tetramethyldiphosphane disulfide)cadmium perchlorate, 3102  
 \* Carbonyl-bis(triphenylphosphine)iridium–silver diperchlorate, 3898  
 \* 5-*p*-Chlorophenyl-2,2-dimethyl-3-hexanone, 3664  
 Copper(II) perchlorate, : Polyfunctional amines, 4057  
 Copper(II) perchlorate, : *N*-(2-Pyridyl)acylacetamides, 4057  
 2(5-Cyanotetrazole)pentaamminecobalt(III) perchlorate, 0974  
 \* 1,5-Cyclooctadiene-bis(4-chloropyridine *N*-oxide)rhodium(I)  
 perchlorate, 3761  
 Diamminenitratocobalt(II) nitrate, 4202  
 Diamminepalladium(II) nitrate, 4562  
 Diamminepalladium(II) nitrite, 4559  
*cis*-Diammineplatinum(II) nitrite, 4560  
 Diamminesilver permanganate, 0018  
*trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III)  
 perchlorate, 3376  
 \* Dicarbonyl(phenanthroline *N*-oxide)rhodium(I) perchlorate, 3626  
 \* Dicarbonylpyrazinerhodium(I) perchlorate, 2147  
 \* *trans*-Dichlorobis[1,2-phenylenebis(dimethylarsine)]palladium(IV)  
 diperchlorate, 3808  
 \* Di[*N,N'*-Ethylenebis(2-oxidoacetophenoneiminato)copper(II)]  
 oxovanadium(IV) diperchlorate, 3893  
 Dihydrazinecobalt(II) chlorate, 4049  
 Dihydrazinemanganese(II) nitrate, 4570  
 Dihydrazinesilver nitrate, 0019  
 6,6'-Dihydrazino-2,2'-bipyridylnickel(II) perchlorate, 3303  
 Dipyridinesilver(I) perchlorate, 3267  
 \* Di[tris(1,2-diaminoethane)chromium(III)] triperoxodisulfate, 3592  
 \* Di[tris(1,2-diaminoethane)cobalt(III)] triperoxodisulfate, 3593

Hexaamminechromium(III) nitrate, 4234  
 Hexaamminechromium(III) perchlorate, 4129  
 Hexaamminecobalt(III) chlorate, 4125  
 Hexaamminecobalt(III) hexanitrocobaltate(3-), 4219  
 Hexaamminecobalt(III) iodate, 4208  
 Hexaamminecobalt(III) nitrate, 4210  
 Hexaamminecobalt(III) perchlorate, 4126  
 Hexaamminecobalt(III) permanganate, 4209  
 Hexaamminenickel chlorate, 4074  
 Hexaamminenickel perchlorate, 4075  
 Hexahydroxylaminecobalt(III) nitrate, 4211  
 \* Hexakis(pyridine)iron(II) tridecacarbonyltetraferate(2-), 3906  
 \* Hexamethylenetetrammonium tetraperoxochromate(V)?, 3779  
 \* Hexaureachromium(III) nitrate, 2623  
 \* Hexaureagallium(III) perchlorate, 2620  
 4-[2-(4-Hydrazino-1-phthalazinyl)hydrazino]-4-methyl-2-pentanone(4-hydrazino-1-phthalazinyl)hydrazonedinickel(II) tetraperchlorate, 3836  
 Isonicotinamidepentaammineruthenium(II) perchlorate, 2618  
 \* Mercury(II) perchlorate, 4078  
 Octaamine- $\mu$ -hydroxy[ $\mu$ -(peroxy-*O:O'*)]dirhodium(3+) perchlorate, 4138  
 Octaamine- $\mu$ -hydroxy[ $\mu$ -(superoxo-*O,O'*)]dirhodium(4+) nitrate, 4597  
 \* Oxybis(*N,N*-dimethylacetamidetriphenylstibonium) perchlorate, 3911  
 Pentaammineaquacobalt(III) chlorate, 4124  
 Pentaamminechlorocobalt(III) perchlorate, 4123  
 Pentaamminedinitrogenosmium(II) perchlorate, 4072  
 Pentaamminenitratocobalt(III) nitrate, 4207  
 Pentaamminenitrochromium(III) nitrate, 4233  
 Pentaamminephosphinatochromium(III) perchlorate, 4053  
 Pentaamminephosphinatocobalt(III) perchlorate, 4050  
 Pentaamminepyrazineruthenium(II) perchlorate, 1792  
 Pentaamminepyridineruthenium(II) perchlorate, 2048  
 Pentaamminethiocyanatocobalt(III) perchlorate, 0519  
 Pentaamminethiocyanatoruthenium(III) perchlorate, 0520  
 \* Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3778  
 \*  $\mu$ -Peroxobis[ammine(2,2',2''-triaminotriethylamine)cobalt(III)](4+) perchlorate, 3591  
 \* Tetraacrylonitrilecopper(I) perchlorate, 3510  
 \* Tetra(3-aminopropanethiolato)trimercury perchlorate, 3582  
 Tetraamminebis(dinitrogen)osmium(II) perchlorate, 4071  
 Tetraammine-2,3-butanediimineruthenium(III) perchlorate, 1794  
 Tetraamminecadmium permanganate, 3956  
 Tetraamminecopper(II) bromate, 0264  
 Tetraamminecopper(II) nitrate, 4276  
 Tetraamminecopper(II) nitrite, 4275  
 Tetraamminecopper(II) sulfate, 4274  
 Tetraamminedithiocyanatocobalt(III) perchlorate, 0969

- Tetraamminehydroxynitratoplatinum(IV) nitrate, 4594  
 Tetraamminepalladium(II) nitrate, 4588  
 Tetraamminezinc peroxodisulfate, 4586  
 1,4,8,11-Tetraazacyclotetradecanenickel(II) perchlorate, 3376  
 Tetrakis( $\mu_3$ -2-amino-2-methylpropanolato)tetrakis( $\mu_2$ -2-amino-2-methylpropanolato)hexacopper(II) perchlorate, 3883  
 Tetrakis(3-methylpyrazole)cadmium sulfate, 3716  
 Tetrakis(3-methylpyrazole)manganese(II) sulfate, 3717  
 Tetrakis(4-*N*-methylpyridinio)porphinecobalt(III)(5+) perchlorate, 3908  
 Tetrakis(4-*N*-methylpyridinio)porphineiron(III)(5+) perchlorate, 3909  
 Tetrakis(pyrazole)manganese(II) sulfate, 3538  
 \* Tetrakis(thiourea)manganese(II) perchlorate, 1785  
 Triamminenitratoplatinum(II) nitrate, 4582  
 Triamminetrinitrocobalt(III), 4204  
 \* 1,4,7-Triazacyclononanetricarbonylmolybdenum hydride perchlorate, 3185  
 \* 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate, 3186  
 1,2,4-Triazolo[4,3-*a*]pyridine–silver nitrate, 2270  
 Trihydrazinealuminium perchlorate, 0064  
 Trihydrazinecadmium chlorate, 3950  
 Trihydrazinecobalt(II) nitrate, 4205  
 Trihydrazinenickel(II) nitrate, 4592  
 Tris(2,2'-bipyridine)chromium(II) perchlorate, 3874  
 Tris(2,2'-bipyridine)silver(II) perchlorate, 3873  
 Tris(2,3-diaminobutane)nickel(II) nitrate, 3589  
 Tris(1,2-diaminoethane)chromium(III) perchlorate, 2619  
 Tris(1,2-diaminoethane)cobalt(III) nitrate, 2622  
 Tris(1,2-diaminoethane)ruthenium(III) perchlorate, 2621  
 Tris(4-methoxy-2,2'-bipyridine)ruthenium(II) perchlorate, 3886  
 Tris(3-methylpyrazole)zinc sulfate, 3540  
 Tris(1,10-phenanthroline)cobalt(III) perchlorate, 3890  
 Tris(1,10-phenanthroline)ruthenium(II) perchlorate, 3889  
 \* 1,4,7-Trithia[7]ferrocenophene–acetonitrilecopper(I) perchlorate, 3710  
 See AMMINECHROMIUM PEROXOCOMPLEXES, [14] DIENE-N<sub>4</sub> COMPLEXES  
 CLATHROCHELATED METAL PERCHLORATES, HYDRAZINEMETAL NITRATES  
 METAL PERCHLORATES: organic ligands, POLYAZACAGED METAL PERCHLORATES  
 SOLVATED OXOSALT INCIDENTS, URANYL MACROCYCLIC PERCHLORATE LIGANDS

## ANTHRAQUINONE DYES

Mizgireva, S. B., *Chem. Abs.*, 1987, **106**, 139802

In a DTA study of 14 anthraquinone dyes, most had high flash points (225–335°C) and ignition points (320–375°C). Purpurin dianilide [107528-40-5] was exceptional with the much lower values of 110 and 155°C, respectively.

## APROTIC SOLVENTS

1. Buckley, A., *J. Chem. Educ.*, 1965, **42**, 674
2. Banthorpe, D. V., *Nature*, 1967, **215**, 1296

Many aprotic (non-hydroxylic) solvents are not inert towards other reagents and care is necessary when using untried combinations of solvents and reagents for the first time. A further potential hazard which should be considered is that some aprotic solvents, notably dimethyl sulfoxide [1] and dimethylformamide [2], as well as having dramatic effects upon reaction rates, may greatly promote the toxic properties of solutes because of their unique ability to penetrate synthetic rubber protective gloves and the skin. Butyl rubber gloves are reputed to be more satisfactory than other types. The ether and cyclic ether solvents are also subject to peroxidation in storage. Individually indexed compounds are:

- N,N*-Dimethylacetamide, 1656
- Dimethylformamide, 1259
- † Dimethyl sulfoxide, 0921
- † 1,4-Dioxane, 1617
- † Furan, 1439
- N*-Methylformamide, 0866
- † Tetrahydrofuran, 1612
- Tetrahydrothiophene-1,1-dioxide, 1622

## AQUA REGIA

Fawcett, H. H., *Chem. Eng. News*, 1955, **33**, 897, 1406, 1622, 1844

Aqua regia (nitric and hydrochloric acids, 1:4 by vol., a powerful oxidant), which had been used for cleaning purposes, was stored in screw-capped winchesters. Internal pressure developed overnight, one bottle being shattered. Aqua regia decomposes with evolution of gas and should not be stored in tightly closed bottles (and preferably not at all).

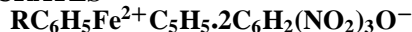
See Nitric acid: Alcohols

## Sodium

Chatt, J. *Biographical Memoirs*, Royal Society, 1996, 98.

Addition of a piece of sodium to aqua regia produces spectacular sparks.

## ARENOCYCLOPENTADIENYLIRON(II) PICRATES

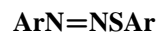


Federman Neto, A. *et al.*, *An. Acad. Bras. Cienc.*, 1982, **54**, 331–333

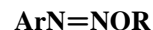
The products of condensing substituted benzenes and ferrocene with Al/AICl<sub>3</sub> were isolated as the picrate salts, which were light-sensitive and explosive.

See other PICRATES

## ARENEDIAZO ARYL SULFIDES



See DIAZONIUM SULFIDES AND DERIVATIVES

**ARENEDIAZOATES**

Houben-Weyl, 1965, Vol. 10.3, 563–564

Alkyl and aryl arenediazoates ('diazoethers') are generally unstable and even explosive compounds. They are produced by interaction of alcohols with (explosive) bis(arenediazo) oxides, or of *p*-blocked phenols with diazonium salts. The thio analogues are similar. Individually indexed compounds are:

Methyl benzenediazoate, 2799

Methyl 4-bromobenzenediazoate, 2737

Methyl 2-nitrobenzenediazoate, 2782

2-(4-Nitrophenoxyazo)benzoic acid, 3601

\* Potassium methanediazoate, 0449

\* Potassium 1-phenylethanediazoate, 2964

See related DIAZONIUM SULFIDES AND DERIVATIVES

**ARENEDIAZONIUM OXIDES**

This group of internal diazonium salts (previously named diazooxides) contains those which are, like many other internal diazonium salts, explosively unstable and shock-sensitive materials.

Other early names of the 1,2-diazonium oxides were based on the benzoxadiazole cyclised structure. For a long time it was doubted that 1,2,3-Benzoxadiazoles had existence, outside the speculative mathematics of theoretical chemists, but more recent researches suggest photochemical equilibrium with the diazonium form and possible predominance in non-polar solvents. Equilibrium implies similar explosive powers though it is possible that sensitivities differ.

Individually indexed compounds are:

Benzenediazonium-4-oxide, 2189

5-Benzoylbenzenediazonium-2-oxide, 3597

3-Bromo-2,7-dinitrobenzo[*b*]thiophene-5-diazonium-4-oxide, 2883

4-Chloro-2,5-dinitrobenzenediazonium 6-oxide, 2066

3,4-Difluoro-2-nitrobenzenediazonium 6-oxide, 2067

3,6-Difluoro-2-nitrobenzenediazonium 4-oxide, 2068

3,5-Dinitrobenzenediazonium 2-oxide, 2087

4,6-Dinitrobenzenediazonium 2-oxide, 2088

3,5-Dinitro-4-hydroxybenzenediazonium 2-oxide, 2090

3,5-Dinitro-2-methylbenzenediazonium-4-oxide, 2666

3,5-Dinitro-6-methylbenzenediazonium-2-oxide, 2667

2,3,5-Trinitrobenzenediazonium-4-oxide, 2072

See DIAZONIUM CARBOXYLATES

5-Diazoniotetrazolide, *also* Benzenediazonium-4-sulfonate

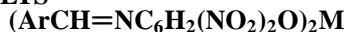
**ARYL CHLOROFORMATES (ARYL CARBONCHLORIDATES) ArOCO.Cl**

Water

Muir, G. D., private comm., 1968

During the preparation of aryl chloroformates, it is essential to keep the reaction mixture really cold during water washing to prevent vigorous decomposition. Phenyl and naphthyl chloroformates may be distilled, but benzyl chloroformate is too thermally unstable.

## 2-ARYLIDENEAMINO-4,6-DINITROPHENOL SALTS



1. Srivastan, R. S. *et al.*, *Def. Sci. J.*, 1979, **29**, 91–96
2. Srivastan, R. S., *Def. Sci. J.*, 1982, **32**, 219–223

The 4'-dimethylaminobenzylidene derivatives form explosive cadmium, mercury and zinc salts [1], and the 4'-nitro analogue forms explosive cadmium, cobalt, copper, iron, mercury, nickel and zinc salts of limited thermal stability [2]. All are constituted with a 1:2 metal:ligand ratio.

See 2-Benzylideneamino-4,6-dinitrophenol

## ARYLMETALS

ArM

This reactive group includes the individually indexed compounds:

- \* 3-Benzocyclobutenylpotassium, 2904
- \* Bis( $\eta$ -benzene)chromium(0), 3511
- \* Bis( $\eta$ -benzene)iron(0), 3512
- \* Bis( $\eta$ -benzene)molybdenum(0), 3514
- \* Bis(cyclopentadienyl)phenylvanadium, 3705
- Dicumenechromium(0), 3767
- 1,3-Dilithiobenzene, 2178
- 1,4-Dilithiobenzene, 2179
- \* Diphenyldistibene, 3500
- Diphenylmagnesium, 3482
- Diphenylmercury, 3480
- Diphenyltin, 3502
- \* Lithium diphenylhydridotungstate(2-), 3503
- \* Lithium hexaphenyltungstate(2-), 3892
- Naphthylsodium, 3253
- Phenylgold, 2221
- Phenyllithium, 2259
- Phenylsilver, 2217
- Phenylsodium, 2287
- \* Phenylvanadium(V) dichloride oxide, 2246
- Tetraphenyllead, 3850
- 2-,3- or 4-Tolylcopper, 2745
- Triphenylaluminium, 3749
- Triphenylchromium tetrahydrofuranate, 3751
- \* Triphenyllead nitrate, 3753

See also ALKYL METALS

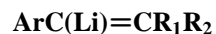


## ARYLTHALLIC ACETATE PERCHLORATES



See Perchloric acid: Ethylbenzene, etc.

## 1-ARYL-1-VINYLLITHIUM DERIVATIVES



Knorr, R. *et al.*, *Tetrahedron Lett.*, 1977, 3969

In the preparation and use of a series of 5 variously substituted 1-aryl-1-vinyl lithium derivatives (*Ar* = phenyl, dimethylphenyl or isopropylphenyl;  $R_1$  = H, Me or 4-tolyl;  $R_2$  = D, Me or 4-tolyl), all operations had to be under purified nitrogen to prevent explosion.

See related ALKYL METALS

## ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

1. Bretherick, L. in *Chemical Process Hazards with Special Reference to Plant Design-V*, 1–15, Kneale, M. (Ed.), Symp. Ser. No. 39a, London, IChE, 1975
2. Grewer, T., *Runaway Reactions*, 1981, Paper 2/E, 1–18
3. Coates, C. F. *et al.*, *Runaway Reactions*, 1981, Paper 4/Y, 1–18; *Chem. & Ind.*, 1981, 84–88
4. Dollimore, D., *Chem. & Ind.*, 1981, 196
5. Kohlbrand, H. T., *Chem. Eng. Progr.*, 1985, **81**(4), 52
6. Gustin, J. L., *J. Loss Prev.*, 1993, **6**(5), 275
7. Fukayama, I. *et al.*, *Bull. Fac. Eng. Yokohama Natl. Univ.*, 1984, **33**, 59–68
8. Yoshida, T. *et al.*, *Kogyo Kagaku*, 1987, **48**(5), 311–316 (*Chem. Abs.*, 1988, **108**, 58900)
9. Cronin, J. L. *et al.*, *Hazards from Pressure*, IChE Symp. Ser. No. 102, 113–132, Oxford, Pergamon, 1987
10. Itoh, M., *Kogyo Kagaku*, 1988, **49**(1), 47–52 (*Chem. Abs.*, 1988, **109**, 8938)
11. Kaneko, Y. *et al.*, *Kogyo Kagaku*, 1988, **49**, 168–175 (*Chem. Abs.*, 1988, **109**, 233687)
12. RSST Brochure, Fauske Associates, 1988, Burr Ridge (IL)

Literature sources of information available to early 1974 and related to assessment of reactive chemical hazards are listed, grouped and discussed in relation to the type of information made available and their application to various situations. Eighty references are given, and those considered suitable for the nucleus of a small safety library are indicated. Toxic hazards are not covered [1]. Relatively simple procedures (oven or Dewar flask tests at normal or elevated pressures) can give a good indication of the potential for exothermic decomposition and runaway reaction hazards, as shown by initial exotherm temperatures, quasi-adiabatic self-heating curves and induction times obtained by these methods [2]. A reliable programme to screen existing, new or modified processes or products for thermal instability has been devised, suitable for a small batch manufacturing installation. This involves a progressive series of tests using simple equipment, for which constructional details are given [3]. Certain practical aspects of the programme were criticised [4]. The Dow reactive chemicals testing programme used to assess

the potential hazards in pilot plant operations is outlined [5]. A Rhone Poulenc procedure based on literature, calculation and calorimetry is described in detail [6].

A simple evaluation method has been developed to assess the hazards of substances, including those regarded as non-explosive, involving thermal sensitivity, mechanical energy sensitivity and detonation sensitivity tests [7]. A method has been developed for predicting the fire and explosion hazards of new chemicals based upon two measurements of thermal properties. These are the heat of decomposition by sealed cell DSC, and the extrapolated decomposition onset temperature by ASTM E-537. These results are used in conjunction with scatter diagrams derived from the results of various standard explosive testing methods and known explosive substances [8]. A simple Insulated Exotherm Test for assessing thermal decomposition hazards, and a Power Compensated Dewar Calorimeter for measuring heat release in liquid systems are key elements in a strategy to assess thermal hazards in batch chemical manufacturing operations [9]. The method in [8] above has been further developed by running comparative tests on different DSC and DTA instruments and analysing the results statistically. Some specific practical problems are identified [10]. A method to determine the detonation/deflagration propagation capabilities of moderately unstable (borderline) chemicals using a propagation tube test has been developed, and the results compared with those from standard explosive tests and DSC methods. Added aluminium oxide was used as inert dephlegmator, and its mixtures with ammonium nitrate (95–100%), 1,3-dinitrobenzene (60–70%), 2,4-dinitrotoluene (70–80%), and dinitrosopentamethylene tetramine (70–80%) would propagate detonation, and dibenzoyl peroxide with 10–15% water content would propagate deflagration [11]. A new and relatively simple test instrument, the Reactive System Screening Tool (RSST) for the rapid assessment of self heating and runaway reaction potential has been described. The sample is contained in an open 10 ml spherical glass cell fitted with internal heater, thermocouple, magnetic stirrer and reagent port. The cell fits into a lagging jacket within a sealable 0.5 l stainless outer pressure vessel of 34 bar working pressure which is fitted with pressure sensor, relief line and reagent syringe. The control unit, which may be interfaced with a personal computer, will set heating rates between 0.1°C/min. and very high rates, to simulate exposure of the sample to fire conditions. For volatile materials, back pressure (e.g. 20 bar) may be applied to suppress evaporation effects. The equipment may be used to acquire data applicable to thermal evaluation or to DIERS vent-sizing purposes, and the test results are comparable with those from other thermal assessment tests. Results for methanol–acetic anhydride, and for styrene–benzoyl peroxide systems are presented graphically [12].

*See* PRESSURE RELIEF (reference 6)

The last decade has seen great and rapid advances in many of the specialised areas of this broad topic, and some of these are covered in the topic headings:

- \*ACCELERATING RATE CALORIMETRY
- CALORIMETRY
- CHEMICAL STABILITY/REACTIVITY ASSESSMENT
- COMPUTATION OF REACTIVE CHEMICAL HAZARDS
- EXOTHERMIC DECOMPOSITION REACTIONS

HEAT FLOW CALORIMETRY  
HIGH RATE DECOMPOSITION  
MAXIMUM REACTION HEAT  
PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION  
REACTION SAFETY CALORIMETRY  
RUNAWAY REACTIONS  
THERMAL EXPLOSIONS  
SCALE OF WORK  
THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS  
THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

### ATOMIC ABSORPTION SPECTROSCOPY (AAS)

1. Bretherick, L., *Hazards in the Chemical Laboratory*, 34, London, Royal Society of Chemistry, 3rd edn., 1981
2. Everett, K., *Chem. Brit.*, 1983, **19**, 108
3. Melucci, R. C., *J. Chem. Educ.*, 1983, **60**(3), 238
4. Everson, R. J., *Chem. Eng. News*, 1987, **65**(25), 2
5. Anon., *Fire Prev.*, 1988, (213), 44–45

Care is necessary with acetylene-fed AAS burners to prevent air being drawn up the liquid drainage line, when explosion is likely [1]. While setting up an AAS instrument for use with nitrous oxide–acetylene, an explosion occurred shortly after switching from compressed air to the oxide, when the flame became unstable. This was attributed to the outdoor location of the nitrous oxide cylinder (at 5°C) and the expansion cooling (4°C) occurring in the reducing valve, combining to reduce the oxide flow to the point of flame instability and flashback [2]. It was proposed that in student laboratories, air–acetylene flame sources should be replaced by air–natural gas flames to improve safety aspects with very little fall-off in detection limits in instrumental AA metal determinations [3]. Three further incidents involving explosions in AAS installations are reported. One involved accidental contamination of the acetylene inlet line by liquid acetone from an overfilled acetylene cylinder. The other explosions involved leakage of acetylene gas inside the instrument cases and ignition by the electrical controls. Fitting of acetylene sensors inside such instruments to prevent further incidents is suggested [4]. Acetylene gas leaking from a supply tube was ignited by the source flame and a minor explosion occurred, and appears to have damaged both gas supply lines, which led to a second major explosion and fire. This involved some 6 m<sup>3</sup> of acetylene and 18 m<sup>3</sup> of nitrous oxide, and caused severe structural damage [5].

*See* Perchloric acid: Acetylene, Nitrous oxide

*See* Silver acetylde (reference 3)

### AUTOIGNITION INCIDENTS

Some incidents which have involved autoignition under unexpected circumstances may be found under the entries:

Calcium stearate, 3896

Methaneboronic anhydride–pyridine complex, 0427

Phenylchlorodiazirine, 2673  
Thiophosphoryl chloride difluoride, 3980  
See MILK POWDER

## AUTOIGNITION TEMPERATURE

1. Hilado, C. J. *et al.*, *Chem. Eng.*, 1972, **79**(19), 75–80
2. *Fire Hazard Properties of Flammable Liquids, Gases, Solids*, No. 325M, Boston, NFPA, 1969
3. Shimy, A. A., *Fire Technol.*, 1970, **6**, 135–139
4. Madej, T. *et al.*, *Chem. Abs.*, 1978, **89**, 203300
5. Hilado, C. J. *et al.*, *Fire Technol.*, 1972, **8**, 218–227
6. Bodurtha, 1980, 29
7. Hedden, K. *et al.*, *Chem. Ing. Tech.*, 1979, **51**, 806–809
8. Lewis, D. J., *Proc. 7th Symp. Chem. Process Hazards*, Symp. Ser. No. 58, 257–271, Rugby, IChE, 1980
9. Affens, W. A. *et al.*, *Loss Prev.*, 1980, **13**, 83–88
10. Coffee, R. D., *Loss Prev.*, 1980, **13**, 74–82
11. D’Onofrio, E. J., *Loss Prev.*, 1980, **13**, 84–97
12. Sheldon, M., *Fire Prev.*, 1983, (161), 31–37
13. Suzuki, T., *Fire Mater.* 1994, **18**(2), 81
14. Ashmore, F. S. *et al.*, *Loss Prev. Bull.*, 1987, (075), 1–10
15. Snee, T. J., *Loss Prev. Bull.*, 1988, (091), 25–38
16. Bond, 1991, 21

Autoignition temperature (AIT) is the temperature at which a material in contact with air undergoes oxidation at a sufficiently high rate to initiate combustion without an external ignition source. Although only those compounds with unusually low AIT’s (225°C or below) have been included in this Handbook, there is a compilation of data for over 300 organic compounds, which also includes the theoretical background and discussion of the effect of variations in test methods upon AIT values obtained [1]. Further AIT data are given in the tabulated publication [2]. Semi-empirical formulae, based only on molecular structure, have been developed which allow AITs to be calculated for hydrocarbons and alcohols, usually with a reasonable degree of accuracy. Flammability limits, flash points, boiling points and flame temperatures may also be calculated for these classes [3]. An equation has been developed which relates the AIT of vapours and gases to the reciprocal of their induction times to self ignition [4]. The effect of iron oxide in lowering the AITs of 21 organic compounds to around 290°C [5] may mean in practical terms that this is the maximum AIT for organic compounds in contact with rusted steel or iron [6].

An improved method for determining the AIT of solids has been described, and the effect of catalytically active inorganics on the reactivity and ignition temperature of solid fuels has been studied. Sodium carbonate markedly lowers the ignition temperatures of coal and coke [7]. The volume of the vessel (traditionally a 200 ml flask) used to determine AIT has a significant effect on the results. For volumes of

1m<sup>3</sup> or greater, AIT values are appreciably lower than those measured in the standard equipment, and due allowance should be made for this [8]. The importance of the cool flame in the 2-stage autoignition process has been reviewed [9], and the transition of the cool flame via an intermediate blue flame to the hot ignition stage is discussed in detail [10]. The relationships of the 2 stages were studied for ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol and bis(2-methoxyethyl) phthalate. The latter was observed to give a transition from a cool flame to a hot flame 122°C below its minimum AIT [11]. The topic, including theoretical background, variations in testing methods and application of results, has been surveyed and summarised [12]. A procedure for calculating autoignition temperatures of organics from molecular properties. Good agreement is claimed for most of the 250 compounds examined [13].

In a further survey of AITs and their practical application, the four main factors affecting the AIT are given as: the temperature of surfaces in contact with the mixture; the contact time between these; whether the surface is active or inert; contaminants which enhance or inhibit combustion [14]. AITs are pressure sensitive, generally decreasing with increased air pressure, as also with oxygen enrichment [16]. The values determined for the various fire-related properties of combustibles (flash point, flammability limits, minimum ignition energy, and autoignition temperature) are all dependent on the particular methods used for determination, and this is especially true of the latter values, where the factors affecting the result are not well understood. The relationship between vessel size and the AITs determined therein has been studied experimentally, together with the kinetics of the slow oxidation processes which lead to ignition. Practical methods to reduce the risk of autoignition, specifically in resin manufacture are discussed, but similar considerations are likely to apply to any process involving hot fuel-air mixtures [15].

## AUTOXIDATION

1. Davies, 1961, 11
2. Ingold, K. U., *Chem. Rev.*, 1961, **61**, 563
3. Kirk-Othmer, 1978, Vol. 3, 128–133

Autoxidation (interaction of a substance with molecular oxygen at below 120°C without flame [1]) has often been involved in the generation of hazardous materials from reactive compounds exposed to air. Methods of inhibiting autoxidation of organic compounds in the liquid phase has been reviewed [2,3].

See PEROXIDISABLE COMPOUNDS,  $\alpha$ -PHENYLAZO HYDROPEROXIDES

$\alpha$ -Phenylazobenzyl hydroperoxide, 3609

Oxygen: Cyclohexane-1,2-dione bis(phenylhydrazone), 4831

## AZIDE COMPLEXES OF COBALT(III)

1. Druding, L. F. *et al.*, *J. Coord. Chem.*, 1973, **3**, 105
2. Druding, L. F. *et al.*, *Anal. Chem.*, 1975, **47**(1), 176–177
3. Siebert, H. *et al.*, *Z. Anorg. Chem.*, 1982, **489**, 77–84

A series of 12 complexes of Co(III) with both ionic and covalent azide groups was prepared and most were easily detonable as dry salts, especially at elevated temperatures [1]. Polarography is an accurate and safe method of analysis for azides [2]. Hexaammine-cobalt, -chromium and -rhodium hexaazidocobaltates are explosive, particularly in the dry state [3].

*See also* AMMINOMETAL AZIDES

*See related* METAL AZIDES

## AZIDES

—N<sub>3</sub>

Many compounds of both organic and inorganic derivation, which contain the azide function, are unstable or explosive under appropriate conditions of initiation, not all have been given entries. The large number of compounds having entries has been subdivided for convenience on the basis of structure.

ACYL AZIDES, AMMINECOBALT(III) AZIDES, AZIDE COMPLEXES OF COBALT(III)

METAL AZIDES, NON-METAL AZIDES

ACYL AZIDES, 2-AZIDOCARBONYL COMPOUNDS, ORGANIC AZIDES

## 2-AZIDOCARBONYL COMPOUNDS

CO—C—N<sub>3</sub>

1. Boyer, J. H. *et al.*, *Chem. Rev.*, 1954, **54**, 33
2. Weyler, J. *et al.*, *J. Org. Chem.*, 1973, **38**, 3865

Certain 2-azidocarbonyl compounds and congeners have long been known as unstable substances [1]. Some members of a group of 2,5-dialkyl-3,6-diazido-1,4-benzoquinones decompose violently on melting [2]. Individually indexed compounds are:

Azidoacetaldehyde, 0772

Azidoacetic acid, 0774

Azidoacetone, 1190

Azidoacetone oxime, 1215

2,5-Diazido-3,6-dichlorobenzoquinone, 2054

\* Ethyl  $\alpha$ -azido-*N*-cyanophenylacetimidate, 3397

Ethyl 2-azido-2-propenoate, 1890

Ethyl 2,3-diazidopropionate, 1903

Tetraazido-1,4-benzoquinone, 2633

*See* 2-AZIDO-2-FLUOROCARBOXYLATES

## 2-AZIDO-2-FLUOROCARBOXYLATES

N<sub>3</sub>CFRCOOR'

Preparative hazard

Takeuchi, Y. *et al.*, *J. Fluorine Chem.*, 1994, **68**(2), 149

The activating effect of the azide makes the fluorine labile, so that there is a risk of excess azide incorporation when attempting preparation by nucleophilic substitution of bromofluorocarboxylates, giving more explosive products than anticipated.

*See* ORGANIC AZIDES, 2-AZIDOCARBONYL COMPOUNDS

## AZIRIDINES

Several derivatives of the highly reactive aziridine (ethylenimine) show explosive instability. Individually indexed compounds are:

† Aziridine, 0863

1,1'-Biaziridiny, 1593

Bis(*O*-salicylidenaminopropylaziridine)iron(III) perchlorate, 3853

1-Bromoaziridine, 0783

1-Chloroaziridine, 0786

*See other* STRAINED-RING COMPOUNDS

## AZOCARBABORANES

Aono, K. *et al.*, *J. Chem. Soc., Dalton Trans.*, 1981, 1190–1195

In the preparation of 1,1'-azo-2-R-1,2-dicarbodecaborane(14) by oxidation of the aminocarbaborane anions in liquid ammonia, toluene or other inert solvent must be added before evaporation of ammonia to prevent explosions. Individually indexed compounds are:

1,1'-Azo-1,2-dicarbodecaborane(14), 1796

1,1'-Azo-2-phenyl-1,2-dicarbodecaborane(14), 2624

## AZO COMPOUNDS



Vasin, A. Ya. *et al.*, *Chem. Abs.*, 1983, **99**, 39872

The lower concentration limits for ignition of air suspensions of 9 azo dyes have been studied. Individually indexed members of the group of unstable azo compounds are:

4-Aminophenylazobenzene, 3487

Azobenzene (Diphenyldiazene), 3483

2,2'-Azobis(2-amidiniopropane) chloride, 3089

2,2'-Azobis(2-amidiniopropane) peroxodisulfate, 3091

2,2'-Azobis(2,4-dimethylvaleronitrile), 3668

Azo-*N*-chloroformamidine, 0792

2,2'-Azo-3,5-dinitropyridine, 3238

Azoformaldoxime, 0815

Azoformamide, 0816

Azoisobutyronitrile, 3011

2,2'-Azoisovaleronitrile, 3345

Azomethane, 0910

Azo-*N*-methylformamide, 1601

Azo-*N*-nitroformamidine, 0825

3,3'-Azo-(1-nitro-1,2,4-triazole), 1401

\* 2-Azoxyanisole, 3653

\*  $\alpha$ -(4-Bromophenylazo)benzyl hydroperoxide, 3606

\*  $\alpha$ -(4-Bromophenylazo)phenylethyl  $\alpha$ -hydroperoxide, 3648

\* 2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3156

1-(4-Chloro-2-nitrobenzeneazo)-2-hydroxynaphthalene, 3697

- 5-(Diazomethylazo)tetrazole, 0719  
 Dicyanodiazene, 1005  
 Diethyl azoformate, 1528  
 5-(4-Dimethylaminobenzeneazo)tetrazole, 3161  
 Dimethyl azoformate, 1528  
 3,4-Dimethyl-4-(3,4-dimethyl-5-isoxazolylazo)isoxazolin-5-one, 3309  
 1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3702  
 \* Diphenyldistibene, 3500  
 \* 2,2-Diphenyl-1,3,4-thiadiazoline, 3647  
 \* Disodium dicyanodiazene, 1006  
 Disodium 5-tetrazolazocarboxylate, 1012  
 \* Isopropyldiazene, 1274  
 \* Methyldiazene, 0474  
 Methyl 3-methoxycarbonylazocrotonate, 2830  
 \*  $\alpha$ -Phenylazobenzyl hydroperoxide, 3609  
 \*  $\alpha$ -Phenylazo-4-bromobenzyl hydroperoxide, 3607  
 \*  $\alpha$ -Phenylazo-4-fluorobenzyl hydroperoxide, 3608  
 \* Potassium azodisulfonate, 4663  
 Potassium 4-nitrobenzeneazosulfonate, 2175  
 Silver 1-benzeneazothiocarbonyl-2-phenylhydrazide, 3605  
 Sodium 5(5'-hydroxytetrazol-3'-ylazo)tetrazolide, 0682

#### ***N*-AZOLIUM NITROIMIDATES**



1. Katritzsky, A. R. *et al.*, *J. Chem. Soc., Perkin Trans 1*, 1973, 2624–2626
2. University of Southern California, *Chem. Abs.* 1994, **120**, 80853

Some of the internal salts derived from *N*-heterocycles are dangerously explosive solids, sensitive to modest heating and to impact, also liable to violent spontaneous decomposition, even in solution. A related *N*-nitroimide (hetero-N–NH–NO<sub>2</sub>) was also explosive. It is possible the benzotriazolium imidates were also, in fact, the tautomeric nitroaminobenzotriazoles. None of their potassium salts exploded [1]. Related chemistry has been examined with a view to new explosives, in particular 1,4-bis(nitroamino)-1,4-diazabicyclo[2.2.2]octane, said to be surprisingly stable. The individually indexed unstable compounds are:

Benzimidazolium 1-nitroimidate, 2704

Benzotriazolium 1-nitroimidate, 2281

Benzotriazolium 2-nitroimidate, 2282

4-Nitroamino-1,2,4-triazole, 0777

*See other* HIGH-NITROGEN COMPOUNDS, *N*-NITRO COMPOUNDS

#### **BENZENE ISOMERS**



Editor's comments.

There are some 40 structural isomers which seem stable enough to be isolated. Six enjoy individual entries in Part I, others are less well described. All will be of higher energy than benzene, itself endothermic, all should be suspected



capable of causing explosion. To a lesser degree, non-aromatic isomers of substituted benzenes will also be suspect.

See ENDOTHERMIC COMPOUNDS

## BATS

1. Anon., *Chemical Engineer*, 1993, 546/7, 33
2. Various, *Chem. Eng. News*, 1993, **71**(38), 64; **71**(41), 60

An explosion demolishing an empty building was dubiously attributed to ignition of methane evolved from bat droppings [1]. There was much argument as to the probability of this [2], the eventual conclusion being that sewer gas from a septic tank was responsible.

See also INDIGESTION

## BATTERIES

1. Anon., *Loss Prev. Bull.*, 1992, (108), 28
2. Anon., *Universities' Safety Assoc. Safety News*, 1979, (12), 20–21
3. See entries under Lithium
4. *Battery Hazards and Accident Prevention*, Levy, S. C. & Bro, P., New York, Plenum Press, 1994

Electrical batteries have associated explosion dangers. These are best known as gas evolution and explosion consequent upon over charging during recharge [1] or connection with reversed polarity: Of 3 HP7 zinc-carbon batteries inserted into a calculator, one was inserted wrongly with reversed polarity. After 2 days, when it was taken out to rectify the error, the battery 'exploded', the carbon rod being ejected with considerable force [2]. With more powerful cells, the risk is increasingly the chemical energy contained in the cell [3]. Short circuits can also serve as ignition sources in flammable surroundings. A book covering all aspects of safety with many types of cell has been published. It gives accounts of many incidents [3].

Silver: Electrolytes, Zinc; STEEL

## BENZYL COMPOUNDS

## PhCH<sub>2</sub>–

Several benzyl derivatives exhibit potentially hazardous properties arising from the activation by the adjacent phenyl group, either of the substituent or of a hydrogen atom. Halides, in particular, are prone to autocatalytic Friedel Crafts polymerisation if the aromatic nucleus is not deactivated by electron withdrawing substituents.

Individually indexed compounds are:

- Barium *N*-perchlorylbenzylamide, 3649
- Benzyl alcohol, 2806
- Benzylamine, 2812
- Benzyl azide, 2779
- Benzyl bromide, 2735
- Benzyl chloride, 2738
- Benzyl dimethylamine, 3168

Benzyl fluoride, 2746  
 Benzyl nitrate, 2765  
 Benzyloxyacetylene, 3133  
 \* Benzylsilane, 2832  
 \* Benzylsodium, 2787  
 1-Benzyl-3-(4-tolyl)triazene, 3657  
 1,2-Bis(chloromethyl)benzene, 2946  
 4-Bromomethylbenzoic acid, 2926  
 2-Chloro-5-nitrobenzyl alcohol, 2715  
 4-Chloro-2-nitrobenzyl alcohol, 2716  
 4-Chloro-3-nitrobenzyl alcohol, 2717  
 5-Chloro-2-nitrobenzyl alcohol, 2718  
 6-Chloro-2-nitrobenzyl bromide, 2671  
 2-Chloro-4-nitrobenzyl chloride, 2678  
 4-Chloro-2-nitrobenzyl chloride, 2679  
 Dibenzyl ether, 3655  
 Dibenzyl phosphite, 3658  
 Dibenzyl phosphorochloridate, 3650  
 Mercury(II) *N*-perchlorylbenzylamide, 3651  
 3-Methoxybenzylamine, 2997  
 4-Methoxybenzyl chloride, 2962  
 4-Methylbenzyl chloride, 2959  
 2-Nitrobenzyl alcohol, 2769  
 3-Nitrobenzyl alcohol, 2770  
 4-Nitrobenzyl alcohol, 2771  
 2-Nitrobenzyl chloride, 2713  
 Phenylacetonitrile, 2935  
 2,2'-[1,4-Phenylenebis(azidomethylidene)]bis(propanedinitrile), 3622  
 Tribenzylarsine, 3822  
*See also* 2-HALOMETHYL-FURANS OR THIOPHENES, NITROBENZYL COMPOUNDS,  $\alpha$ -PHENYLAZO HYDROPEROXIDES

## BIS(ARENEDIAZO) OXIDES

(ArN=N)<sub>2</sub>O

1. Bamberger, E., *Ber.*, 1896, **29**, 451
2. Kaufmann, T. *et al.*, *Ann.*, 1960, **634**, 77

Action of alkalis on diazonium solutions, or of acids on alkali diazoates to give a final pH of 5–6, causes these compounds ('diazoanhydrides') to separate as oils or solids. Many of these are violently explosive (some exceeding nitrogen trichloride in effect), sensitive to friction and heat or contact with aromatic hydrocarbons [1,2]. Individually indexed compounds are:

Bis(benzeneazo) oxide, 3490  
 Bis(4-chlorobenzenediazo) oxide, 3456  
 Bis(toluenediazo) oxide, 3654  
 Bis(2,4,5-trichlorobenzenediazo) oxide, 3431

*See related* BIS(ARENEDIAZO) SULFIDES, BELOW

**BIS(ARENEDIAZO) SULFIDES**

Some of the products of interaction of diazonium salts with sulfides may have this structure. Relevant entries are:

Bis(benzenediazo) sulfide, 3491

Bis(4-nitrobenzenediazo) sulfide, 3467

See DIAZONIUM SULFIDES AND DERIVATIVES

**BIS(DIFLUOROAMINO)ALKYL NITRATES**

Reed, S. F., *J. Org. Chem.*, 1972, **37**, 3329–3330

Prepared from tetrafluorohydrazine and alkenyl nitrates, these compounds are dangerously explosive. Purification is difficult, as they are sensitive to heat and shock. Preparation by nitration of the alcohol is a more practical route.

See other DIFLUOROAMINO COMPOUNDS

**BIS(FLUOROOXY)PERHALOALKANES**

Hazardous preparation and products

Sekiya, A. *et al.*, *Inorg. Chem.*, 1980, **19**, 1328–1330

The compounds are all strong oxidants and explosive, requiring very careful handling. Individually indexed compounds are:

1,1-Bis(fluorooxy)hexafluoropropane, 1061

2,2-Bis(fluorooxy)hexafluoropropane, 1062

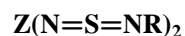
1,1-Bis(fluorooxy)tetrafluoroethane, 0641

2-Chloro-1,1-bis(fluorooxy)trifluoroethane, 0595

1,1,4,4-Tetrakis(fluorooxy)hexafluorobutane, 1374

See Fluorine: Fluorocarboxylic acids, etc., 4310

See related HYPOHALITES

**BIS(SULFUR)DIIMIDES**

Appel, R. *et al.*, *Chem. Ber.*, 1976, **109**, 2444

During the preparation of a series of the bis(diimides), ( $\text{Z} = (\text{CH}_2)_2$  or  $_3$ ;  $\text{R} = \text{Me}$ ,  $\text{Et}$ ), work-up operations must be at below  $100^\circ\text{C}$  to avoid violent decomposition.

See other N–S COMPOUNDS

**BITUMEN**

1. Agaev, A. S. *et al.*, *Chem. Abs.*, 1975, **82**, 88310

2. Hoban, T. W. S. *et al.*, *J. Loss Prevention*, 1994, **7**(3), 217

Factors leading to ignition or explosion during preparation of high-melting bitumens by air-blowing petroleum residues were identified as control of vapour temperature (often above AIT), presence of lower hydrocarbon vapours, and lack of control of free oxygen content. Measures for controlling these are discussed [1]. Bitumen storage tank fires are instanced, and the causes discussed [2]

See Oxygen: Hydrocarbons

## BLEACHING POWDER



1. Mellor, 1956, Vol. 2, Suppl. 1, 564–567
2. *Accid. Bull. No. 30*, Washington, Amer. Railroad Assoc. Bur. Explos., 1921
3. Gill, A. H., *Ind. Eng. Chem.*, 1924, **16**, 577
4. ‘Leaflet No. 6’, London, Inst. Chem., 1941

Bleaching powder is effectively a mixture of calcium hypochlorite, calcium hydroxide and a non-hygroscopic form of calcium chloride [1] and may therefore be regarded as a less active form (39% available chlorine) of oxidant than undiluted calcium hypochlorite (49% chlorine). There is a long history of explosions, many apparently spontaneous, involving bleaching powder. On storage or heating, several modes of decomposition are possible, one involving formation of chlorate which may increase the hazard potential. Of the 3 possible routes for thermal decomposition, that involving liberation of oxygen predominates as the water content decreases, and at 150°C the decomposition becomes explosive [1]. Material which has been stored for a long time is liable to explode on exposure to sunlight, or on overheating of tightly packed material in closed containers [2]. The spontaneous explosion of material packed in drums was attributed to catalytic liberation of oxygen by iron and manganese oxides present in the lime used for manufacture [3]. Traces of metallic cobalt, iron, magnesium or nickel may also catalyse explosive decomposition [1]. When the lever-lid of a 6-month-old tin of bleaching powder was being removed, it flew off with explosive violence, possibly owing to rust-catalysed slow liberation of oxygen [4].

### Bis(2-chloroethyl) sulfide

Mellor, 1956, Vol. 2, Suppl. 1, 567

Interaction is very exothermic and ignition may occur, particularly in presence of water.

### Wood

Anon., *ABCM Quart. Safety Summ.*, 1933, **4**, 15

A mixture of sawdust and bleaching powder ignites when moistened.

See other METAL HYPOCHLORITES, OXIDANTS

## BLEVE

1. Prugh, R. W., *Chem. Eng. Progress*, 1991 (Feb.), 66
2. Venart, J. E. S. *et al.*, *Process Safety Progr.*, 1993, **12**(2), 67
3. Birk, A. M. *et al.*, *J. Loss Prev.*, 1994, **7**(6), 474
4. Birk, A. M. *et al.*, *Chem. Abs.*, 1998, **129**, 323897d

A Boiling Liquid Expanding Vapour Explosion, or BLEVE, is an industrial event related to the laboratory ‘bump’ occasioned when the inadequately mixed bottom of a vessel of liquid becomes superheated, then explosively boils. In the industrial version, rupture of a pressurised container is usually involved. Although strictly speaking a non-reactive physical hazard, chemical fires and explosions, with fatalities, often follow. Means of estimating risk and prevention, with a list of incidents are given[1]. A more ferocious version, the Boiling Liquid Compressed Bubble

Explosion, or BLCBE, involving multiple site initiation during the explosive stage, is described [2]. A study of Bleves in propane tanks is combined with a procedure for predicting whether a tank will BLEVE or merely produce a jet leak on over-heating [3]. The relationship between BLEVE conditions and subsequent fireballs has been studied [4]

*See also* VAPOUR CLOUD EXPLOSIONS

## BLOWING AGENTS

1. Morisaki, S. *et al.*, *J. Haz. Mat.*, 1981, **5**, 49–63
2. Bond, J., *Hazards from Pressure*, IChE Symp. Ser. No. 102, 37–44, Oxford, Pergamon, 1987

Six blowing agents (\* in the list below), which generate gas (mainly N<sub>2</sub>) by thermal decomposition and are used to create plastic foams, were examined by DSC at up to 50 bar pressure. The very significant increase in heat release under pressure (especially air pressure) suggests that sealed containers of the materials may explode violently if subjected to heating [1]. Decomposition of a hydrazide blowing agent in a large feed hopper was probably initiated by friction from the mechanical feed-screw in the base. The exothermic decomposition activated the explosion suppression system which added to the volume of gas produced and caused rupture of the hopper [2].

Individually indexed compounds are:

2,2'-Azobis(2,4-dimethylvaleronitrile), 3668

Azoformamide\*, 0816

Azoisobutyronitrile\*, 3011

2,2'-Azoisovaleronitrile\*, 3345

Azo-*N*-methylformamide, 1601

3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane\*, 1954

4,4'-Oxybis(benzenesulfonylhydrazide)\*, 3525

4-Toluenesulfonylhydrazide\*, 2827

*See also* RADICAL INITIATORS

## BORANES (BORON HYDRIDES)

Wright, S. W. *et al.*, *Chem. Eng. News*, 1992, **70**(35), 4

Many boranes and their complexes are air sensitive and pyrophoric. Boranes and their complexes apparently disproportionate to higher boranes and hydrogen on storage, pressurising their containers.

Aluminium chloride, Sulfur dioxide

Bonnetot, B. *et al.*, *Inorg. Chim. Acta*, 1989, **156**(2), 183

Intimate mixtures or complexes of the above and salts of decahydrodecaborate(2-) left after evaporation of excess liquid sulfur dioxide exploded on grinding. The same could presumably happen with derivatives of other boranes.

## Carbon tetrachloride

1. Hermanek, S., *Chem. Abs.*, 1976, **84**, 38384
2. *491M*, 1975, 92

Carbon tetrachloride is not recommended as an eluting solvent in the chromatographic separation of boranes, carbaboranes or their derivatives because of the danger of explosion [1]. Use of a carbon tetrachloride extinguisher on a diborane fire caused a violent explosion [2].

Carbon tetrachloride is not recommended as an eluting solvent in the chromatographic separation of boranes, carbaboranes or their derivatives because of the danger of explosion [1]. Use of a carbon tetrachloride extinguisher on a diborane fire caused a violent explosion [2].

*See also* ALKYLBORANES, ALKYLHALOBORANES, HALOBORANES

Individually indexed compounds are:

- \* Ammonium decahydrodecaborate(2-), 0199
- \* 1,1'-Azo-[2-methyl-1,2-dicarbodecaborane(14)], 2624
- \* Bis(borane)-hydrazine, 0143
- \* Bis(dimethylaminoborane)aluminium tetrahydroborate, 1795
- \* *N,N'*-Bis(trimethylsilyl)aminoborane, 2612
- Borane, 0135
- \* Borane-ammonia, 0141
- \* Borane-bis(2,2-dinitropropylhydrazine), 0137
- Borane-dimethylsulfide, 0136
- \* Borane-hydrazine, 0142
- \* Borane-phosphorus trifluoride, 0140
- \* Borane-pyridine, 0139
- \* Borane-tetrahydrofuran, 0138
- \* *N-tert*-Butyl-*N*-trimethylsilylaminoborane, 2878
- \* *B*-Chlorodimethylaminodiborane, 0962
- \* Cyanoborane oligomer, 0393
- Decaborane(14), 0198
- \* Diammineboronium heptahydrotetraborate, 0190
- \* Diammineboronium tetrahydroborate, 0167
- † Diborane(6), 0166
- \* Dimethylaminodiborane, 0967
- \* Disodium tridecahydrononaborate(2-), 0195
- \* Heptakis(dimethylamino)trialuminium triboron pentahydride, 3676
- Hexaborane(10), 0191
- Hexaborane(12), 0192
- Pentaborane(11), 0189
- † Pentaborane(9), 0188
- \* Phosphorus azide difluoride-borane, 4316
- Poly[borane(1)], 0134
- Tetraborane(10), 0181
- \* Tetraphosphorus hexaoxide-bis(borane), 4868

*See* 1,3-DIAZA-2-BORACYCLOALKANES *See other* NON-METAL HYDRIDES

## BORON COMPOUNDS

This class contains the groups:

ALKYLBORANES, ALKYLHALOBORANES  
AZOCARBABORANES, BORANES, CARBABORANES  
DIAZONIUM TETRAHALOBORATES, HALOBORANES

### *tert*-BUTYL ESTERS

**Me<sub>3</sub>COCO.R**

Hodgson, P. K. G. *et al.*, *J. Chem. Soc., Perkin Trans. 2*, 1978, 854

Preparation of *tert*-butyl esters from the acid and 2-methylpropene under pressure in glass vessels led to explosions. A safe procedure in a steel cylinder is described.

### *tert*-BUTYL PEROXOPHOSPHATE DERIVATIVES

**Me<sub>3</sub>COOP(O)(OR)<sub>2</sub>**

Rieche, A. *et al.*, *Chem. Ber.*, 1962, **95**, 381–388

Although dialkyl *tert*-butylperoxophosphate derivatives are relatively stable, the diaryl esters and bis(*tert*-butylperoxo) esters decompose violently on attempted isolation. Individually indexed compounds are:

*O*–*O*-*tert*-Butyl diphenyl monoperoxophosphate, 3712

*O*–*O*-*tert*-Butyl di(4-tolyl) monoperoxophosphate, 3763

*tert*-Butyl peroxophosphoryl dichloride, 1644

Di(*O*–*O*-*tert*-butyl) ethyl diperoxophosphate, 3374

*See related* PEROXYESTERS, PHOSPHORUS ESTERS

## CALORIMETRY

Individual entries:

ACCELERATING RATE CALORIMETRY (ARC)  
ADIABATIC CALORIMETRY  
ASSESSMENT OF REACTIVE CHEMICAL HAZARDS  
CHEMICAL STABILITY/REACTIVITY ASSESSMENT  
DIFFERENTIAL SCANNING CALORIMETRY (DSC)  
DIFFERENTIAL THERMAL ANALYSIS (DTA)  
HEAT FLOW CALORIMETRY  
OXYGEN BOMB CALORIMETRY  
REACTION SAFETY CALORIMETRY  
THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

## CAN OF BEANS

Foote, C. S., private comm., 1965

An unopened can of beans, placed in a laboratory oven originally at 110°C but later reset to 150°C, exploded causing extensive damage. Comments were judged to be superfluous.

*See* Diprotium monoxide, 4475

## CARBABORANES

(Cyclic boranes with hetero C atoms)

Carbon tetrachloride

See BORANES: carbon tetrachloride

## CARBONACEOUS DUSTS

*Explosion and Ignition Hazards*, Rept. 6597, Washington, US Bur. Mines, 1965  
Hazards of 241 industrial dusts which may explode or burn because of their carbon content are defined, covering particle size and chemical composition in 10 categories.

See also DUST EXPLOSION INCIDENTS, PETROLEUM COKE

Carbon, (reference 6), 0298

## CARBONYLMETALS

$M(CO)_n$

Bailar, 1973, Vol. 1, 1227

The explosive 'carbonylalkali-metals', previously formulated as monomeric compounds, are either dimeric acetylene derivatives of the general formula  $MOC\equiv COM$ , or are trimers of the latter and formulated as salts of hexahydroxybenzene. Many true carbonylmetal complexes are air-sensitive and pyrophoric, not always immediately. Individually indexed compounds are:

- Bis(dicarbonylcyclopentadienyliron)–bis(tetrahydrofuran)magnesium, 3835
- \* Bis[dicarbonyl(cyclopentadienyl)tributylphosphinemolybdenum]–tetrakis(tetrahydrofuran)magnesium, 3913
- \* Bis(2-methyl-1,8-naphthyridine)tetracarbonyldirrhodium(I) perchlorate, 3833
- \* Bis(1,8-naphthyridine)tetracarbonyldirrhodium(I) perchlorate, 3791
- \* Caesium pentacarbonylvandate(3–), 1811
- \* Carbonyl(pentasulfur pentanitrido)molybdenum, 0535
- Decacarbonyldirhenium, 3386
- \* Dicarbonyl- $\pi$ -cycloheptatrienyltungsten azide, 3123
- \* Dicarbonylmolybdenum diazide, 0995
- \* Dicarbonyl- $\eta$ -trichloropropenyldinickel chloride dimer, 3233
- \* Dicarbonyltungsten diazide, 1013
- Dodecacarbonyltetracobalt, 3420
- Dodecacarbonyltriiron, 3428
- Hexacarbonylchromium, 2056
- Hexacarbonylmolybdenum, 2628
- Hexacarbonyltungsten, 2636
- Hexacarbonylvandium, 2635
- \* Hexakis(pyridine)iron(II) tridecacarbonyltetraferate(2–), 3906
- \* Lithium octacarbonyltrinicelate, 3109
- Nonacarbonyldiiron, 3111
- Octacarbonyldicobalt, 2881
- † Pentacarbonyliron, 1814
- \* Potassium pentacarbonylvandate(3–), 2049



- \* Potassium tricarbonyltris(propynyl)molybdate(3-), 3471
- \* Sodium pentacarbonylrhenate, 2051
- \* Sodium tetracarbonylferrate(2-), 1376
- \* Tetracarbonylmolybdenum dichloride, 1358
- † Tetracarbonylnickel, 1805
- \* Tetrakis(pyridine)bis(tetracarbonylcobalt)magnesium, 3867
- \* 1,4,7-Triazacyclononanetricarbonylmolybdenum hydride perchlorate, 3185
- \* 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate, 3186
- \* Tris(bis-2-methoxyethyl ether)potassium hexacarbonylniobate(1-), 3856

### CATALYST HANDLING SAFETY

1. Fulton, J. W., *Chem. Eng.* (NY), 1987, **94**(12), 99–101
2. Habermehl, R., *Chem. Eng. Progr.*, 1988, **84**, 16–19
3. Reynolds, M. P. *et al.*, *Chem. Ind.* (Dekker), 1996, **68**, 371

Safety aspects of drum storage, pellet screening, dust removal, reactor loading and unloading, and activation of process catalysts are discussed [1], and reprocessing aspects are considered, with disposal as a last resort [2]. Hydrogenation catalysts introduce their own problems [3].

*See also* HYDROGENATION CATALYSTS

### CATALYTIC HYDROGENATION AUTOCLAVES

Harak, J., *Stud. Surf. Sci. Catal.*, 1986 (27, Catal. Hydrog.), 578–611

Measures and equipment needed for safe control of autoclaves used for laboratory, pilot plant, or industrial scale catalytic hydrogenation are discussed, including the need for early recognition of onset of hazardous conditions.

CATALYTIC NITRO REDUCTION PROCESSES

HYDROGENATION CATALYSTS

HYDROGENATION INCIDENTS

### CATALYTIC IMPURITY INCIDENTS

Incidents where presence of impurities, often in trace (catalytic) amounts, has significantly reduced stability or enhanced reactivity are under the entries:

Acetic anhydride, : Ethanol, Sodium hydrogen sulfate, 1534

† Acrylaldehyde, 1145

Adipic acid, 2441

Ammonium perchlorate, : Impurities, 4004

Azidoacetic acid, 0774

† Aziridine, : Acids, 0863

Benzoyl azide, 2698

Benzyl chloroformate, 2931

1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0803

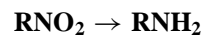
Bromine trioxide, 0259

2-Butanone oxime, 1654

2-Butyne-1,4-diol, 1526

Butyraldehyde oxime, 1655  
 Carbon, : Unsaturated oils, 0298  
 Chlorine, : Carbon disulfide, 4047  
 † 1-Chloro-2,3-epoxypropane, : Contaminants, 1162  
 Cyanogen chloride, 0323  
 \* Diethyl phosphorochloridate, 1681  
 † 1,1-Difluoroethylene, 0700  
 † Diketene, : Acids, or Bases, or Sodium acetate, 1441  
*N,N*-Dimethylacetamide, 1656  
 2,4-Dinitrotoluene, 2726  
 4-Ethoxy-2-methyl-3-butyn-2-ol, 2844  
 Ethylene oxide, : Contaminants, 0829  
 Ethyl oxalyl chloride, 1456  
 Hydrogen peroxide, : Coal, 4477  
 Hydrogen peroxide, : Copper(II) chloride, 4477  
 † Isopropyl chloroformate, 1560  
 Maleic anhydride, : Bases, or Cations, 1404  
 Mercury(II) oxalate, 0982  
 Methylammonium nitrate, 0506  
 4-Methylbenzyl chloride, 2959  
 \* Methyl isocynoacetate, 1470  
*N*-Methylmorpholine oxide, 1997  
 Nickel, : Hydrogen, Oxygen, 4820  
 Nitric acid, : Sulfur dioxide, 4436  
 Oxygen (Gas), : Carbon disulfide, Mercury, Anthracene, 4831  
 Oxygen (Liquid), : Carbon, Iron(II) oxide, 4832  
 Oxygen difluoride, : Hexafluoropropene, Oxygen, 4317  
 Potassium chlorate, : Manganese dioxide, 4017  
 † Propionyl chloride, : Diisopropyl ether, 1163  
 † Propylene oxide, : Sodium hydroxide, 1225  
 Silver azide, 0023  
 Silver nitride, 0038  
 Sodium carbonate, 0552  
 Sodium peroxoborate, 0155  
 Tetrafluoroammonium tetrafluoroborate, 0133  
 Triallyl phosphate, 3184  
 Trifluoromethanesulfonic acid, : Acyl chlorides, Aromatic hydrocarbons, 0375  
 Trimethyl phosphate, 1318  
 See DIAZONIUM TETRAHALOBORATES (reference 5)  
 See INDUCTION PERIOD INCIDENTS

## CATALYTIC NITRO REDUCTION PROCESSES



1. MacNab, J. I., *Runaway Reactions*, 1981, Paper 3/S, 1–15
2. Stoessel, F., *J. Loss Prev.*, 1993, **6**(2), 79

Catalytic reduction of aromatic nitro compounds to the amines is highly exothermic ( $\Delta H = -548 \pm 12$  kJ/mol) and has high potential for hazard in the event of cooling- or other process-failure. The total reaction proceeds *via* nitroso and hydroxylamino intermediates, both of which are reactive and may undergo undesired condensation or disproportionation reactions, and the thermochemistry of all these possibilities was investigated. The reduction or disproportionation of the hydroxylamino intermediate (which is of low thermal stability) is identified as the fastest and most exothermic step (despite which it can frequently be concentrated or trapped); implications for process safety are considered in detail and verified by experiment with typical compounds and intermediates [1]. A calorimetric study of the hazards inherent in hydrogenation of nitroaromatics was made, using nitrobenzene as model compound [2]. Individual incidents of this type are:

2-Chloro-5-methylphenylhydroxylamine, 2796

3,4-Dichlorophenylhydroxylamine, 2243

2-Nitroanisole, : Hydrogen

1,1,1-Tris(azidomethyl)ethane, 1937

Tris(hydroxymethyl)nitromethane, 1664

*See also* CATALYTIC HYDROGENATION AUTOCLAVES, CALORIMETRY

## CATHODIC CORROSION PROTECTION

Bond, 1991, 43; *ibid.*, 63

Cathodic protection systems have started a number of hydrocarbon fires, either by direct current sparking to earth, or from thermite reactions causing sparks when rusty lumps of iron fall on magnesium electrodes.

*See* THERMITE REACTIONS

## CELLULOSE



Gray, B. F. *et al.*, *J. Chem. Technol., Biotechnol.*, 1984, **34A**(8), 453–463

Spontaneous ignition hazards and criteria for safe storage of stockpiles of cellulosic materials were investigated on the laboratory scale, using piles of sieved bagasse pith of various sizes and shapes. Temperature profiles were measured and critical temperatures for ignition determined with high accuracy. The important part played by moisture was investigated, and the need for improvement in scaling extrapolation procedures is stressed. The results are consistent with those for wood flour, and conclusions are applicable to all cellulosic materials at high temperatures.

Energy of exothermic decomposition of finely fibrous cellulose in range 275–335°C was measured as 0.32 kJ/g.

*See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Calcium oxide

*See* Calcium oxide: Water (reference 2)

Oxidants

*See* Calcium permanganate: Cellulose

Fluorine: Miscellaneous materials, 4310  
Magnesium perchlorate: Cellulose, etc., 4084  
*N*-Methylmorpholine oxide, 1997  
Nitric acid: Cellulose, 4436  
Perchloric acid: Cellulose and derivatives, 3998  
Perchloric acid: Hydrofluoric acid, Structural materials, 3998  
Potassium chlorate: Cellulose, 4017  
Potassium nitrate: Cellulose, 4650  
Sodium chlorate: Paper, etc., or: Wood, 4039  
Sodium nitrite: Wood, 4720  
Sodium nitrate: Fibrous material, 4721  
Sodium peroxide: Fibrous materials, 4803  
Zinc permanganate: Cellulose, 4710  
BLEACHING POWDER: Wood  
PERCHLORATES: Organic matter

#### Water

1. Longauerova, D. *et al.*, *Chem. Abs.* 1993, **118**, 26762
2. Kletz, T. A., *Process Safety Progress*, 1995, **14**(4), 274

A storage tank for neutral sulphite woodpulp exploded. Investigation showed bacterial contamination, producing hydrogen and hydrogen sulphide in the headspace, which subsequently suffered electrostatic ignition [1]. A similar incident with ignition from welding operations is reported; in this case not bulk wet woodpulp, but recycled water from pulping operations was the source of the hydrogen [2]. [NB, most shirts and all kitchen paper are made of cellulose, neither the above phenomena, nor a very mild exotherm on hydration, justify the statement in another recent work on reactive chemicals that cellulose and water are an unsafe combination — Editor]

See COTTON, WOOD PULP

#### CELLULOSE NITRATE

(MCA SD-96, 1970); FPA H118, 1982

1. Kirk-Othmer, 1979, Vol. 5, 129–137
2. Anon., *Accidents*, 1961, **46**, 12
3. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 13
4. *MCA Case History No. 1614*
5. Fifen, R. A., *Progr. Astronaut. Aeronaut.*, 1984, **90**, 177–237
6. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62–74
7. Grewer, T. *et al.*, *Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
8. Roberts, T. A. *et al.*, *J. Loss Prev.*, 1992, **5**(5), 311
9. Dosoudel, T. *et al.*, *Chem. Abs.*, 1994, **121**, 13250

Cellulose nitrate is very easily ignited and burns very rapidly or explosively, depending on the degree of confinement, degree of nitration and state of subdivision. Unless very pure and stabilised, it deteriorates in storage and may ignite

spontaneously [1]. Removal of the emulsion coating from celluloid film base gives unstable material which may ignite on prolonged storage in an enclosed space [2]. Unused but aged centrifuge tubes made of 'nitrocellulose' plasticised with dibutyl phthalate, ignited and exploded while being steam-sterilised in an autoclave at 125°C. The violent decomposition was attributed to the age of the tubes, the high temperature and the presence of the steam, (leading to hydrolysis and formation of free nitric acid) [3]. During hacksaw cutting of a pipe containing cellulose nitrate residues, a violent explosion occurred [4]. The ignition and combustion chemistry of cellulose nitrate has been reviewed, including the decomposition and catalysis mechanisms [5]. The finely divided nitrate is also a very significant dust explosion hazard, maximum explosion pressures above 17.4 bar, with maximum rate of rise above 1.42 kbar/s have been recorded [6]. Values for the critical ignition temperature of 60 and 41°C for induction periods of 7 and 60 days, respectively, have been recorded. Autocatalytic combustion is exhibited [7]. Details of storage separation distances for cellulose nitrate sufficient to prevent thermal radiation propagating deflagration from one container to the next are given [8]. Water in nitrocellulose powders does not always have the expected stabilising effects. Detonation velocities can increase and 25% water was shown to facilitate the deflagration to detonation transition [8].

#### Amines

MRH 4.81/tr. (for all 8 amines)

1. Anon., *ABCM Quart. Safety Summ.*, 1956, **27**, 2
2. Thurlow, G. K. *et al.*, private comm., 1973
3. Kaila, E., *Chem. Abs.*, 1958, **52**, 19121<sub>f</sub>

Cellulose nitrate of high surface area (dry or alcohol-wet guncotton or scrap) spontaneously ignited in contact with various amines used as curing agents for epoxy resins. These included 1,2-diaminoethane, *N*-2-hydroxyethyl-1,2-diaminoethane, diethylenetriamine, triethylenetetramine, *N*-2-hydroxyethyltriethylenetetramine, tetraethylenepentamine, 2-hydroxyethylamine, 2-hydroxyethyl dimethylamine, 2-hydroxypropylamine, 3-dimethylaminopropylamine, morpholine, and diethylamine. Ethylamine and dibutylamine caused charring but not ignition [1]. Similar results were found during an investigation of the compatibility of cellulose nitrate with a range of amine and amide components used in paint manufacture. Preliminary small-scale (12 g) tests in which ethyl acetate solutions of cellulose nitrate and the other components were mixed in a lagged boiling tube showed large exotherms (which boiled the solvent off) with 1,4-diazabicyclo[2.2.2]octane, 2,4,6-tris(dimethylamino)phenol, morpholine and benzyldimethylamine. Smaller exotherms were shown by dodecylamine, dodecyl dimethylamine (both fat-derived, containing homologues) and a polyamide resin, Versamid 140.

Subsequent tests in which small portions of these undiluted liquid amines and dried cellulose nitrate linters were contacted (with a little added butyl acetate for the solid phenol) under various conditions, gave ignition with the first 3 amines, and exotherms to 110°C with foaming decomposition for the remaining 4. Other amine resin components showed slight or no exotherms in either test [2]. Contact of cellulose nitrate with a little butylamine caused explosive reaction [3].

Iron red pigment, Plasticiser

Penczek, P. *et al.*, *Chem. Abs.*, 1976, **85**, 63924

During roller-blending to disperse iron red pigment (iron(III) oxide) into plasticised cellulose nitrate, the mixture became a gel after 15 passes and tended to self-ignite.

Iron(II) sulfate

Yan, Z., *Chem. Abs.*, 1983, **99**, 106948

Presence of iron(II) sulfate reduces the stability of the nitrate by a factor of 2.5.

Other reactants

Yoshida, 1980, 274

MRH values calculated for 13 materials all indicate likely catalytic decomposition effects with traces of them.

Potassium iodide

Morrow, S. I., *Anal. Calorim.*, 1977, **4**, 185–191

Low levels of potassium iodide strongly retard the thermal decomposition of thin films of cellulose nitrate.

*See related* ALKYL NITRATES *See other* PYROPHORIC MATERIALS

## CHARCOAL

Pfeil, N., *Loss Prevention and Safety Promotion in the Process Industries*, Vol II, (Mewis, J. J., Pasman, H. J. and De Rademaker, E. E. Eds.), 161, Amsterdam, Elsevier, 1995

Autoignition of fresh charcoal, but not gunpowder prepared from it, is known to have happened in the black powder industry. (Optimum charcoal for gunpowder production is well short of being fully carbonised).

*See* Carbon

## CHEMICAL PLANT SAFETY

1. Kirk Othmer, 1996, Vol. 19, 190
2. Ullmann, 1995, B7, B8, especially B8, 311
3. *Loss Prevention in the Process Industries*, Lees, F. P., Oxford, Butterworth-Heinemann, 2nd Edn. (3 Volumes), 1996
4. *The Safe Handling of Chemicals in Industry*, Carson P. A., Mumford, C. J., Harlow (Essex), Longmans 1989: (originally two volumes, later extended to four)

Much writing on this subject, from introductory essays to multivolume books covering all aspects, including the legislative and bureaucratic, has latterly appeared. Remarkably little of it is directly relevant to the purposes of this book, which is not surprising since it is slips, trips, falls and moving transport accidents which injure and kill chemical workers, far more than do fire and explosion, though these are themselves well ahead of poisoning in the accident statistics. Public concern is otherwise focussed. Some English-language examples are given above.

## CHEMICAL STABILITY/REACTIVITY ASSESSMENT

Fenlon, W. J., *Proc. Intern. Sympos. Prev. Major Chem. Accid.*, Washington, 1987, A.27–A.41, New York, AIChE, 1987

In the Technical Safety Laboratory of Eastman Kodak, the role played by calorimetric methods (such as High Pressure DSC and ARC techniques) in assessing the stability of chemicals and processes, though a central one, is but part of a range of techniques used for this overall purpose. The relations between these methods is discussed and presented in the form of logic flow diagrams.

*See* ASSESSMENT OF REACTIVE CHEMICAL HAZARDS  
COMPUTATION OF REACTIVE CHEMICAL HAZARDS  
REACTION SAFETY CALORIMETRY

## CHEMICAL VAPOUR DEPOSITION (CVD)

Hammond, M. L., *Solid State Technol.*, 1980, **23**(12), 104–109

Hazards associated with the use of cleaning, etching and doping materials and procedures in semi-conductor CVD are codified, with 7 references.

*See also* GAS HANDLING

## CHLORINATED PARAFFINS

Carbon black, Lead(IV) oxide, Manganese(IV) oxide

Chlorinated paraffins are viscous liquids or low-melting solids, depending on the chlorine content (40–80%) and the paraffin type. In general they are thermally unstable, tending to eliminate hydrogen chloride. In the absence of an inhibitor (usually a material which will react readily with traces of hydrogen chloride), they will soon turn brown or black at ambient temperature. Epoxides or glycols are often used as inhibitors at around 1% concentration, and chlorinated paraffins stabilised with propane-1,2-diol or epoxidised soya oil may be heated to 100°C with little change, though for limited periods, as the inhibitor becomes depleted with time.

*See* Lead(IV) oxide: Carbon black, etc.

*See related* HALOALKANES, HALOCARBONS

## N-CHLORINATED PHOSPHORUS AMIDES



Preparative hazard

*See* Chlorine: Dimethyl phosphoramidates

## CHLORINATED POLY(DIMETHYLSILOXANES)



Sosa, J. M., *Thermochim. Acta*, 1975, **13**, 100–104

Chlorinated silicone oil (DC200, with 15, 30 or 40% chlorine content; structure shown has 32%) decomposed violently on heating. Thermal stability decreased with increasing chlorine content and was investigated by TGA and DSC techniques.

## CHLORINATED RUBBER

Metal oxides or hydroxides

1. Anon., *Chem. Trade J.*, 1962, **151**, 672
2. Anon., *Euro. Chem. News*, 1963, (May 24th), 29
3. 'Rept. GCS 27130', London, ICI, 1963
4. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 12

Intimate mixtures of chlorinated rubber and zinc oxide or powdered zinc, with or without hydrocarbon or chlorinated solvents, react violently or explosively when heated at about 216°C. If in milling such mixtures local overheating occurs, a risk of a violent reaction exists. Such risks can be minimised by controlling milling temperatures, by cooling, or by using a mixture of maximum possible fluidity [1]. Similar reactions have been observed with antimony or lead oxides, or aluminium, barium or zinc hydroxides [2]. The full report [3] has been abstracted [4].

*See related* HALOALKENES

## CHLORINE-CONTAINING SYSTEMS

1. Mal'tseva, A. S. *et al.*, *Chem. Abs.*, 1975, **82**, 45981
2. Dokter, T., *Explosion hazards of methyl chloride and chlorine-containing systems*, PhD thesis, Twente University, Netherlands. 1987
3. Gustin J-L., *Ind. Chem. Libr.*, 1996 **8** (Roots of Organic Development), 431, Elsevier

Explosive limits and hazards of various binary and ternary systems containing chlorine or its compounds are reviewed and discussed [1]. The safety aspects of operating a proposed pilot plant for the continuous production of dichloromethane and chloroform from chloromethane and chlorine have been studied in an explosion hazards analysis. The study has been augmented by experimental investigation of many of the safety parameters revealed in the study for which no results were available. Such parameters include flammability limits, burning velocities and quenching diameters, detonation limits and velocities, ignition energies and autoignition temperatures in the gaseous system chloromethane–dichloromethane–chlorine–hydrogen chloride; autoignition temperatures of chloromethane and dichloromethane in chlorine. Additionally, the formation of the highly explosive nitrogen trichloride during chlorination of materials containing ammonium salts or other nitrogen source was studied [2]. A review covering auto-ignition, deflagration and detonation of chlorination reactions has appeared more recently [3].

Chlorine drying towers

*See* Hydrogen: Oxygen, Sulfuric acid

*See* Chlorine

## CHLORITE SALTS

$\text{ClO}_2^-$

1. Mellor, 1941, Vol. 2, 284; 1956, Vol. 2, Suppl. II (Halogens), 573–575
2. Pascal, 1960, Vol. 16, 263



Many of the salts which have been prepared are explosive and sensitive to heat or impact. These include chlorites of copper (violent on impact), hydrazine (monochlorite, inflames when dry), nickel (explodes at 100°C but not on impact), silver (at 105° or on impact), sodium, tetramethylammonium, mercury, thallium and lead (which shows detonator properties). Several other chlorites not isolated and unstable in solution include mono-, di- and tri-methylammonium chlorites. The metal salts are powerful oxidants [1]. Chlorites are much less stable than the corresponding chlorates, and most will explode under shock or on heating to around 100°C [2]. Individually indexed compounds are:

Barium chlorite, 0204

Calcium chlorite, 3925

Hydrazinium chlorite, 4008

Lead(II) chlorite, 4102

Lithium chlorite, 4020

Mercury(I) chlorite, 4080

Mercury(II) chlorite, 4077

Methylammonium chlorite, 0500

Nickel chlorite, 4093

Potassium chlorite, 4016

Silver chlorite, 0010

Sodium chlorite, 4038

Tetramethylammonium chlorite, 1742

Thallium(I) chlorite, 4043

*See also* OXOSALTS OF NITROGENOUS BASES

## CHLOROFLUOROCARBONS

*RSC Lab. Hazard Data Sheet No. 75, 1988*

Information is given on Freons 11, 12, 13, 21, 22, 113, 114: trichlorofluoro-, dichlorodifluoro-, chlorotrifluoro-, dichlorofluoro- and chlorodifluoro-methane; 1,1, 2-trichloro-1,2,2-trifluoro-, and 1,2-dichloro-tetrafluoro-ethane, respectively.

*See* Chlorodifluoromethane

1,2-Dichlorotetrafluoroethane

Trichlorofluoromethane

*See also* HALOCARBONS

## N-CHLORONITROAMINES

**RN(Cl)NO<sub>2</sub>**

Grakauskas, V. *et al.*, *J. Org. Chem.*, 1972, **37**, 334

*N*-Chloronitroamines and the derived *N*-chloro-*N*-nitrocarbmates are explosive compounds and decompose rapidly in storage.

*See* *N*-Fluoro-*N*-nitrobutylamine

*See other* *N*-HALOGEN COMPOUNDS, *N*-NITRO COMPOUNDS

## CHLOROPHYLL

Ichimura, S. *et al.*, Japan Kokai, 74 86 512, 1974

Chlorophyll adsorbed on clay, or powdered unicellular green algae (chlorella) can be caused to explode by focussed irradiation from a powerful ruby laser.

*See other* IRRADIATION DECOMPOSITION INCIDENTS

## CLATHROCHELATED METAL PERCHLORATES

Goedeken, V. L., *Inorg. Synth.*, 1980, **20**, 89

In the tris(2,3-butanedione dihydrazone) complexes of e.g. iron(II), nickel or cobalt(II or III) salts, the metal atom is effectively enclosed in an open ended chelating cylinder. The end of the cylinder can be closed by treating the complex with acidified aqueous formaldehyde, when at each end of the cylinder the 3 amino groups are converted to a hexahydrotriazine ring to give the clathrochelate salt. When the metal salts are perchlorates (and the formaldehyde is acidified with perchloric acid), the products must be regarded as treacherously unstable, like other perchlorate salts containing oxidisable matter, with avoidance of heating either the solids or the conc. solutions.

Individually indexed compounds are:

5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo [8.8.4.1<sup>3,17</sup>.1<sup>8,12</sup>]tetracos-4,6,13,15,19,21-hexaene-*N*<sup>4</sup>,*N*<sup>7</sup>,*N*<sup>13</sup>,*N*<sup>16</sup>,*N*<sup>19</sup>,*N*<sup>22</sup> cobalt(II) perchlorate, 3768

5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo [8.8.4.1<sup>3,17</sup>.1<sup>8,12</sup>]tetracos-4,6,13,15,19,21-hexaene-*N*<sup>4</sup>,*N*<sup>7</sup>,*N*<sup>13</sup>,*N*<sup>16</sup>,*N*<sup>19</sup>,*N*<sup>22</sup> iron(II) perchlorate, 3769

5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo [8.8.4.1<sup>3,17</sup>.1<sup>8,12</sup>]tetracos-4,6,13,15,19,21-hexaene-*N*<sup>4</sup>,*N*<sup>7</sup>,*N*<sup>13</sup>,*N*<sup>16</sup>,*N*<sup>19</sup>,*N*<sup>22</sup> nickel(II) perchlorate, 3770

*See* AMMINEMETAL OXOSALTS, [14] DIENE-N<sub>4</sub> COMPLEXES

POLYAZACAGED METAL PERCHLORATES

TETRAAZAMACROCYCLANEMETAL PERCHLORATES

## CLEANING BATHS FOR GLASSWARE

Stahr, H. M. *et al.*, *Anal. Chem.*, 1982, **54**, 1456A

As a safer and cheaper alternative to the use of sulfuric acid–dichromate mixtures (chromic acid, and of the hazardous nitric acid–ethanol, or sulfuric acid–permanganate mixtures), a sulfuric acid–ammonium persulfate bath is recommended as long-lasting and economical. However, any such oxidant mixture should be used with caution, and only when necessary. In the absence of significant adherent residues on glassware, one of the proprietary detergent formulations should give adequate cleaning, except perhaps for the most rigorous surface chemistry or trace analysis requirements.

*See* Chromic acid

Nitric acid: Alcohols (reference 2), 4600

Nitric acid: Glassware, 4436

Potassium permanganate: Sulfuric acid, etc. (references 2,3), 4709

See also PLANT CLEANING INCIDENTS

## COAL

1. Rigsby, L. S., *J. Coal Qual.*, 1983, **2**(2), 16–20
2. Grossman, S. L. *et al.*, *Coal Sci. Technol.* 1995, 24(Coal Sci. Vol. I), 469, 473.
3. Grossman, S. L. *et al.*, *Erdöl, Erdgas, Köhle*, 1996, **112**(7/8), 322
4. Marzec, A., *Chem. Abs.*, 1997, **127**, 164191e

All aspects of self-heating of coal during storage and transportation are considered, and the main factors are identified as temperature, rank, particle size, moisture and pyrites contents [1]. Although explosions are always attributed to methane, in fact bituminous coal emits hydrogen during warm storage by an oxidative decomposition mechanism, which can be a danger if ventilation is poor [2,3,4].

Sodium carbonate

See AUTOIGNITION TEMPERATURE (reference 7)

See also SELF-HEATING AND IGNITION INCIDENTS

## COMMERCIAL ORGANIC PEROXIDES

C—OO—

1. Boyars, C., *AD Rept. No. 742770*, Richmond (Va.), USNTIS, 1972
2. Lee, P. R., *J. Appl. Chem.*, 1969, **19**, 345–351
3. Leleu, *Cahiers*, 1980, (99), 279
4. Gehrke, H., *Zentr. Arbeitsmed. Arbeitsschutz*, 1977, **27**, 7–10
5. Venable, E., *Chem. Eng. News*, 1982, **60**(42), 94
6. Stull, 1977, 21
7. Wagle, U. D. *et al.*, *Safety in Polyethylene Plants*, 1978, **3**, 62–68
8. Nakagawa, S., *Chem. Abs.*, 1979, **91**, 210654
9. de Groot, J. J. *et al.*, *Runaway Reactions*, 1981, Paper 3/V, 1–17
10. de Groot, J. J. *et al.*, *Ind. Eng. Chem., Proc. Des. Dev.*, 1981, **20**, 131–138
11. Mohan, V. K. *et al.*, *J. Haz. Mat.*, 1982, **5**, 197–220
12. Fisher A., *Ger. Offen.*, 2 637 940, 1978
13. *NFPA 43B*, Quincy (Ma), Natl. Fire Prot. Assocn., 1986

This group of compounds is widely used in industry as a radical source for initiation of polymerisation. They are available from several manufacturers in a very wide range of formulations in various diluents to reduce operational hazards. These were classified into 6 hazard levels and of the many materials available, the first list below of 6 compounds (all dry and unformulated except for that suffixed \*, which is water-wetted) were included in the highest risk category. This specified the material as being sensitive to friction or mechanical shock equivalent to the dissipation of 1 kg m or less of energy within the sample.

Existing and proposed methods of evaluating transportation hazards of organic peroxides exposed to impact, explosive shock or thermal surge stimuli were reviewed, and a hazard classification system proposed [1]. Commercial 2-butanone peroxide ('MEK peroxide') as a 40% solution in dimethyl phthalate was previously

thought to be safe in normal storage or transport situations, but several road- and rail-tanker explosion incidents showed evidence of detonation. Application of steady-state thermal explosion theory allowed the prediction of critical mass and induction period in relation to temperature in bulk storage. The critical mass seems likely to have been attained in some of the incidents [2]. MEK peroxide diluted with mixed phthalate–phosphate esters and mixed with powdered charcoal gave accelerated decomposition above 35–40°C, with thick fumes [3]. (Catalysis by trace metals in the charcoal seems a likely factor). This peroxide is also used as a hardener in on-site production of polyester–concrete structural elements, and a violent explosion occurred which was attributed to incorrect storage conditions [4]. MEK peroxide is, of course, also an oxidant and will ignite acetone or other combustibles on contact, and may lead to explosion [5]. The result of calculations of the exothermic potential from thermal decomposition of neat MEK peroxide ( $Q = 218.5$  kJ/mol, 1.79 kJ/g, leading to adiabatic product gas temperature of 832°C and a peak pressure of 32 bar) is related to the effects of a catastrophic transportation incident involving 17 t of mixed peroxides initiated by a small MEK peroxide fire [6].

A method was developed for the large-scale testing of the decomposition characteristics of commercial peroxides held in closed vessels of 2–120 l capacity fitted with bursting disks and temperature/pressure recording facilities. The results on *tert*-butyl peroxyvalate and *tert*-butyl peroxy-2-ethylhexanoate suggest that adequate pressure relief vents can be designed based on a constant area per unit volume of container [7]. The course and rate of pressure development when 20 organic peroxides were heated in a new pressure vessel test appear to offer a better assessment of potential hazards and pressure-relief requirements [8]. Thermal phenomena involved in the self-heating decomposition processes of organic peroxides have been investigated under isothermal, adiabatic and temperature-scanning conditions. A new rapid test method had been developed for assessing the effect of impurities upon stability [9]. Both simulated and experimental investigations of worst probable hazards likely from exothermic decomposition of bulk tanks (10 m<sup>3</sup>) of commercial organic peroxides are described, and emergency procedures formulated [10]. A range of 6 commercial organic peroxides and hydrogen peroxide was screened using a variety of tests and a simplified classification of peroxides into 3 groups is proposed [11]. The use of expanded sodium borate as a carrier for organic peroxides is claimed to improve resistance to fire and detonation, and allows their safe use as catalysts, especially in aqueous systems [12]. A recent US National Fire Code covers requirements for safe storage of commercial formulated mixtures [13].

Individually indexed commercial peroxides are:

Acetyl cyclohexanesulfonyl peroxide, 3033

Bis(3-carboxypropionyl) peroxide, 2990

Bis(2,4-dichlorobenzoyl) peroxide, 3623

Bis(2-hydroperoxy-2-butyl) peroxide, 3078

Bis(1-hydroperoxycyclohexyl) peroxide, 3553

*O*-*O*-*tert*-Butyl hydrogen monoperoxymaleate, 3015

Diisopropyl peroxydicarbonate, 3034  
1-Hydroperoxy-1'-hydroxydicyclohexyl peroxide, 3555  
2-Phenyl-2-propyl hydroperoxide, 1387  
*See* CYCLIC PEROXIDES, RADICAL INITIATORS

### COMPLEX ACETYLIDES

$K_m[M(C\equiv C)_n]$

1. Bailar, 1973, Vol. 4, 810
2. Nast, R. *et al.*, *Chem. Ber.*, 1962, **95**, 1470–1483
3. Nast, R. *et al.*, *Z. Anorg. Chem.*, 1955, **279**, 146–156

The title salts, where M is Cr(III), Co(II or III), Cu(0 or I), Au(I), Fe(II or III), Mn(II or III), Ni(0 or II), Pd(0), Pt(0 or II) or Ag(I) are frequently explosive [1], several of the analogous sodium salts being similar. A series of dialkynyl-palladates and -platinate [2] and a tetraalkynylnickelate [3] are pyrophoric, while other tetraalkynylnickelates are explosive [3]. Most react violently with water. Individually indexed compounds are:

(Many of the equivalent sodium salts are similar)

- \* Bis(trimethylphosphine)nickel(0)–acetylene complex, 3093
- Potassium bis(phenylethynyl)palladate(2–), 3699
- Potassium bis(phenylethynyl)platinate(2–), 3700
- Potassium bis(propynyl)palladate, 2308
- Potassium bis(propynyl)platinate, 2309
- Potassium diethynylpalladate(2–), 1394
- Potassium diethynylplatinate(2–), 1395
- Potassium hexaethynylcobaltate(4–), 3446
- Potassium hexaethynylmanganate(3–), 3448
- Potassium tetraethynylnickelate(2–), 2896
- Potassium tetraethynylnickelate(4–), 2897
- Potassium tetrakis(propynyl)nickelate(4–), 3513
- \* Potassium tricarbonyltris(propynyl)molybdate(3–), 3471
- Sodium hexakis(propynyl)ferrate(4–), 3759

*See other* ACETYLENIC COMPOUNDS

### COMPLEX HYDRIDES

$[MH_n],[EH_n]$

1. Gaylord, 1956
2. Semenenko, K. N. *et al.*, *Russ. Chem. Rev.*, 1973, 1–13
3. Ashby, E. C., *Rept. AD-A057764*, Richmond (Va.), NTIS, 1978
4. Ashby, E. C., *J. Organomet. Chem.*, 1980, **200**, 1–10

This group of highly reactive compounds includes several which have found extensive use in preparative chemistry [1]. Properties and reactions of several covalent tetrahydroborates have been reviewed [2]. Preparation and properties of several new hydrides are given which are of interest as high-energy fuels in propellant systems [3,4]. Individually indexed compounds are:

- \* Aluminium dichloride hydride diethyl etherate, 0061
- Aluminium tetrahydroborate, 0058

Beryllium tetrahydroborate, 0157  
 Beryllium tetrahydroborate–trimethylamine, 1337  
 Bis(cyclopentadienyl)niobium tetrahydroborate, 3324  
 Bis(dimethylaminoborane)aluminium tetrahydroborate, 1795  
 Caesium hexahydroaluminat(3–), 0067  
 Caesium lithium tridecahydrononaborate, 0194  
 Calcium tetrahydroborate, 0158  
 Cerium(III) tetrahydroaluminat, 0089  
 Copper(I) tetrahydroaluminat, 0068  
 \* Diammineboronium tetrahydroborate, 0167  
 Disodium tridecahydrononaborate(2–), 0195  
 Hafnium(IV) tetrahydroborate, 0182  
 Heptakis(dimethylamino)trialuminium triboron pentahydride, 3676  
 Lithium dihydrocuprate, 4271  
 Lithium pentahydrocuprate(4–), 4273  
 \* Lithium tetradeuteroaluminat, 0069  
 Lithium tetrahydroaluminat, 0075  
 Lithium tetrahydroborate, 0145  
 Lithium tetrahydrogallate, 4407  
 Magnesium tetrahydroaluminat, 0085  
 Manganese(II) tetrahydroaluminat, 0086  
 Potassium hexahydroaluminat(3–), 0077  
 Potassium tetrahydrozincate, 4516  
 Potassium trihydromagnesate  
 Silver hexahydrohexaborate(2–), 0027  
 Sodium dihydrobis(2-methoxyethoxy)aluminat, 2575  
 Sodium tetradecahydrononaborate, 0196  
 Sodium octahydrotriborate, 0177  
 Sodium tetrahydroaluminat, 0076  
 Sodium tetrahydroborate, 0147  
 Sodium tetrahydrogallate, 4408  
 \* Tricyclopentadienyluranium tetrahydroaluminat, 3688  
 Uranium(III) tetrahydroborate, 0178  
 Uranium(IV) tetrahydroborate etherates, 0183  
 Zirconium(IV) tetrahydroborate, 0184  
*See other REDUCANTS See also METAL HYDRIDES, NON-METAL HYDRIDES*

## COMPRESSED GASES

1. Crowl, D. A. *Plant/Oper. Progr.* 1992, **11**(2), 47  
 Since the whole theme of this book is concerned with unexpected or concealed sources of energy, it is relevant to reiterate that compressed gases may contain a large content of kinetic energy over and above that potentially available from chemical reaction energy possibilities for the gas. A procedure for calculating available kinetic energy from rupture of compressed gas containers is found in

[1]. Compression heating, or just pressure, may explode many unstable gases, or combustible mixtures thereof, during only slight compression.

See GAS CYLINDERS

#### COMPUTATION OF REACTIVE CHEMICAL HAZARDS

1. Treweek, D. N. *et al.*, *J. Haz. Mat.*, 1976, **1**, 173–189
2. Domalski, E. S. *et al.*, *Proc. 4th Int. Symp. Transp. Haz. Cargoes*, 1975, USNTIS PB 254214
3. *CHETAH, Chemical Thermodynamic and Energy Release Evaluation Program*, Philadelphia, ASTM, 1975
4. Sherwood, R. M., *Chem. Brit.*, 1975, **11**, 417
5. Treweek, D. N. *et al.*, *Ohio J. Sci.*, 1980, **80**(4), 160–166
6. Yoshida, T. *et al.*, *Chem. Abs.*, 1981, **95**, 64605
7. Yoshida, T. *et al.*, *Primary Evaluation of Incompatibility and Energy Release in Proc. 4th Symp. Chem. Problems. Conn. Stab. Explosives*, (Hansson, J., Ed.), Tokyo, 1976
8. Yoshida, T. *et al.*, *Chem. Abs.*, 1983, **95**, 7923
9. Yoshida, T. *et al.*, *Chem. Abs.*, 1982, **93**, 188632
10. Davies, C. A. *et al.*, in *Chem. Process Haz. Rev.*, (Hoffmann, J. M. & Mason, D. C., eds.), ACS Symp. Ser. 274, Ch. 9, 81–90, 1985
11. Frurip, D. J. *et al.*, *Plant/Oper. Progr.*, 1989, **8**(2), 100–104
12. Shanley, E. S. *et al.*, *J Loss Prev. Process Ind.*, 1995, **8**(5), 261
13. Harrison, B. K., private communication, 1998

During past decades, several computational methods for predicting instability (or ‘self-reactivity’) and mutual reactivity (‘other chemical reactivity’) have been developed and tested. These have been variously based on structural and calculated thermodynamic parameters, amplified in some cases with experimentally determined data, to produce hazard rating systems.

These methods were jointly evaluated for their ability to predict successfully instability in a range of compound types. It was concluded that the relationship between the parameters considered and chemical stability was too obtuse for conventional statistical analysis. However, application of pattern-recognition techniques to statistical analysis was more fruitful, and 13 of the more promising parameters were evaluated successfully. Total under- and over-estimation error was below 10% relative to generally accepted forms of consensus grading into the 3 stability categories of explosive, hazardous decomposition or polymerisation, and non-hazardous. The methods appear to have great potential in minimising hazards in storage, transfer and transportation of chemicals [1].

In an alternative assessment of the effectiveness of these computer programs, it was concluded that explosive power was over-emphasised in relation to the more practically important aspect of sensitivity to initiation, and many compounds were being indicated as hazardous when they were not. There was also no provision for considering polymerisation as a hazardous possibility, and there was little quantitative data on this. The parameter best correlating with material sensitivity is the bond-dissociation energy. It was recommended that regulations specifying the

handling and transport of chemicals should be based on the concept of known self-reactivity of functional groups present (nitro, nitramine, peroxide, azide, etc.) [2].

One of the computer programs [3] is relatively simple to apply, and gives estimates of the maximum energy release possible for any covalent compound or mixture of compounds containing C, H, O, N, and up to 18 other specified elements. Reactions and products may be specified if known, but the only essential input from the user is the amount and structure of each compound involved, the latter expressed in terms of the number of standard groups or skeletal fragments present in the structure. The graded results serve as a screening guide to permit decisions on which reaction systems need more detailed and/or experimental investigation [4]. In view of the difficulties which attend the use of thermodynamic parameters to try to predict mutual reactivity possibilities between pairs of compounds ('other chemical reactivity'), a computational method has been developed which combines two existing reactivity-ranking procedures (NAS hazard rating system, and Lewis acid-base rating) which gives results within a 10% error margin of the experimental results of the Dow binary hazard classification system (measurement of exotherm and gas evolution on mixing two typical components). It is intended to incorporate this refinement into the CHETAH program [5]. The early program was used fairly successfully to correlate the calculated maximum heat of decomposition for various types of explosive materials (nitrate esters, nitramines, nitroaromatics, formulated explosives, and organic peroxides) with their performance in various standard tests and the heat of decomposition determined by sealed-cell DSC. Correlation was fairly good across the range of comparisons [6].

The EITP (Evaluation of Incompatibility from Thermodynamic Properties) program was originally applied to reduce the possibilities of fires occurring in chemical stores situated in earthquake zones, through collapse of shelving and indiscriminate mixing of reactive chemicals from broken containers. The program calculates for mixtures of 2 or more chemicals the maximum reaction heat (MRH) which is possible, and the proportions necessary for this. Working from case histories of incidents it was then possible to set threshold values for MRH below which no ignition was likely, so that storage schedules to segregate any potentially reactive chemicals could be prepared and implemented [7]. A second revised version (REITP2) was prepared and evaluated against the results of various instrumental tests for purposes more closely related to specific chemical stability problems in explosives and chemical intermediates and products [8]. The REITP program is effective for initial estimation of the degree of hazard arising from decomposition of unstable materials, while the sealed-cell DSC procedure gives more detail on the course and likely consequences of decomposition [9].

A general account of how the CHETAH program may be applied to estimation of chemical hazards in relation to process research and development has been given [10]. Progressively enhanced and user-friendly versions of CHETAH, which give an overall hazard assessment and are capable of running on personal computers are available from ASTM [11]. Comments critical of the criteria used for hazard evaluation in the 1994 CHETAH program [12] led to amendments and enhancements incorporated in the 1998 Windows version. The pure compound physical properties databank has since been expanded from 400 to 1500 compounds and the



number of structural Benson groups used in thermodynamic calculations to >730. An additional criterion, the Calculated Maximum Adiabatic Reaction Temperature (CART) is incorporated. Input of drawn structures via the CHEMDRAW package, with automatic subsequent calculations, is imminent. The new Windows version 7.3 is expected in 1999 [13].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS  
CHEMICAL STABILITY/REACTIVITY ASSESSMENT  
EXOTHERMICITY  
EXPLOSIBILITY (references 3–5)  
MAXIMUM REACTION HEAT

## CONDUCTING POLYMERS

See PERCHLORATE-DOPED CONDUCTING POLYMERS

## COOL FLAMES

1. Coffee, R. D., *Cool Flames*, Chapter 18, 323–338 in *Safety and Accident Prevention in Chemical Operations*, Fawcett, H. H. & Wood, W. S., (Eds.), New York, Wiley, 2nd edn., 1982
2. D'Onofrio, E. J., *Loss. Prev.*, 1980, **13**, 99–95
3. Kolodner, H. J. *et al.*, *Proc. 3rd Intl. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 2, 345–355, SSCI, Basle, 1980
4. Baronnet, R. *et al.*, *Oxid. Commun.*, 1983, **4**(1–4), 83–95
5. Coffee, R. D., *Loss Prev. Bull.*, 1988, (081), 19–23

The complex and incompletely understood phenomena of cool flames and their close relationship with autoignition processes is discussed in considerable detail. As the temperature of mixtures of organic vapours with air is raised, the rate of autoxidation (hydroperoxide formation) will increase, and some substances under some circumstances of heating rate, concentration and pressure will generate cool flames at up to 200°C or more below their normally determined AIT. Cool flames (peroxide decomposition processes) are normally only visible in the dark, are of low temperature and not in themselves hazardous. However, quite small changes in thermal flux, pressure, or composition may cause transition to hot flame conditions, usually after some delay, and normal ignition will then occur if the composition of the mixture is within the flammable limits.

Conditions most conducive to transition from cool flame to hot ignition are those encountered during sudden loss of vacuum and ingress of air during (or soon after) high temperature vacuum distillation processes. Many of the unexplained cases of ignition during these or similar processing operations of organic materials may be attributable to this transition [1]. In a study of the relationships of cool flame temperature, autoignition temperature and ignition delay times of a series of glycols in several sizes of containing vessels, it was found that ethylene glycol shows extremely long delay times. The transition from cool flame to hot ignition was demonstrated experimentally under conditions simulating progressive vacuum failure during vacuum distillation [2]. The same phenomenon, observed when air was admitted during vacuum distillation of a mixture of triethylene glycol

diacetate with 36% of acetic acid, was investigated experimentally prior to pilot scale preparation of the ester, when nitrogen rather than air was admitted to break vacuum [3]. A semi-empirical correlation between cool flame behaviour of an organic compound and structure has been developed, but further experimental work is necessary [4]. A brief account of the nature and significance of cool flames in relation to process safety is presented [5].

For an example, See †2,2-Dimethoxypropane, 1895  
See AUTOXIDATION, AUTOIGNITION INCIDENTS

## COOLING BATHS

Anon., *Sichere Chemiearbeit*, 1992, **44**(6), 70; *Jahresbericht*, 1991, 72

A substantial explosion, followed by a fire causing fatal burns to the experimenter, occurred when working with butyllithium in tetrahydrofuran cooled by a propan-2-ol/solid carbon dioxide freezing bath. It was considered that the explosion might have been fueled by isopropanol vapour in air. This explanation was rejected since the alcohol should have been below its flash point. However, making up such cooling baths, containing flammable solvents, does disperse considerable quantities of vapour and mist before the mix is fully cooled. There is a period of potential hazard, as there may be when the bath warms above the flash point once more.

## COPPER CHROMITE CATALYST



### Alcohols

Budniak, H., *Chem. Abs.*, 1975, **83**, 134493

Copper chromite catalyst, after use in high-pressure hydrogenation of fatty acids to alcohols, is pyrophoric, possibly owing to presence of some metallic copper and/or chromium. Separation of the catalyst from the product alcohols at 130°C in a non-inerted centrifuge led to a rapid exotherm and autoignition at 263°C.

### Ammonium perchlorate

See Ammonium perchlorate: Catalysts (reference 2)

See other HYDROGENATION CATALYSTS

## CORROSION INCIDENTS

1. Hammer, N. E., *Dangerous Prop. Ind. Mater. Rept.*, 1981, **1**(8), 2–7
2. Asakura, S. *et al.*, *Chem. Abs.*, 1982, **96**, 147574
3. Maddison, T. E., *Loss Prev. Bull.*, 1987, (076), 31–38

Hazards created by corrosion involving consumer products, industrial installations, utility systems and dangerous wastes are reviewed [1]. Auto-accelerating corrosion reactions of copper components in acidic media which could lead to sudden plant failure have been studied [2]. Seven cases involving catastrophic failure of large glass-reinforced plastic (GRP) storage tanks are described, most stemming from corrosive attack of the GRP structural elements by the contained liquors, sometimes

after failure of a polymeric liner. Plastics are not commonly considered to be subject to corrosive attack [3].

Some examples of these incidents are:

Aluminium, : Butanol, 0048  
Aluminium, : Mercury(II) salts, 0048  
Aluminium, : Metal nitrates, Sulfur, Water, 0048  
Aluminium, : Water, 0048  
Ammonium sulfide, : Zinc, 4577  
Calcium chloride, : Zinc, 3923  
Chlorine, : Aluminium, 4047  
Chlorine, : Steel, 4047  
Gallium, : Aluminium alloys, 4406  
Magnesium, : Methanol, 4690  
Magnesium, : Halocarbons, 4690  
Magnesium, : Water, 4690  
Magnesium chloride, : Air, Mild steel, Water, 4081  
Mercury, : Metals, 4600  
Methacrylic acid, 1530  
Orthophosphoric acid, : Chlorides, Stainless steel, 4505  
Potassium, (references 4–5a), 4645  
Sodium sulfide, : Glass, 4811  
Uranium, : Nitric acid, Trichloroethylene, 4923

## **COTTON**

### **Oils**

Anon., *Textil-Rundschau*, 1957, **12**, 273

Cotton waste in contact with fatty oils (especially of unsaturated character) is much more subject to self-heating and autoignition than animal fibres. Various factors affecting storage hazards of baled cotton, including the aggravating effects of moisture, are discussed. Mineral oils, though generally less subject to oxidative heating than vegetable oils, have also been involved in autoignition incidents

*See* CELLULOSE

## **COUMARONE-INDENE RESIN**

The finely powdered resin is a significant dust explosion hazard.

*See entry* DUST EXPLOSION INCIDENTS (reference 22)

## **CRITICAL IGNITION TEMPERATURE**

Kotoyori, T., *J. Loss Prev. Proc. Ind.*, 1989, **2**, 16–21

Materials of limited thermal stability may self-heat and eventually ignite through progressive accelerating decomposition if they are stored or processed above the critical ignition temperature (CIT). Knowledge of this is therefore essential for

defining safe conditions for processing or storing such materials. Existing tests to determine this temperature involve a series of runs with adiabatic storage of samples at different (increasing) temperatures until ignition is observed. This temperature is not an absolute value, but depends on sample size and induction period allowed. In the BAM heat accumulation storage test, samples are the largest standard commercial package, and the induction time is set at 7 days, the result being the self-accelerating decomposition temperature (SADT). Naturally, this test requires many kg of material to complete.

A new small-scale test has been developed which needs only a few g of thermally unstable material, which may be contained in an open cell version of the apparatus if aerobic processes are involved, otherwise in a closed cell apparatus, both with full temperature control and monitoring systems. Such materials may be divided into 2 types, depending on the behaviour of a sample after introduction into adiabatic storage at elevated temperature. The first type, which after attaining the adiabatic temperature shows a steady further increase in temperature in line with Frank-Kamenetski's thermal explosion theory, exhibit thermal combustion (TC) behaviour. In the second type, after adiabatic temperature has been reached, the sample shows a sudden rapid rate of rise, exhibiting autocatalytic (AC) behaviour as chain branching and acceleration set in. Of 8 materials examined in this test, five showed TC behaviour (azoisobutyronitrile, dibenzoyl peroxide, dinitrosopentamethylene tetramine, 4,4'-oxybis(benzenesulfonylhydrazide) and calcium hypochlorite), while 3 showed AC behaviour (cellulose nitrate, dilauroyl peroxide and toluenesulfonylhydrazide). CIT values, largely comparable with the BAM results, are given in the individual entries:

Azoisobutyronitrile, 3011

Calcium hypochlorite, 3924

Dibenzoyl peroxide, 3639

Didodecanoyl peroxide, 3857

3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1954

4,4'-Oxybis(benzenesulfonylhydrazide), 3525

4-Toluenesulfonylhydrazide, 2827

*See entries* DEFLAGRATION INCIDENTS, HIGH RATE DECOMPOSITION

## **CROWN ETHERS**

As cyclic polyethers (polyethylene oxides), some of this group of aprotic complexing solvents may be subject to peroxidation, though no reports have been so far noted.

*See* 1,4,7,10,13,16-Hexaoxacyclooctadecane ('18-Crown-6')

Bromoform, Potassium hydroxide, etc.

*See* Bromoform: Cyclic polyethylene oxides, Potassium hydroxide

## CRYOGENIC LIQUIDS

1. Zabetakis, M. G., *Safety with Cryogenic Fluids*, London, Heywood, 1967
2. *Safety Panel, British Cryogenics Council, Cryogenics Safety Manual – A Guide to Good Practice*, Oxford, Butterworth-Heinemann, 3rd edn., 1991
3. *Safety Problems in Handling Low-Temperature Industrial Fluids*, 1964, IChE Symp. papers, published in *Chem. Engr.*, 1965, **43**(185), CE7–10; (186), CE36–48
4. Bernstein, J. T., *Cryogenics*, 1973, **13**, 600–602
5. *B.S. Code of Practice*, BS 5429: 1976
6. Timmerhaus, K. D. *et al.*, *Adv. Cryog. Eng.* 1977, 1978, **23**, 721–729
7. *Recommended Safety Precautions for Handling Cryogenic Liquids*, Crawley, Edwards High Vacuum, 1979
8. Ordin, P. M., *Liqu. Cryog.*, 1983, **1**, 1–57
9. Hofmann, M. J., *J. Chem. Educ.*, 1986, **63**(6), A149–150
10. Ryan, K. P. *et al.*, *Microscope*, (Oxford), 1987, **147**, 337–340
11. Rouault, F. C., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 537–556, Heidelberg, ISSA, 1987
12. Currie, J. L., *Cryogenics*, 1988, **28**, 830–834
13. Anon., *Sichere Chemiearbeit*, 1997, **49**(1), 10

The monograph presents concisely in 6 chapters the principles of safety applicable to cryogenics, with safety data sheets for 15 cryogenic fluids [1]. The revised safety manual covers the operation and maintenance of plant for producing, storing and handling commercial gases which liquefy at low temperatures, and precautions in the use of these materials [2]. The symposium covered possible fire and explosion hazards in general terms, as well as in detail for liquid hydrogen, acetylene, natural gas, and a low-temperature nitrogen-washing process for ammonia synthesis gas [3]. Safety aspects of sampling and handling cryogenic liquids were reviewed [4] and the Code of Practice provides users of liquid oxygen, nitrogen, argon, natural gas, etc. with a basic appreciation of the problems associated with the small-scale use and storage of these materials [5]. Aspects of cryogenic systems involving physiological materials and high pressure are discussed [6], and a 16-page booklet briefly covers essential aspects of the title topic [7]. The recent review of safety in handling and use of cryogenic fluids includes 69 references [8], and safe practices in their laboratory use are presented [9].

In a review of the use of various cryogenic liquids for rapid freezing of biological specimens for cryo-sectioning, hazards attendant on the use of liquid propane and similar cryogens are discussed. Upon evaporation, the volume of mixture with air within the explosive range may be 14,000 times that of the volume of original liquid, and this may be a significant proportion of the free space in a confined work area. Precautions including the use of nitrogen blanketing, a fume cupboard, and adequate ventilation are discussed [10]. The use of a computer controlled interlocked interactive sequencing system to prevent mistakes in loading road tankers with cryogenic liquids is described [11]. The role of the Cryogenics Safety Manual (reference 2 above) as a training guide is discussed, and the major changes in the scheduled 1988 revision are highlighted [12].

A cryogenic storage vial frozen in liquid nitrogen exploded on rewarming to just above ambient temperature, injuring a worker. It is considered that liquid nitrogen seeped round the contracted and hardened seal, which resealed on warming. It is suggested caps be loosened immediately on removal from storage and (impractically?) that vials be filled to the brim, leaving no room for liquid gases [13].

Some examples of cryogens are:

† Propane, 1271

Nitrogen (Liquid), 4735

Oxygen (Liquid), 4832

† Hydrogen (Liquid), 4454

See Argon, Liquid nitrogen

See also LIQUEFIED GASES

### CRYSTALLINE HYDROGEN PEROXIDATES

1. Castrantas, 1965, 4
2. Emeléus, 1960, 432
3. Kirk-Othmer, 1966, Vol. 11, 395
4. Mellor, 1971, Vol. 8, Suppl. 3, 824
5. Editor's comments, 1999
6. Jones, D. P. *et al.*, *J. Chem. Soc., Dalton Trans.*, 1980, 2526–2532

Many compounds will crystallise out with hydrogen peroxide in the crystal lattice, analogous to crystalline hydrates. A few (some of which are listed below) sequester the peroxide preferentially from water. These complexes represent a form of concentrated hydrogen peroxide distributed at a molecular level, which may react violently in close contact (grinding or heating) with oxidisable materials [1–4]. If the host is itself oxidisable, this molecular distribution makes detonability highly probable [5]. Some examples of true peroxodicarbonates (MOCO.OOCO.OM) have been prepared, but they do not behave as oxidants, immediately hydrolysing in water to hydrogen peroxide [6]. Individually indexed compounds are:

1,4-Diazabicyclo[2.2.2]octane hydrogen peroxidate, 2473

Potassium citrate tri(hydrogen peroxidate), 2258

Potassium fluoride hydrogen peroxidate, 4300

Sodium borate hydrogen peroxidate, 0154

Sodium carbonate hydrogen peroxidate, 0552

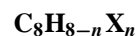
Sodium pyrophosphate hydrogen peroxidate, 4816

Triethylamine hydrogen peroxidate, 2570

Urea hydrogen peroxidate, 0476

See Hydrogen peroxide: Nitric acid, Thiourea

### CUBANES



1. Eaton, P. E., *Angew. Chem. (Int.)*, 1992, **31**(11), 1421
2. Eaton, P., *Chem. Abs*, 1993, **119**, 75812
3. Schmitt, R. J. *et al.*, *Chem. Abs*, 1994, **121**, 112782
4. Piermarini, G. J. *et al.*, *Propellants, Explos., Pyrotech.*, 1991, **16**(4), 188

5. Su, Z. *et al.*, *Proc. Int. Pyrotech. Semin.*, 1991, (17th) Vol. 1, 224  
 6. Eaton, P. E. *et al.*, *J. Amer. Chem. Soc.*, 1997, **119**(41), 9591

All cubanes are high energy materials and should be handled with due precautions for potential explosives [1]. The ring system has almost 700 kJ/mol strain energy (more, per unit weight, than the detonation energy of TNT) and is under study as a basis for high power explosives [2,3]. Cubane itself explodes spontaneously at 3 GPa pressure, the 1,4-dinitro derivative not until >7 GPa [4]. The slightly less strained homocubanes are also studied as explosives [5]. Cubane acyl azides are sensitive and powerful primary explosives; they should be handled only in dilute solution [6]. Individual cubanes are:

- 1,4-Dinitropentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane, 2918  
 Pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane, 2942  
 Pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane-1,2-dicarboxylic acid, 3261  
*See other* STRAINED-RING COMPOUNDS

## CYANIDES

CN<sup>-</sup>

### Hypochlorites

- Wallace, V., *Chem. Eng. News*, 1978, **56**(4), 3
- Kirk-Othmer, 3rd Edn., Vol. 7, 322

Care is necessary in using hypochlorite solutions to destroy cyanide wastes by oxidation to cyanates. This reaction goes readily, even at high pH, but the secondary oxidation of cyanate to nitrogen and carbon dioxide is very pH dependent. This is slow at pH 11 but runs away at 10–10.3, with subsequent sudden release of nitrogen gas. Disposal operations should be conducted to avoid the combination of high pH, excess of hypochlorite and moderate or high concentrations [1]. On the other hand, pH above 9 is recommended to avoid nitrogen trichloride formation [2]. Addition of 0.5 ml of cyanide solution to 5 ml of stirred hypochlorite destroyed a gas meter with the violent gas evolution [1].

*See* Nitrogen trichloride

*See other* GAS EVOLUTION INCIDENTS

*See* METAL CYANIDES (AND CYANO COMPLEXES)

## CYANO COMPOUNDS

-C≡N, C≡N<sup>-</sup>

Metal cyanides are readily oxidised and those of some heavy metals show thermal instability. The covalent cyano group is endothermic, and hydrogen cyanide and many organic nitriles are unusually reactive under appropriate circumstances, and *N*-cyano derivatives are reactive or unstable. The class includes the groups:

- 3-CYANOTRIAZENES, METAL CYANIDES (AND CYANO COMPLEXES)  
 DIISOCYANIDE LIGANDS

Individually indexed compounds are:

- † Acetonitrile, 0758
- † Acrylonitrile, 1107
- \* Allyl isothiocyanate, 1471

- 3-Aminopropionitrile, 1212
- \* Ammonium thiocyanate, 0479
- Azidoacetonitrile, 0714
- 2,2'-Azobis(2,4-dimethylvaleronitrile), 3668
- Azoisobutyronitrile, 3011
- 2,2'-Azoisovaleronitrile, 3345
- Bis(acrylonitrile)nickel(0), 2312
- Bis(2-cyanoethyl)amine, 2397
- \* 1,3-Bis(isocyanomethyl)benzene, 3257
- \* Bis(trifluoromethyl)cyanophosphine, 1053
- \* Butane-1,4-diisocyanate, 2376
- † Butyl isocyanate, 1931
- † Butyronitrile, 1563
  - Caesium cyanotridecahydrodecaborate(2-), 0518
  - Calcium cyanamide, 0316
  - 2-Carbamoyl-2-nitroacetonitrile, 1116
- \* Carbonyl diisothiocyanate, 1342
- † 2-Chloroacrylonitrile, 1074
  - 2-Chlorobenzylidenemalononitrile, 3333
  - 4-Chlorobutyronitrile, 1487
  - 2-Chloro-1-cyanoethanol, 1130
- \* 4-Chlorophenyl isocyanate, 2648
- \* Chlorosulfonyl isocyanate, 0324
  - Cyanamide, 0404
  - Cyanoacetic acid, 1113
  - Cyanoacetyl chloride, 1075
- \* Cyanoborane oligomer, 0393
  - N-Cyano-2-bromoethylcyclohexylamine, 3178
  - Cyanocyclopropane, 1463
  - Cyanodiazocetyl azide, 1346
  - 2-Cyanoethanol (3-Hydroxypropanenitrile), 1181
  - Cyanoforn, 1383
  - Cyanofornyl chloride, 0600
  - Cyanogen bromide, 0313
  - Cyanogen chloride, 0323
  - Cyanogen fluoride, 0323
  - Cyanoguanidine, 0813
  - Cyanohydrazonoacetyl azide, 1083
- \* Cyanonitrene, 0540
  - 2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2668
  - 4-Cyano-3-nitrotoluene, 2917
  - 3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-)oxide, 2630
  - 2-Cyano-2-propanol, 1566
- † 1-Cyanopropene, 1464
- † 3-Cyanopropene, 1465
  - 1-Cyano-2-propen-1-ol, 1467



- 2-Cyano-2-propyl nitrate, 1506
- \* 3-Cyanopropyne, 1416
- † Cyanotrimethylsilane, 1665
- 2-Cyano-1,2,3-tris(difluoroamino)propane, 1432
- Diazidomalononitrile, 1347
- Diazidomethylenecyanamide, 1017
- 2,3-Diazidopropiononitrile, 1121
- Diazomalononitrile, 1344
- 2-Diazonio-4,5-dicyanoimidazolid, 2050
- \* 1,2-Dibromo-1,2-diisocyanatoethane polymers, 3165
- \* Dibutylthallium isocyanate, 3193
- † Dicyanoacetylene, 1801
- 1,4-Dicyano-2-butene, 2311
- Dicyanodiazene, 1005
- Dicyanofurazan, 1803
- Dicyanofurazan *N*-oxide, 1804
- † Dicyanogen, 0996
- \* Dicyanogen *N,N'*-dioxide, 0998
- Dicyanoiodonium triflate, 1048
- (Difluoroamino)difluoroacetonitrile, 0630
- \* 1,6-Diisocyanatohexane, 3008
- \* Diisocyanatomethane, 1079
- \* 2,4-Diisocyanatotoluene, 3117
- \* 1,4-Diisocyanobutane, 2372
- \* 1,5-Diisocyanopentane, 2825
- \* Disodium dicyanodiazene, 1006
- \* Disulfur thiocyanate, 1003
- \* 3-Ethoxycarbonyl-4,4,5,5-tetracyano-3-trimethylplumbyl-4,5-dihydro-3*H*-pyrazole, 3611
- Ethyl cyanoacetate, 1889
- Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2359
- \* Ethyl isocyanide, 1178
- Fumarodinitrile, 1397
- \* Germanium isocyanate, 1377
- Glutarodinitrile, 1870
- Glycolonitrile, 0760
- \* Hexaethyltrialuminium trithiocyanate, 3695
- Hydrogen Cyanide, 0380
- † Isobutyronitrile, 1565
- \* Isocyanoamide, 0407
- \* 2-Isocyanoethyl benzenesulfonate, 3143
- \* Isopropylisocyanide dichloride, 1561
- Malononitrile, 1078
- Mercaptoacetonitrile, 0767
- Methyl 3,3-diazido-2-cyanoacrylate, 1824
- † Methyl isocyanate, 0761

- \* Methyl isocyanide, 0759
- \* Methyl isocyanoacetate, 1470
- \* 1-Naphthyl isocyanate, 3390
- 2-Nitrobenzotrile, 2662
- Nitrosyl cyanide, 0541
- \* Oxopropanedinitrile, 1341
- Perfluoro-*N*-cyanodiaminomethane, 0637
- Phenylacetoneitrile, 2935
- 2,2'-[1,4-Phenylenebis(azidomethylidene)]bis(propanedinitrile), 3622
- \* 2-Phenylethyl isocyanate, 3139
- \* Phosphorus tricyanide, 1343
- \* Phosphoryl dichloride isocyanate, 0327
- † Pivalonitrile, 1929
- † Propionitrile, 1179
- Silver 3-cyano-1-phenyltriazene-3-ide, 2670
- Succinodinitrile, 1433
- Sulfinylcyanamide, 0542
- \* Sulfur thiocyanate, 1002
- \* Tetraacrylonitrilecopper(I) perchlorate, 3510
- Tetracyanoethylene, 2629
- Tetracyanoethylnitrogold, 3814
- Tetramethylsuccinodinitrile, 3007
- \* Thiocarbonyl azide thiocyanate, 1011
- \* Thiocyanogen, 1001
- Trichloroacetoneitrile, 0607
- Trinitroacetoneitrile, 1009
- \* Vinyl isocyanide, 1109

### 3-CYANOTRIAZENES



Bretschneider, H. *et al.*, *Monatsh.*, 1950, **81**, 981

Many aromatic 3-cyanotriazenes are shock-sensitive, explosive compounds.

*See other* HIGH-NITROGEN COMPOUNDS, TRIAZENES

### CYCLIC PEROXIDES

1. Swern, 1970, Vol. 1, 37; 1972, Vol. 3, 67, 81

2. Nixon, J. R. *et al.*, *J. Org. Chem.*, 1978, **43**, 4052, footnote 18

Generally produced *inter alia* during peroxidation of aldehydes or ketones, the lower members are often violently explosive. Dimeric and trimeric ketone peroxides are the most dangerous group of organic peroxide, exploding on heating, touching or friction [1]. Some bromo- and hydrido-cyclic peroxides exploded repeatedly during microanalytical combustion [2]. Individually indexed compounds are:

2,2'-Biphenyldicarbonyl peroxide, 3631

1,6-Diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4]tetradecane, 2476

2,3-Dibromo-5,6-epoxy-7,8-dioxabicyclo[2.2.2]octane, 2298  
 3,6-Dichloro-3,6-dimethyltetraoxane, 1492  
 4,5-Dichloro-3,3,4,5,6,6-hexafluoro-1,2-dioxane, 1355  
 2,3:5,6-Diepoxy-7,8-dioxabicyclo[2.2.2]octane, 2339  
 3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane, 3052  
 2,5-Dimethyl-2,5-dihydrothiophene-2,5-endoperoxide, 2387  
 Dimethyldioxirane, 1227  
 3,6-Dimethyl-1,2,4,5-tetraoxane, 1625  
 1,4-Dimethyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene, 2388  
 7,8-Dioxabicyclo[4.2.2]-2,4,7-decatriene, 2955  
*cis*-1,4-Dioxenedioxetane, 1538  
 3,6-Dioxo-1,2-dioxane, 1445  
 3,6-Di(spirocyclohexane)-1,2,4,5-tetraoxane, 3546  
 1,6-Di(4'-tolyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3796  
 9,10-Epidioxyanthracene, 3630  
 1,4-Epidioxy-1,4-dihydro-6,6-dimethylfulvene, 2984  
 1,4-Epidioxy-2-*p*-menthene, 3347  
*endo*-2,3-Epoxy-7,8-dioxabicyclo[2.2.2]oct-5-ene, 2336  
 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane, 3195  
 3- or 4-Methoxy-5,6-benzo-6*H*-1,2-dioxin, 3154  
 3-Methoxy-3-methyl-5,6-benzo-6*H*-1,2-dioxin, 3313  
 3-Methoxy-4-methyl-5,6-benzo-6*H*-1,2-dioxin, 3314  
 1-(*cis*-Methoxyvinyl)-1,4-endoperoxy-2,5-cyclohexadiene, 3153  
 Methyltrifluoromethylidioxirane, 1102  
 3-Methyl-1,2,4-trioxolane, 1235  
 4a,8a,9a,10a-Tetraaza-2,3,6,7-tetraoxaperhydroanthracene, 2478  
 3,3,4,5-Tetrachloro-3,6-dihydro-1,2-dioxin, 1390  
 3,3,6,6-Tetrakis(bromomethyl)-9,9-dimethyl-1,2,4,5,7,8-hexoxonane, 3173  
 Tetramethyl-1,2-dioxetane, 2508  
 3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, 2517  
 7,7,10,10-Tetramethyl-1,2,5,6-tetroxocane-3,4-dione, 3349  
 3,6,9-Triethyl-1,2,4,5,7,8-hexoxonane, 3196  
 Tri(spirocyclopentane)1,1,4,4,7,7-hexoxonane, 3693  
 See Hydrogen peroxide: Ketones, Nitric acid  
 See also COMMERCIAL ORGANIC PEROXIDES, DIOXETANES

## DEFLAGRATION INCIDENTS

See entries CRITICAL IGNITION TEMPERATURE, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION(reference 3)

Some incidents involving deflagration may be found under:

Ammonium dichromate  
 4-Chloronitrobenzene  
 1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene  
 Hydroxylaminium sulfate

4-Nitrobenzoic acid  
2-Nitrosophenol (1,2-Benzoquinone monoxime)  
Sodium 3-nitrobenzenesulfonate

## DEFLAGRATION TO DETONATION

Chatrathi, K. *et al.*, *Process Safety Progr.*, 1996, **15**(4), 237

A study of deflagration to detonation transition in pipes, for gas/air and dust mixtures, has been made and reported. Obviously it depends upon the exact mixture, but departures from the straight and narrow generally facilitate this transition from slight to seriously destructive over-pressures.

*See also* DUST EXPLOSION INCIDENTS, GEOMETRY OF VESSELS AND PIPEWORK, VAPOUR CLOUD EXPLOSIONS

## DEVARDA'S ALLOY

**Cu—Al—Zn**

1. Cameron, W. G., *Chem. & Ind.*, 1948, 158
2. Chaudhuri, B. B., *Chem. & Ind.*, 1948, 462

The analytical use of the alloy to reduce nitrates is usually accompanied by the risk of a hydrogen explosion, particularly if heating is effected by flame. Use of a safety screen and flameless heating, coupled with displacement of hydrogen by an inert gas, are recommended precautions [1]. The explosion was later attributed to gas pressure in a restricted system [2].

*See other* ALLOYS, GAS EVOLUTION INCIDENTS

## DIACYL PEROXIDES

**RCO.OOCO.R, RSO<sub>2</sub>.OOSO.R<sub>2</sub>**

1. Swern, 1970, Vol. 1, 70
2. Mageli, O. L. *et al.*, US Pat. 3 956 396, 1976
3. Fujimori, K., *Org. Peroxides, Chichester, John Wiley*, 1992, 319

Most of the isolated diacyl (including sulfonyl) peroxides are solids with relatively low decomposition temperatures, and are explosive, sensitive to shock, heat or friction. Several, particularly the lower members, will detonate on the slightest disturbance. Autocatalytic (self-accelerating) decomposition, which is promoted by tertiary amines, is involved [1]. Solvents suitable for preparation of safe solutions of diacetyl, dipropionyl, diisobutyryl and di-2-phenylpropionyl peroxides are disclosed [2]. The class is reviewed, including hazards and safety measures [3]. Cyclic diacyl peroxides are more stable, but scarcely to be trusted. Individually indexed compounds are:

- Acetyl cyclohexanesulfonyl peroxide, 3033
- 2,2'-Biphenyldicarbonyl peroxide, 3631
- \* Bis(2-azidobenzoyl) peroxide, 3628
- Bis(bromobenzenesulfonyl) peroxide, 3453
- Bis(3-carboxypropionyl) peroxide, 2990
- Bis(4-chlorobenzenesulfonyl) peroxide, 3458
- Bis(3,4-dichlorobenzenesulfonyl) peroxide, 3445
- Bis(2,4-dichlorobenzoyl) peroxide, 3623

Bis(fluoroformyl) peroxide, 0625  
 Bis-3-(2-furyl)acryloyl peroxide, 3640  
 Bis(trichloroacetyl) peroxide, 1361  
 Bis(trifluoroacetyl) peroxide, 1367  
 Diacetyl peroxide, 1537  
 Dibenzenesulfonyl peroxide, 3499  
 Dibenzoyl peroxide, 3639  
 Di-3-camphoroyl peroxide, 3807  
 Dicrotonoyl peroxide, 2986  
 Dicyclohexylcarbonyl peroxide, 3667  
 Didodecanoyl peroxide, 3857  
 Di-2-furoyl peroxide, 3245  
 Dihexanoyl peroxide, 3554  
 Diisobutyryl peroxide, 3032  
 Diisopropyl peroxydicarbonate, 3034  
 Dimethanesulfonyl peroxide, 0931  
 Di-2-methylbutyryl peroxide, 3354  
 Di-1-naphthoyl peroxide, 3831  
 3,6-Dioxo-1,2-dioxane, 1445  
 Dipropionyl peroxide, 2442  
 Dipropyl peroxydicarbonate, 3035  
 Di-4-toluenesulfonyl peroxide, 3656  
 Peroxodisulfuryl difluoride, 4328  
 Phthaloyl peroxide, 2900  
 Potassium benzenesulfonylperoxosulfate, 2257  
 Potassium *O-O*-benzoylmonoperoxosulfate, 2684  
 \* *O*-Trifluoroacetyl-*S*-fluoroformyl thioperoxide, 1050  
 See PEROXIDES, PEROXYCARBONATE ESTERS

## DIALKYL HYPONITRITES

## RON=NOR

1. Partington, J. R. *et al.*, *J. Chem. Soc.*, 1932, **135**, 2593
2. Mendenhall, G. D. *et al.*, *J. Amer. Chem. Soc.*, 1982, **104**, 5113
3. Ogle, C. A. *et al.*, *J. Org. Chem.*, 1983, **48**, 3728–3733

The violence of the explosion when the ethyl ester was heated at 80°C was not so great as reported previously. The propyl and butyl esters explode if heated rapidly, but decompose smoothly if heated gradually [1]. Dialkyl hyponitrites with alkyl groups below C<sub>6</sub> are shock-sensitive [2]. The shock-sensitivity decreases with increasing MW, and it was not possible to detonate esters above C<sub>6</sub>. The aryl esters were insensitive and the alkyl esters became so on dilution with solvent [3].

Individually indexed compounds are:

Dibutyl hyponitrite, 3069  
*trans*-Di-*tert*-butyl hyponitrite, 3070  
 Diethyl hyponitrite, 1690  
 Diisopropyl hyponitrite, 2538  
 Dimethyl hyponitrite, 0913

Dipropyl hyponitrite, 2539  
*See related* AZO COMPOUNDS

## DIALKYL MAGNESIUMS

**R<sub>2</sub>Mg**

Alcohols, Ammonia, Carbon dioxide or Water  
Sidgwick, 1950, 233

This series, either as the free alkyls or their ether complexes, is extremely reactive, igniting in air or carbon dioxide and reacting violently or explosively with alcohols, ammonia or water. Individually indexed compounds are:

Diethylmagnesium, 1687  
Dimethylmagnesium, 0908  
Diphenylmagnesium, 3482  
*See other* ALKYL METALS

## DIALKYL PEROXIDES

**ROOR**

1. Castrantas, 1965, 12
2. Swern, 1970, 1, 38, 54
3. Davies, 1961, 75
4. Uetake, K. *et al.*, *Bull. Chem. Soc. Japan*, 1979, **52**, 2136

The high and explosive instability of the lower dialkyl peroxides decreases rapidly with increasing chain length and degree of branching, the di-*tert*-alkyl peroxides being amongst the most stable of the group [1,2]. Though many 1,1-bis(peroxides) have been reported, few have been purified because of the higher explosion hazards, compared with the monofunctional peroxides [3]. Samples of 4 pure liquid dialkyl peroxides were thermally decomposed in TGA–DSC equipment to provide information for hazard prevention [4]. Individually indexed compounds are:

- \* Bis(2-hydroperoxy-4-methyl-2-pentyl) peroxide, 3566
- 2-(4-Bromophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3709
- 2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3711
- † Di-*tert*-butyl peroxide, 3074
- \* 2,2-Di(*tert*-butylperoxy)butane, 3565
- Diethyl peroxide, 1699
- Dimethyl peroxide, 0923
- Dipropyl peroxide, 2547
- Ethyl methyl peroxide, 1282

*See* PEROXIDES

## DIALKYL ZINCS

**R<sub>2</sub>Zn**

1. Sidgwick, 1950, 266
2. Noller, C. R., *J. Amer. Chem. Soc.*, 1929, **51**, 597
3. Houben-Weyl, 1973, Vol. 13.2a, 560, 576

The dialkylzincs up to the dibutyl derivatives readily ignite and burn in air. The higher alkyls fume but do not always ignite [1]. During preparation of dialkylzincs,

reaction of the copper–zinc alloy with mixed alkyl bromides and iodides must begin (exotherm, often after a long induction period), before too much halide mixture is added, or violent explosions may occur [2]. Reactions with water may be explosive [3].

*See other* INDUCTION PERIOD INCIDENTS

#### Acyl halides

Houben-Weyl, 1973, Vol. 13.2a, 781

Too-fast addition of acyl halides during preparation of ketones may lead to explosive reactions.

#### Alkyl chlorides

Noller, C. R., *J. Amer. Chem. Soc.*, 1929, **51**, 599

During interaction to give hydrocarbons, too much chloride must not be added before reaction sets in (induction period), or explosions may occur.

*See other* INDUCTION PERIOD INCIDENTS

#### Methanol

Houben-Weyl, 1973, Vol. 13.2a, 855

Contact of the neat liquids with uncooled methanol is explosively violent and leads to ignition. For analysis, ampouled samples of dialkylzincs must first be frozen in liquid nitrogen before being broken under methanol–heptane mixtures at  $-60^{\circ}\text{C}$ .

*See* Zinc ethoxide: Nitric acid

Individually indexed compounds are:

Dibutylzinc, 3080

Diethylzinc, 1718

Diisobutylzinc, 3081

Diisopentylzinc, 3371

Dimethylzinc, 0935

Dipropylzinc, 2551

*See other* ALKYL METALS

### 1,3-DIAZA-2-BORACYCLOALKANES

#### Alcohols

Merriman, J. S. *et al.*, *Inorg. Synth.*, 1977, **17**, 165

These heterocycles react readily with protic solvents, and alcohols in particular may occasionally cause explosive solvolysis reactions.

*See related* BORANES

### DIAZIRINES

1. Schmitz, E. *et al.*, *Org. Synth.*, 1965, **45**, 85

2. Liu, M. T. H., *Chem. Eng. News*, 1974, **52**(36), 3

3. Terpinski, J. *et al.*, *Magn. Reson. Chem.*, 1987, **25**, 923–927

Diazirine and several of its 3-substituted homologues, formally cyclic azo compounds, are explosive on heating or impact [1]. The shock-sensitivity of all diazirine compounds and the inadvisability of their handling in the undiluted state have again been stressed [2]. In a description of the synthesis of 27 3-(4-substituted)halodiazirines, the need is stressed to handle the compounds at below 30°C to prevent thermal decomposition, or, for the pure compounds, explosion [3].

Individually indexed compounds are:

3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2645  
3-Chloro-3-methoxydiazirine, 0734  
Chloro-(4-methoxyphenyl)diazirine, 2928  
3-Chloro-3-methyldiazirine, 0733  
3-Chloro-3-trichloromethyldiazirine, 0610  
3-Chloro-3-trifluoromethyldiazirine, 0593  
Diazirine, 0405  
Diazirine-3,3-dicarboxylic acid, 1080  
Difluorodiazirine, 0342  
Dipotassium diazirine-3,3-dicarboxylate, 1340  
3-Fluoro-3-(trifluoromethyl)-3*H*-diazirine, 0631  
3-Methyldiazirine, 0808  
3,3-Pentamethylenediazirine, 2422  
Potassium hydrogen diazirine-3,3-dicarboxylate  
3-Propyldiazirine, 1594  
Spiro(homocubane-9,9'-diazirine)(Spiro[3*H*-diazirine-3,9'-pentacyclo[4,3,0,0<sup>2,5</sup>0<sup>3,8</sup>0<sup>4,7</sup>]nonane]), 3127  
*See related* AZO COMPOUNDS

## DIAZAZOLES

1. Hui, H. *et al.*, *Tetrahedron Lett.*, 1982, **23**, 5115–5118  
2. Magee, W. L. *et al.*, *J. Org. Chem.*, 1987, **52**, 5538–5548  
Four 4-diazo-1,2,3-triazole derivatives, though stable in dichloromethane solution, exploded violently when heated as solids [1]. Several diazo-triazoles, -pyrazoles and -imidazoles were found to be explosively unstable in varying degrees [2].

Individually indexed compounds are :

5-Amino-3-phenyl-1,2,4-triazole, : Nitrous acid  
5-*tert*-Butyl-3-diazo-3*H*-pyrazole  
5-Cyano-4-diazo-4*H*-1,2,3-triazole  
2-Diazo-2*H*-imidazole  
3-Diazo-5-phenyl-3*H*-pyrazole  
3-Diazo-5-phenyl-3*H*-1,2,4-triazole  
4-Diazo-1,2,3-triazole  
3-Diazo-3*H*-1,2,4-triazole  
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate



## DIAZO COMPOUNDS

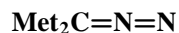
CN<sub>2</sub>

In this group of reactive and unstable compounds, the common structural feature is an N=N unit double-bonded to a carbon atom. Individually indexed compounds are:

- 1-Benzoyl-1-phenyldiazomethane, 3638
- 1,6-Bis(4-chlorophenyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3743
- \* Bis(dimethylarsinyldiazomethyl)mercury, 2467
- Bis(ethoxycarbonyldiazomethyl)mercury, 2978
- 2-Buten-1-yl diazoacetate, 2377
- tert*-Butyl diazoacetate, 2423
- tert*-Butyl 2-diazoacetoacetate, 3009
- 5-*tert*-Butyl-3-diazo-3*H*-pyrazole, 2831
- Cyanodiazocetyl azide, 1346
- 5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1345
- Diazoacetaldehyde, 0710
- Diazoacetone, 0675
- Diazoacetyl azide, 0679
- 2-Diazocyclohexanone, 2375
- Diazocyclopentadiene, 1832
- 2-Diazo-2*H*-imidazole, 1082
- 1-Diazoindene, 3116
- Diazomalonic acid, 1081
- Diazomalnonitrile, 1344
- Diazomethane, 0406
- 5-(Diazomethylazo)tetrazole, 0719
- Diazomethyldimethylarsine, 1240
- 3-Diazo-5-phenyl-3*H*-pyrazole, 3118
- 4-Diazo-5-phenyl-1,2,3-triazole, 2910
- 3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2909
- 3-Diazopropene, 1135
- $\alpha$ -Diazo- $\gamma$ -thiobutyrolactone, 1434
- 4-Diazo-1,2,3-triazole, 0678
- 3-Diazo-3*H*-1,2,4-triazole, 0677
- Di-*tert*-butyl diazomalonate, 3411
- Dicyclopropyldiazomethane, 2824
- Dideuterodiazomethane, 0336
- Diethyl diazomalonate, 2828
- Dinitrodiazomethane, 0545
- 1,6-Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3744
- Disilver diazomethanide, 0306
- Ethyl diazoacetate, 1503
- Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1853
- Lithium diazomethanide, 0379
- 3-Methoxy-2-nitrobenzoyldiazomethane, 3124
- Methyl diazoacetate, 1138
- 2-Nitrophenylsulfonyldiazomethane, 2700

Phenyldiazomethane, 2725  
Poly(diazomethylenemercury), 0522  
Sodium diazomethanide, 0383  
Tetrachlorodiazocyclopentadiene, 1807  
2,2,2-Trifluorodiazooethane, 0664  
*See*  $\alpha$ -DIAZO- $\beta$ -OXOSULFONES, DIAZOMETHANE SALTS

### DIAZOMETHANE SALTS



Bertrand, G. *et al.*, *Angew. Chem. (Int.)*, 1994, **33**(5), 534.  
The disilver, dilithium and 'dimercury' salts of this anion [128234-64-0] are too explosive for safe handling. The bis(trimethylstannyl) derivative is a safer substitute.  
*See* DIAZO COMPOUNDS

### DIAZONIUM CARBOXYLATES

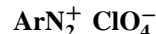


Several of these internal diazonium salts, prepared by diazotisation of anthranilic acids, are explosive in the solid state, or react violently with various materials. Individually indexed compounds (including analogous sulfonates) are:

- Benzenediazonium-2-carboxylate, 2659
- Benzenediazonium-3 or 4-carboxylate, 2661
- \* Benzenediazonium-2-sulfonate, 2192
- \* Benzenediazonium-4-sulfonate, 2193
- \* 2-Carboxy-3,6-dimethylbenzenediazonium chloride, 3138
- \* 1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3392
- 3,5-Dimethylbenzenediazonium-2-carboxylate, 3128
- 4,6-Dimethylbenzenediazonium-2-carboxylate, 3129
- 4-Hydroxybenzenediazonium-3-carboxylate, 2663
- \* 2-Hydroxy-6-nitro-1-naphthalenediazonium-4-sulfonate, 3240
- 4-Iodobenzenediazonium-2-carboxylate, 2639

*See other* DIAZONIUM SALTS

### DIAZONIUM PERCHLORATES



1. Hofmann, K. A. *et al.*, *Ber.*, 1906, **39**, 3146; 1910, **43**, 2624
2. Vorländer, D., *Ber.*, 1906, **39**, 2713–2715
3. Burton, H. *et al.*, *Analyst*, 1955, **80**, 4

The diazonium perchlorates are extremely explosive, shock-sensitive materials when dry, some even when damp [1,2]. The salt derived from diazotised *p*-phenylenediamine was considered to be more explosive than any other substance known in 1910 [3]. Individually indexed compounds are:

- 4-Aminobenzenediazonium perchlorate, 2304
- Benzene-1,4-bis(diazonium perchlorate), 2160
- Benzenediazonium perchlorate, 2232
- 4,4'-Biphenylenebis(diazonium) perchlorate, 3457

1(2'-Diazoniophenyl)2-methyl-4,6-diphenylpyridinium diperchlorate, 3847  
1(2', 3', or 4'-Diazoniophenyl)-2,4,6-triphenylpyridinium diperchlorate, 3870  
1- or 2-Naphthalenediazonium perchlorate, 3247  
3-Nitrobenzenediazonium perchlorate, 2155  
2-Toluenediazonium perchlorate, 2740  
*See other* DIAZONIUM SALTS

## DIAZONIUM SALTS



1. Houben-Weyl, 1965, Vol. 10.3, 32–38
2. Doyle, W. H., *Loss Prev.*, 1969, **3**, 14
3. Anon., *Sichere Chemiearbeit*, 1993, **45**(1), 8
4. Fogel'zang, A. E. *et al.*, *Chem. Abs.*, 1974, **81**, 155338
5. Bartsch, R. A. *et al.*, *J. Amer. Chem. Soc.*, 1976, **98**, 6753–6754
6. Storey, P. D., *Runaway Reactions*, 1981, Paper 3/P, 1–9
7. Mustacchi, H. *et al.*, *Ger. Offen. DE 3 202 208*, 1982
8. Grewer, Th. *et al.*, *Thermochim. Acta*, 1993, **225**(2), 201

A few diazonium salts are unstable in solution, and many are in the solid state. Of these, the azides, chromates, nitrates, perchlorates (outstandingly), picrates, sulfides, triiodides and xanthates are noted as being explosive, and sensitive to friction, shock, heat and radiation. In view of their technical importance, diazonium salts are often isolated as their zinc chloride (or other) double salts, and although these are considerably more stable, some incidents involving explosive decomposition have been recorded.

During bottom discharge of an undefined diazonium chloride preparation, operation of a valve initiated explosion of the friction-sensitive chloride which had separated from solution. The latter did not occur with the corresponding sulfate [2]. Some of a group of industrial diazotisation vessels were closed down, improving gas extraction from those still operated. The ventline later blocked on one vessel and, when attempts were made to open it, disassembled itself explosively. Thick deposits of crystalline diazonium salts were found elsewhere in the system, although only slime had been seen previously. It appears that the improved extraction sucked amines and nitrous gases from the vessels, to complete their reaction in the vent line [3]. The combustive and explosive behaviour of solid diazonium salts at various pressures was studied, including benzenediazonium chloride and nitrate, and *m*- and *p*-nitrobenzenediazonium chlorides [4]. Complexation of diazonium anions with crown ethers reduces or suppresses thermal decomposition of the anion, and may prove useful to stabilise shock-sensitive species [5]. The thermal explosion properties of a series of 10 dimethylamino- or morpholino-substituted benzenediazonium tetrafluoroborates or tetrafluorozincates were studied using DSC, to provide data to assist in practical assessment of stability, particularly towards impact [6]. Diazonium 5-sulfoisophthalate salts are more thermally stable and less flammable than the corresponding tetrafluoroborate and tetrachlorozincate salts [7]. A procedure is given for testing impact sensitivity of diazonium salts by a drop-weight procedure. It is applicable to impure materials of commercial practice. Nitrobenzenediazonium

derivatives were found especially sensitive: of critical impact energy 1–2 J [8]. Separately treated groups are:

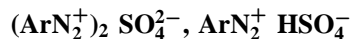
ARENEDIAZONIUM OXIDES, DIAZONIUM CARBOXYLATES  
DIAZONIUM PERCHLORATES, DIAZONIUM SULFATES  
DIAZONIUM SULFIDES AND DERIVATIVES  
DIAZONIUM TETRAHALOBORATES, DIAZONIUM TRIIODIDES

Individually indexed compounds are:

- 5-Amino-3-phenyl-1,2,4-triazole, : Nitrous acid, 2952
- Benzenediazonium chloride, 2230
- Benzenediazonium iodide, 2250
- Benzenediazonium nitrate, 2275
- \* Benzenediazonium-2-sulfonate, 2192
- \* Benzenediazonium-4-sulfonate, 2193
- Benzenediazonium tetrachlorozincate, 3476
- Benzenediazonium tribromide, 2227
- \* 1,10-Bis(diazonio)decaboran(8)ate, 0197
- 4-Bromobenzenediazonium salts, 2131
- 2-Chlorobenzenediazonium salts, 2148
- 3-Chlorobenzenediazonium salts, 2149
- 4-Chloro-2-methylbenzenediazonium salts, 2719
- 5-Chlorotoluene-2-diazonium tetrachlorozincate, 3644
- 2-Diazonio-4,5-dicyanoimidazolidine, 2050
- 1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3392
- 3-Diazoniopyrazolide-4-carboxamide, 1399
- 5-Diazoniotetrazolide, 0548
- 2-Naphthalenediazonium trichloromercurate, 3248
- 4-Nitrobenzenediazonium azide, 2209
- 3-Nitrobenzenediazonium chloride, 2151
- 4-Nitrobenzenediazonium nitrate, 2205
- \* Potassium 1-phenylethanediazoate, 2964
- Tetrazole-5-diazonium chloride, 0370
- 2-Toluenediazonium bromide, 2736
- 2- or 3-Toluenediazonium iodide, 2751
- 3-Toluenediazonium salts, 2774
- 2- or 4-Toluenediazonium salts, 2775
- 2,4,6-Tri(2-acetylhydrazino)-1,3,5-trinitrobenzene, : Hydrochloric acid, 3535
- 1,2,4-Triazole-3-diazonium nitrate, 0680
- 3,4,5-Triiodobenzenediazonium nitrate, 2084

See also TETRAZOLES

## DIAZONIUM SULFATES



Bersier, P. *et al.*, *Chem. Ing. Tech.*, 1971, **43**(24), 1311–1315

During investigation after the violent explosion of a 6-chloro-2,4-dinitrobenzenediazonium sulfate preparation made in nitrosylsulfuric acid, it was found that above

certain minimum concentrations some diazonium sulfates prepared in sulfuric acid media could be brought to explosive decomposition by local application of thermal shock. Classed as dangerous were the diazonium derivatives of 6-chloro-2,4-dinitroaniline (at 1.26 mmol/g, very dangerous at 1.98 mmol/g); 6-bromo-2,4-dinitroaniline (very dangerous at 1.76 mmol/g); 2,4-dinitroaniline (2.0 mmol/g). Classed as suspect were the diazonium derivatives above at lower concentrations, and those of 2-chloro-5-trifluoromethylaniline (at 1.84 mmol/g); 2,6-dichloro-4-nitroaniline (0.80 mmol/g); 2-methanesulfonyl-4-nitroaniline (0.80 mmol/g); 2-cyano-4-nitroaniline (1.04 mmol/g). A further 11 derivatives were not found to be unstable. Details of several stability testing methods are given. Individually indexed compounds are:

Benzenediazonium hydrogen sulfate, 2318  
 6-Bromo-2,4-dinitrobenzenediazonium hydrogen sulfate, 2097  
 2-Chloro-4,6-dinitroaniline, : Nitrosylsulfuric acid, 2153  
 6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2102  
 2-Chloro-5-trifluoromethylbenzenediazonium hydrogen sulfate, 2647  
 2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2668  
 2,6-Dichloro-4-nitrobenzenediazonium hydrogen sulfate, 2106  
 2,4-Dinitrobenzenediazonium hydrogen sulfate, 2206  
 2-Methanesulfonyl-4-nitrobenzenediazonium hydrogen sulfate, 2784  
*See* THERMAL STABILITY OF REACTION MIXTURES  
*See other* DIAZONIUM SALTS

## DIAZONIUM SULFIDES AND DERIVATIVES

ArN<sub>2</sub>S-

1. Graebe, C. *et al.*, *Ber.*, 1882, **15**, 1683
2. Bamberger, E. *et al.*, *Ber.*, 1896, **29**, 272
3. Nawiasky, P. *et al.*, *Chem. Eng. News*, 1945, **23**, 1247
4. Hodgson, H. H., *Chem. & Ind.*, 1945, 362
5. Tomlinson, W. R., *Chem. Eng. News*, 1957, **29**, 5473
6. Hollingshead, R. G. W. *et al.*, *Chem. & Ind.*, 1953, 1179
7. Anon., *Angew. Chem. (Nachr.)*, 1962, **10**, 278
8. Parham, W. E. *et al.*, *Org. Synth.*, 1967, **47**, 107
9. Anon., *BCISC Quart. Safety Summ.*, 1969, **40**, 17
10. Zemlyanskii, N. I. *et al.*, *Chem. Abs.*, 1971, **74**, 53204
11. Spencer, H., *Chem. Brit.*, 1977, **13**, 240–241
12. Petullo, G. *et al.*, *Tetrahedron Lett.*, 1985, **24**, 6365–6368

There is a long history of the preparation of explosive solids or oils from interaction of diazonium salts with solutions of various sulfides and related derivatives. Such products have arisen from benzene- and toluene-diazonium salts with hydrogen, ammonium, or sodium sulfides [1,5]; 2- or 3-chlorobenzene-, 4-chloro-2-methylbenzene-, 2- or 4-nitrobenzene- or 1- or 2-naphthalene-diazonium solutions with hydrogen sulfide, sodium hydrogen sulfide or sodium mono-, di- or poly-sulfides [1]–[4,7]. 4-Bromobenzenediazonium solutions gave with hydrogen sulfide at –5°C a product which exploded under water at 0°C [2], and every addition of a drop of 3-chlorobenzenediazonium solution to sodium disulfide solution

at 0°C caused a violent explosion [4]. In general, these compounds appear to be bis(arene-diazo) sulfides or the hydrogen sulfides, since some of the corresponding disulfides are considerably more stable [2].

Interaction of 2-, 3- or 4-chlorobenzenediazonium salts with *O*-alkyldithiocarbonate ('xanthate') solutions [8] or thiophenoxide solutions [9] produces explosive products, possibly arene-diazo aryl sulfides. The intermediate diazonium xanthate produced during the preparation of *m*-thiocresol can be dangerously explosive under the wrong conditions [8], while the reaction of 3-nitrobenzenediazonium chloride with xanthate solution at 70–75°C proceeds with near-explosive evolution of nitrogen [4]. The product of interaction of 2-chlorobenzenediazonium chloride and sodium 2-chlorothiophenoxide exploded violently on heating to 100°C, and the oil precipitated from interaction of potassium thiophenoxide with 3-chlorobenzenediazonium chloride exploded during mixing of the solutions [9].

Interaction of substituted arene-diazonium salts with potassium *O,O*-diphenylphosphorodithioates gave a series of solid diazonium salts which decomposed explosively when heated dry [10]. The unique failure of diazotised anthranilic acid solutions to produce any explosive sulfide derivatives under a variety of conditions has been investigated and discussed [6]. Preparation of diaryl sulfides from interaction of diazonium and thiophenoxide salts led to violent explosions, attributed to presence of some arene-diazo sulfide during subsequent distillation of the diaryl sulfides. Precautions are detailed [11]. A safe method of preparation of diaryl sulfides from diazonium tetrafluoroborates and sodium benzenethiolate in DMF is now available [12].

Individually indexed hazardous reaction pairs are:

4-Chloro-2-methylbenzenediazonium salts, 2719

Hydrogen trisulfide : Benzenediazonium chloride, 4485

1-Naphthalenediazonium salts, 3251

2-Naphthalenediazonium salts, 3252

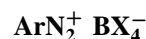
2- or 4-Toluenediazonium salts, 2775

3-Toluenediazonium salts, : Ammonium sulfide, or Hydrogen sulfide, 2774

3-Toluenediazonium salts, : Potassium *O*-ethyl dithiocarbonate

See Hydrogen trisulfide: Benzenediazonium chloride

## DIAZONIUM TETRAHALOBORATES



1. Olah, G. A. *et al.*, *J. Org. Chem.*, 1961, **26**, 2053
2. Doak, G. O. *et al.*, *Chem. Eng. News*, 1967, **45**(53), 8
3. Fletcher, T. L., *Chem. & Ind.*, 1972, 370
4. Pavlath, A. E. *et al.*, *Aromatic Fluorine Compounds*, 15, New York, Reinhold, 1962
5. Coates, C. F. *et al.*, *Runaway Reactions*, 1981, Paper 4/Y, 1–2

Solid diazonium tetrachloroborates decompose very vigorously, sometimes explosively, on heating in absence of solvent. Dry *o*-nitrobenzenediazonium tetrachloroborate is liable to explode spontaneously during storage at ambient temperature [1]. Hazards involved in drying diazonium tetrafluoroborates have been discussed. The

decomposition temperature of any new salt should be checked first on a small sample, and only if it is above 100°C should the bulk be dried and stored. Salts which show signs of decomposition at or below ambient temperature must be kept moist and used immediately [2]. The need to use an inert solvent in any deliberate thermal decomposition is stressed [3], and attention is drawn to an erroneous reference to the use of tetrahydrofuran, which could be hazardous. The presence of nitro substituent groups may greatly increase the decomposition temperature, so that decomposition may become violent or even explosive [4]. The Schiemann thermal decomposition of a tetrafluoroborate salt, previously done repeatedly without incident, became violent on one occasion, causing vessel pressurisation from evolved gas. The presence of impurities had transformed the normally smooth decomposition at 95° to a violent reaction at 84°C [5].

Individually indexed compounds are:

2-Azidomethylbenzenediazonium tetrafluoroborate, 2708

Benzenediazonium tetrafluoroborate, 2223

2-Chloro-3-pyridinediazonium tetrafluoroborate, 1816

5-(4-Diazoniobenzenesulfonamido)thiazole tetrafluoroborate, 3119

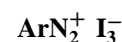
5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3677

2-Nitrobenzenediazonium tetrachloroborate, 2128

3-Pyridinediazonium tetrafluoroborate, 1826

*See other* GAS EVOLUTION INCIDENTS, CATALYTIC IMPURITY INCIDENTS

## DIAZONIUM TRIIODIDES



Carey, J. G. *et al.*, *Chem. & Ind.*, 1960, 7

The products produced by interaction of diazonium salts and iodides are unstable and liable to be explosive in the solid state. They are usually the triiodides, but monoiodides have been isolated under specific conditions from diazotised aniline and *o*-toluidine. Products prepared from diazotised *o*-, *m*- or *p*-nitroanilines, *m*-chloro-, -methoxy-, or -methyl-aniline are too unstable to isolate, decomposing below 0°C.

Individually indexed compounds are:

Benzenediazonium iodide, 2250

Benzenediazonium triiodide, 2254

4-Chlorobenzenediazonium triiodide, 2137

2,4-Dimethylbenzenediazonium triiodide, 2963

2- or 4-Methoxybenzenediazonium triiodide, 2758

4-Toluenediazonium triiodide, 2756

*See other* DIAZONIUM SALTS, IODINE COMPOUNDS

## $\alpha$ -DIAZO- $\beta$ -OXOSULFONES

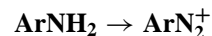


Manteiro, H. J., *Synth. Comm.*, 1987, **17**(8), 983–989

The title compounds were prepared safely by a diazo-transfer reaction onto  $\beta$ -oxosulfones by treatment with 1-ethyl-2-chloropyridinium tetrafluoroborate and sodium azide in presence of sodium acetate.

See DIAZO COMPOUNDS, above

## DIAZOTISATION



1. Houben-Weyl, 1965, Vol. 10.3, 1–112
2. Schierwater, F.-W., *Sichere Chemiearb.*, 1986, **38**(2), 18

In the extensive review of diazotisation, frequent reference is made to the need for close temperature control during processing operations, and to the explosive nature of isolated diazonium salts [1]. Inclusion of methanol in the reaction mixture used to diazotise 2-toluidine, and use of sulfuric acid rather than acetic acid in the ensuing coupling reaction with 2-toluidine to give 2-aminoazotoluene led to formation of a high concentration of methyl nitrite. No explosion occurred, but a fatality resulted from inhaling the fumes escaping from the open port of the reaction vessel [2].

See also Many examples are covered in the group entries:

ARENEDIAZONIUM OXIDES, DIAZONIUM CARBOXYLATES

DIAZONIUM PERCHLORATES, DIAZONIUM SULFATES

DIAZONIUM SULFIDES AND DERIVATIVES

DIAZONIUM TETRAHALOBORATES, DIAZONIUM TRIIODIDES

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

## *I,I*-DI(BENZOYLPEROXY)ARYLIODINES



Plesnicar, B. *et al.*, *Angew Chem. (Intern. Ed.)*, 1970, **9**, 707

Compounds of the general structure above, with X = *m*-chloro or *p*-nitro, and Y = H, *p*-chloro or *o*-methoxy, are extremely powerful oxidants, unstable when dry, and will explode during manipulation at ambient temperature (particularly with metal spatulae), or on heating to 80–120°C. The group exceeds the oxidising power of organic peroxyacids. The individual compounds are:

*I,I*-Bis(3-chlorobenzoylperoxy)-4-chlorophenyliodine, 3793

*I,I*-Bis(3-chlorobenzoylperoxy)phenyliodine, 3794

*I,I*-Bis(4-nitrobenzoylperoxy)-4-chlorophenyliodine, 3789

*I,I*-Bis(4-nitrobenzoylperoxy)-2-methoxyphenyliodine, 3819

*I,I*-Bis(4-nitrobenzoylperoxy)phenyliodine, 3795

[*I,I*Bis(trifluoroacetoxy)iodo]benzene, 3239

See other DIACYL PEROXIDES, IODINE COMPOUNDS, OXIDANTS

## DICHROMATE SALTS OF NITROGENOUS BASES



Gibson, G. M., *Chem. & Ind.*, 1966, 553

The dichromates of 1-phenylbiguanide, its *p*-chloro, *p*-methyl and 1-naphthyl analogues all decompose violently at around 130°C.



Individually indexed compounds are:

Ammonium dichromate, 4246

1-(4-Chlorophenyl)biguanidinium hydrogen dichromate, 3005

Dianilinium dichromate, 3537

Dipyridinium dichromate, 3304

Guanidinium dichromate, 0971

1-Phenylbiguanidinium hydrogen dichromate, 3019

4-Tolylbiguanidinium hydrogen dichromate, 3182

*See other* OXOSALTS OF NITROGENOUS BASES

#### [14] DIENE-N<sub>4</sub> COMPLEXES

1. Goedken, V. L. *et al.*, *J. Amer. Chem. Soc.*, 1972, **94**, 3397

2. Tait, A. M. *et al.*, *Inorg. Synth.*, 1978, **18**, 2–36

3. Peng, S. M. *et al.*, *Inorg. Chem.*, 1978, **17**, 821

The macroheterocyclic ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene (abbreviated to [14] diene-N<sub>4</sub>) forms cationic complexes with iron(II or III), also containing acetonitrile, imidazole, phenanthroline or halogen ligands. When the anion is perchlorate, the products are explosive, sensitive to heat and impact; some appear to decompose on storage (1 week) and become sensitive to slight disturbance [1]. Details are given for avoiding the use of perchloric acid and/or perchlorate salts in this and structurally related series [2]. Some of the compounds containing perchlorate anions must be regarded as extremely hazardous and potentially explosive. Prepare only minimal amounts, and long term storage above 1 month is not recommended [3]. Individually indexed compounds are:

Acetonitrileimidazole-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3828

\* *trans*-Bromoazido(meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) perchlorate, 3553

Bromo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclo-tetradecadieneiron(II) perchlorate, 3722

Chloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3724

Copper(II) perchlorate: Polyfunctional amines, 4057

Copper(II) perchlorate: *N*-(2-Pyridyl)acylacetamides, 4057

Diacetonitrile-5,5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3813

Dichloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(III) perchlorate, 3725

5,5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraaza-4,11,-cyclotetradecadiene-1,10-phenanthrolineiron(II) perchlorate, 3869

Hydroxobis[5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II)] triperchlorate, 3881

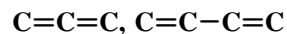
Iodo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3723

Oxybis[aqua-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetra-decadieneiron(II)] tetraperchlorate, 3882

See POLYAZACAGED METAL PERCHLORATES

See other AMMINOMETAL OXOSALTS

## DIENES



The 1,2 and 1,3-dienes (vicinal and conjugated, respectively) are more reactive than the separated dienes.

Oxides of nitrogen

See Nitrogen oxide: Dienes, Oxygen

Individually indexed compounds are:

- 7-Azidobicyclo[2.2.1]hepta-2,5-diene, 2777
- \* 1,4-Benzoquinone diimine, 2310
- \* 1,4-Benzoquinone monoimine, 2260
- † Bicyclo[2.2.1]hepta-2,5-diene, 2789
- † 1,2-Butadiene, 1479
- † 1,3-Butadiene, 1480
- † 2-Chloro-1,3-butadiene, 1451
- \* *N*-Chlorocinnamaldimine, 3126
- † 1,3,5-Cycloheptatriene, 2790
- † 1,3-Cyclohexadiene, 2361
- † 1,4-Cyclohexadiene, 2362
- † 1,3,5,7-Cyclooctatetraene, 2943
- \* 1,3,5-Cyclooctatriene, 2966
- † Cyclopentadiene, 1857
- 2,3-Diazido-1,3-butadiene, 1437
- † Dicyclopentadiene, 3299
- 2,3-Dimethyl-1,3-butadiene, 2407
- \* 3,7-Dimethyl-2,6-octadienal, 3346
- † 1,3-Hexadiene, 2409
- † 1,4-Hexadiene, 2410
- † 1,5-Hexadiene, 2411
- † *cis*-2-*trans*-4-Hexadiene
- † *trans*-2-*trans*-4-Hexadiene, 2412
- 1,3-Hexadien-5-yne, 2290
- † 1,5-Hexadien-3-yne, 2291
- 4,5-Hexadien-2-yn-1-ol, 2328
- 1-Iodohepta-2,4-diene, 2393
- Limonene, 3337
- 1,5-*p*-Menthadiene, 3338
- \* Methoxy-1,3,5,7-cyclooctatetraene, 3149
- † 2-Methyl-1,3-butadiene, 1893
- † 3-Methyl-1,2-butadiene, 1892

- Methylcyclopentadiene, 2363
  - † 2-Methyl-1,3-pentadiene, 2416
  - † 4-Methyl-1,3-pentadiene, 2417
  - \* 2-Nitrosophenol (1,2-Benzoquinone monoxime), 2263
  - † 1,7-Octadiene, 3021
  - \* 1,3,7-Octatrien-5-yne, 2944
  - † 1,2-Pentadiene, 1895
  - † 1,3-Pentadiene, 1896
  - † 1,4-Pentadiene, 1897
  - Perfluorobutadiene, 1364
  - \* Poly(acetylene), 0687
  - \* *cis*-Poly(butadiene), 1484
  - \* Poly(1-pentafluorothio-1,2-butadiyne), 1379
  - † Propadiene (Allene), 1124
    - 1,1,2,3-Tetrachloro-1,3-butadiene, 1389
  - \* 1,1,4,4-Tetrachlorobutatriene, 1360
    - Tetracyclo[4.3.0<sup>3,5</sup>.0<sup>4,6</sup>]nona-1,7-diene, 3125
  - \* 1,1,4,4-Tetrafluorobutatriene, 1363
- See other* PEROXIDISABLE COMPOUNDS

#### **DIESEL ENGINES**

1. Sheldrick, G., *Chem. & Ind.*, 1969, 1823
2. Young, J. A., *CHAS Notes*, 1991, **IX**(5), 2
3. Bond, 1991, 50

In the vicinity of hydrocarbon or solvent spillages, these engines may take in enough fuel with their air supply. In consequence, they cannot be stopped by cutting the supply of fuel from the tank, perpetuating combustion which may not stay internal [1,3]. Precautions against flashback are detailed. Problems can also arise if the engine is driving the pump which is spilling the volatile material [2]. Similar problems could, in principle, occur with gas turbines.

#### **DIFFERENTIAL SCANNING CALORIMETRY (DSC)**

1. Gygax, R. *et al.*, *Therm. Anal.*, 1980, **1**, 541–548
2. Brogli, F. *et al.*, *Therm. Anal.*, 1980, **1**, 549–554
3. Cardillo, P. *et al.*, *Runaway Reactions*, 1981, Paper 3/N, 1–9

The scope and limitations of the use of DSC as a means of investigating the reaction dynamics of potentially hazardous chemical reactions is discussed. For existing processes, examination of production samples taken at various stages of the overall process sequence can identify the stage at which maximum heat production is occurring, as the most critical phase for control requirements. The existence of an induction period can also be established, and use of the instrument in its more sensitive isothermal mode can yield information on consecutive reactions and catalytic effects [1]. The place of DSC in a screening programme to estimate hazards in proposed chemical processes is discussed in detail. The use of pressure-tight encapsulated samples permits rapid assessment of heats of reaction and/or

decomposition and kinetic behaviour under likely process conditions. Selected case studies are included [2]. The part played by DSC in the investigation of the Seveso incident has been discussed [3].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

### DIFFERENTIAL THERMAL ANALYSIS (DTA)

1. Corignan, Y. P. *et al.*, *J. Org. Chem.*, 1967, **32**, 285
2. Prugh, R. W., *Chem. Eng. Progr.*, 1967, **63**(11), 53
3. Krien, G., *Diff. Therm. Anal.*, 1972, **2**, 353–377
4. Duswalt, A. A., *Thermochim. Acta*, 1974, **8**(1–2), 57–58
5. Berthold, W. *et al.*, *Chem. Ing. Tech.*, 1975, **47**, 368–373
6. Giger, G. *et al.*, *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, C14–23, Rugby, IChE, 1983
7. Cassel, R. B., *Perkin-Elmer Therm. Anal. Appl. Study*, 1979, **28**, 1–6

Thermal stabilities of 40 explosive or potentially explosive *N*-nitroamines, aminium nitrates and guanidine derivatives were studied in relation to structure; 14 of the compounds decomposed violently when the exotherm occurred [1]. The value of the DTA technique in assessing hazards of compounds or reaction mixtures is discussed [2]. DTA data on thermally unstable materials (peroxides) as well as explosives was reviewed [3]. The use of various DTA methods for defining processing, storage, and safe reaction conditions has been investigated, and experiences and conclusions were discussed [4]. Use of DTA and DSC methods for predictions in preventing thermal explosions by assessing the stable range of operations in large storage containers are discussed [5,6], with experimental details and exemplification using nonyl nitrate [5] and an unidentified compound [6]. Details of a new ASTM standard method E537-76 for determination of potential explosive hazard by studying the kinetics of thermal decomposition by DTA were discussed [7].

Some of the individual compounds examined are :

Ammonium 1,2-ethylenebis(nitramide)

3-Azoniabicyclo[3.2.2]nonane nitrate

*N,N'*-Diacetyl-*N,N'*-dinitro-1,2-diaminoethane

Diaminoguanidinium nitrate

1,3-Dinitro-2-imidazolidinone

*N,N'*-Dinitro-*N*-methyl-1,2-diaminoethane

1,3,6,8-Tetraazoniatricyclo[6.2.1.1<sup>3,6</sup>]dodecane tetranitrate

1,3,5,7-Tetranitroperhydro-1,3,5,7-tetrazocine

Triaminoguanidinium nitrate

Triaminoguanidinium perchlorate

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

### DIFLUOROAMINOALKANOLS

### F<sub>2</sub>NC(RR')OH

Fokin, A. V. *et al.*, *Chem. Abs.*, 1970, **72**, 78340

A series of 1-difluoroaminoalkanols prepared from difluoramine and an aldehyde or ketone, together with their acetates or bis(ethers), were all shock- and friction-sensitive explosives.

*See other* DIFLUOROAMINO COMPOUNDS

## DIFLUOROAMINO COMPOUNDS

RNF<sub>2</sub>

Freeman, J. P., *Adv. Fluorine Chem.*, 1970, **6**, 321, 323

All organic compounds containing one or more difluoroamino groups should be treated as explosive oxidants and excluded from contact with strong reducing agents. If the ratio of NF<sub>2</sub> to CH<sub>2</sub> groups is above 1:5, the compound will be impact-sensitive. Direct combustion for elemental analysis will be unsafe, but polarography is applicable. Some difluoroamines have been studied as explosives in their own right.

Individually indexed compounds are:

Bis(difluoroamino)difluoromethane, 0362

1,1-Bis(difluoroamino)-2,2-difluoro-2-nitroethyl methyl ether, 1104

1,2-Bis(difluoroamino)ethanol, 0802

1,2-Bis(difluoroamino)ethyl vinyl ether, 1496

4,4-Bis(difluoroamino)-3-fluoroimino-1-pentene, 1867

1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0803

2-Cyano-1,2,3-tris(difluoroamino)propane, 1432

Di-1,2-bis(difluoroaminoethyl) ether, 1497

(Difluoroamino)difluoroacetonitrile, 0630

3-Difluoroamino-1,2,3-trifluorodiaziridine, 0358

*N,N*-Difluorotrifluoromethylamine, 0357

1,1-Difluorourea, 0398

\* Pentafluoroguanidine, 0359

*C,N*-Perfluoro-*N*-aminomethyltriaminomethane, 0649

Perfluoro-*N*-cyanodiaminomethane, 0637

† Tetrafluorohydrazine, 4345

Tetrafluorourea, 0352

Tris(difluoroamino)fluoromethane, 0364

*See* BIS(DIFLUOROAMINO)ALKYL NITRATES *See other* N-HALOGEN COMPOUNDS

## DIFLUOROAMINOPOLYNITROARYL COMPOUNDS

Lerom, M. W. *et al.*, *J. Chem. Eng. Data*, 1974, **19**, 389–392

Several difluoroaminopolynitro derivatives of stilbene, biphenyl, terphenyl and their precursors are explosives, sensitive to initiation by impact, shock, friction or rapid heating.

*See other* DIFLUOROAMINO COMPOUNDS

## DIFLUOROPERCHLORYL SALTS



Organic materials, or Water

Christe, K. O. *et al.*, *Inorg. Chem.*, 1973, **12**, 1358

Difluoroperchloryl tetrafluoroborate, hexafluoroarsenate or hexafluoroplatinate all react violently with organic materials or water. Individual salts are:

Difluoroperchloryl hexafluoroarsenate, 0093

Difluoroperchloryl hexafluoroplatinate, 3991

Difluoroperchloryl tetrafluoroborate, 0123

*See* Chlorine dioxide trifluoride

## DIGESTION

Geological and biological sample preparation for subsequent analysis often involves digestion in highly oxidant media such as nitric or perchloric acid. This is a frequent cause of incidents, which will be found under the entries for digestion reagents. It is also necessary to consider that the apparatus, or parts of it such as mounts and sealing rings, may be constructed of materials themselves digestible.

## DIISOCYANIDE LIGANDS



1. Yaneff, P. V. *et al.*, *J. Organomet. Chem.*, 1979, **179**, 111

2. Howell, J. A. *et al.*, *J. Chem. Soc., Dalton Trans.*, 1981, 301

It is preferable to prepare and use various diisocyanide ligands (trimethylene to octamethylenene diisocyanides, 1,4-dimethylenecyclohexane and 1,3-xylylidene diisocyanides) as solvent solutions rather than as isolated materials, because violent explosions have been observed during vacuum distillation of these ligands [1]. Four such ligands were, however, distilled uneventfully [2]. Individually indexed compounds are:

1,3-Bis(isocyanomethyl)benzene, 3257

1,4-Bis(isocyanomethyl)cyclohexane, 3330

1,4-Diisocyanobutane, 2372

1,6-Diisocyanohexane, 3006

1,8-Diisocyanooctane, 3343

1,5-Diisocyanopentane, 2825

1,3-Diisocyanopropane, 1869

1,1,1-Triazidodinitroethane, 0683

*See related* CYANO COMPOUNDS

## 1,1-DINITRODIFLUORAMINES



Fokin, A. V. *et al.*, *Dokl. Akad. Nauk.*, 1996, **346**(3), 358; *Chem. Abs.*, 1996, **125** 167297

A variety of these compounds were prepared (R = CN, CONH<sub>2</sub>, Me, Ph). Not surprisingly they were explosives very sensitive to shock, friction and heat. They were inclined to distillation during distillation.

*See also* N-HALOGEN COMPOUNDS, POLYNITROALKYL COMPOUNDS

## 1,2-DIOLS



Preparative hazard

See Sodium chlorate: Alkenes, Potassium osmate

## 1,3,4-DIOXAZOLONES

Middleton, W. J., *J. Org. Chem.*, 1983, **48**, 3845–3847

2-Perfluoroalkyl-1,3,4-dioxazolones are a potentially hazardous group of compounds, being capriciously explosive. They are no safer than perfluoroacyl azides as precursors for isothiocyanates.

See other N–O COMPOUNDS, DIOXETANES

## DIOXETANES

1. Mumford, C., *Chem. Brit.*, 1975, **11**, 402

2. Kopecky, K. R. *et al.*, *Can. J. Chem.*, 1975, **53**, 1103–1122

3. Livingstone, R., Rodd, (Supplement to 2nd Edn.), IVa, 1984

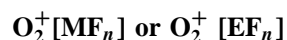
4. Adam, W. *et al.*, *J. Amer. Chem. Soc.*, 1994, **116**(17), 7581

This group of highly strained cyclic peroxides, though thermodynamically unstable, contains some compounds of sufficient kinetic stability to exist as solids at ambient temperature [1]. Interest in these compounds is increasing, most are very unstable, several have proved explosive when isolated [2,3]. Not only are lower 1,2-dioxetanes dangerously unstable but so, above 0°C, are the precursor 1,2-bromohydroperoxides [4].

See Tetramethyl-1,2-dioxetane

See other CYCLIC PEROXIDES, STRAINED-RING COMPOUNDS

## DIOXYGENYL POLYFLUOROSALTS



1. Bailar, 1973, Vol. 2, 778–779

2. Griffiths, J. E. *et al.*, *Spectrochim. Acta*, 1975, **31A**, 1208

Dioxygenyl hexafluoro-antimonate, -arsenate, -phosphate, -platinate and -stannate, also tetrafluoroborate, all react very violently with water, liberating ozone and oxygen [1]. Irradiation for Raman spectroscopy of a range of the title compounds and their nitrosyl analogues in glass or quartz capillaries caused many of them to decompose explosively. A special rotating sapphire/Teflon cell overcame the problem. Compounds examined were dioxygenyl hexafluoro-arsenate, -bismuthate, -ruthenate, -rhodate, -platinate and -aurate; dioxygenyl undecafluorodi-antimonate, -niobate and -tantalate; and their nitrosyl analogues [2].

See other IRRADIATION DECOMPOSITION INCIDENTS

## DIPHENYL BLACK

Anon., *Loss Prev. Bull.*, 1980, (030), 160

A batch of the trisazo dyestuff, after drying at 100–105°C in a circulating air dryer, was left in the unheated dryer overnight. Exothermic decomposition set in after some hours.

*See other* AZO COMPOUNDS

## DIPLUMBANES

## R<sub>3</sub>PbPbR<sub>3</sub>

Sidgwick, 1950, 595

The higher members of the hexaalkyldiplumbane series may disproportionate explosively during distillation.

*See other* ALKYL METALS

## 1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES

Anderson, J. R. *et al.*, *J. Org. Chem.*, 1975, **40**, 2016

Several substituted title salts, intermediates in the preparation of 1,3-diselenole-2-selenones, exploded on heating, ignition or shock. The tetrafluoroborate salts were stable, safe intermediates for large-scale application. Individually indexed compounds are:

1-(4,5-Dimethyl-1,3-diselenonylidene)piperidinium perchlorate, 3340

2-(1,3-Diselena-4,5,6,7-tetrahydroindanylidene)piperidinium perchlorate, 3408

1-(4-Methyl-1,3-diselenonylidene)piperidinium perchlorate, 3174

1-(4-Phenyl-1,3-diselenonylidene)piperidinium perchlorate, 3659

*See other* OXOSALTS OF NITROGENOUS BASES

## DISPOSAL

1. *Hazardous Chemicals: Information and Disposal Guide*, Armour, M. A. *et al.*, Edmonton, University of Alberta, 1984  
*Handbook of Laboratory Waste Disposal*, Pitt, E. & M. J., Chichester (UK), Ellis Horwood, 1985.
2. Chivers, G. E., *Disposal of Hazardous Wastes*, Northwood (Mdx.), Science Reviews Ltd., 1983
3. *Hazardous and Toxic Materials: Safe Handling & Disposal*, Fawcett, H. H., New York, Wiley, 1984
4. *The Disposal of Hazardous Waste from Laboratories*, Proceedings of RSC Chemical Information Group meeting, March 1983, London, RSC, 1983
5. Voegelien, J. F., *J. Chem. Educ.*, 1966, **43**, A151–157
6. Teske, J. W., *J. Chem. Educ.*, 1970, **47**, A291–295
7. Allen, R. O., *J. Chem. Educ.*, 1983, **60**(3), A814
8. Cook, J. D., reference 4 above, 116
9. Ghosh, P. K. *et al.*, *Proc. 11th Int. Sympos. Prev. Occup. Risks Chem. Ind.*, 703–719, Heidelberg, ISSA, 1987

The gap left in the literature on disposal of hazardous laboratory materials by the withdrawal in 1980 of the MCA manual has been filled adequately by new compilations. In addition to providing brief details on general properties, reactive and toxic hazards for each of some 300 laboratory chemicals, detailed directions for



disposal of spills, residues or package lots are available. Disposal methods have been laboratory tested for completeness of reaction, safety and practical utility [1]. All aspects of the implications and operation of UK hazardous waste legislation and the derived practical systems are covered in a 100 page survey, which includes a chapter on disposal of wastes from chemical, biological and radiochemical laboratories [2]. The third reference is concerned more with the long-term implications of past and previous large-scale disposal procedures than with the practical detail of laboratory disposal methods [3]. Many aspects of the complex problems and practical solutions related to disposal of laboratory wastes were covered comprehensively in a symposium [4]. Practical solutions to disposal problems adopted by an explosives research laboratory [5], and by two American universities have been described [6,7], the former including details on the use of explosives to rupture corroded and unusable cylinders of compressed or liquefied gases.

Some of the techniques employed need a remote area for safe operations, which may not be available to laboratories in urban locations. In such cases the services of a specialist chemical disposal contractor may be the most practical solution. It is, however, possible to minimise disposal problems by strict control on quantities ordered for stock (resisting bargain bulk offers), and on stockroom procedures. The reasons for the reluctance of many practising chemists to accept the fact that they are, almost invariably, the person best qualified to deal at the point of origin with difficult or dangerous residues were discussed [8]. Problems encountered and their solutions in disposing of inventories after a chlorine leak in a disused chemical factory are discussed. A large spill of liquid chlorine was largely absorbed in sodium hydroxide. Vinyl chloride was pumped out and removed, hydrogen was released slowly to atmosphere and acetylene was flared off [9].

### **1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE SALTS**

Preparative hazard

*See* Carbon disulfide: Alkali metals

### **DRUMS**

Several accidents in this book, some fatal, involve bursting forty-five gallon (215 litre, 55 gallon US) steel drums, a standard chemical packaging. These are sometimes attributed to setting off an explosion in the headspace of a bulging drum while attempting to vent it. In fact, a bulging drum can contain quite enough mechanical energy to kill, cut pipelines, etc. A bulging drum will eventually burst unattended, but the last straw, which breaks the worker's neck if he is in the wrong position, may be the slight additional stress of handling. The most damage results when the bottom blows out, this creates what, in military terms, is a spigot mortar, allowing the compressed gas in the headspace to transfer most of its energy to the bulk of the drum. Since the bottom is under more stress, both chemical and physical, than the top, having the weight of the contents as well as the gas pressure to resist, such failure is probable in a symmetric drum. Any worker standing above the drum while trying to vent it may then be struck hard beneath the chin by 15 kg

of percussive instrument travelling at modest speed—result a broken neck. Do not stand above bulging drums when trying to vent them. The relatively light, if sharp edged, top plate, though accelerated over a very short distance before the gas vents, is still dangerous. Chemists must beware of storing materials which can either generate gas, react with the drum to produce hydrogen, or be catalysed by it to self-heat to boiling.

See STEEL:apricots

## DRYING

1. *High Vacuum Techniques for Chemical Syntheses and Measurements*, Plesch, P. H., Cambridge, Cambridge University Press, 1989, pp. 140, 141
2. *Purification of Laboratory Chemicals*, Perrin, D. D., Armarego, W. L. F. (Eds.), New York, Pergamon, 3rd edn.
3. *Drying: Principles and Practice*, Keey, R. B., Oxford, Pergamon, 1972
4. *Spray Drying Handbook*, Masters, K., Harlow (Essex), Longmans, 5th edn. 1992
5. *Industrial Drying Equipment Selection and Application*, van't Land, New York, Marcel Dekker, 1991

In the strict chemical sense, the term drying refers to removal of water present in solid or fluid materials by treatment with water-reactive chemicals. In a wider (chemical engineering) context, it also refers to use of physical methods to remove any unwanted liquids (or vapours) from solid, liquid or gaseous phases.

The first reference is largely devoted to small scale and intensive drying of solvents and reagents by chemical methods for use in kinetic work. Chemical drying is commonly a source of hazard since the reagents used are, of their nature, often extremely reactive, and not only with water; a discussion of hazards is given [1]. A good example of such an agent is magnesium perchlorate (Anhydrone) which reacts with a variety of chemicals or solvents to form explosive products or adducts. Generally its use should be avoided. The next reference covers various aspects of laboratory scale purification and possibly less rigorous drying of a wider range of materials [2]. The remaining references cover chemical engineering aspects of industrial drying operations, with attention to safety aspects [3,4,5].

Drying, usually by physical methods, is one of the most common unit operations in both laboratory or industrial scale process chemistry, and since heating is usually employed to remove volatiles, thermally unstable materials may decompose if overheated. As a light-hearted example, when a faulty oven thermostat led to overheating of mercuric thiocyanate, a monstrous 'Pharaoh's serpent' resulted. Drying moist cadmium propionate in an electric oven led to explosive ignition of the diethyl ketone vapour produced as an unforeseen by-product. Drying 3,5-dinitro-2-toluamide had more serious consequences.

Chemical drying of liquids often involves reaction, with or without heating, of a solid which will react selectively with water. Calcium or lithium aluminium hydrides are often used; evolved hydrogen needs safe venting. For the lithal, careful stirring and temperature control is essential to prevent formation of extremely

reactive aluminium, which may react violently with oxygenated or halogenated solvents like dioxane or trichloroethane.

When adsorbents are used to dry gases or liquids, often in a flow system, the adsorbents may need pre- or post-treatment to avoid hazards. Thus, when ethylene was contacted with molecular sieve not previously treated with dilute ethylene, the adsorption exotherm heated the bed to red heat and ruptured the drier. When peroxide-containing ethers are simultaneously dried and purified by chromatography (passage through an alumina column), the peroxides are concentrated on the alumina, which must be treated before disposal.

The drying of solids may involve the removal of volatile solvents. When these are flammable, ignition sources must be excluded to minimise risk of fire or explosion.

Some industrial drying techniques have inherent potential hazards. The conditions prevalent in spray drying, where a solution is sprayed into a hot gas (usually air), are likely to cause electrostatic charge generation, and stringent earthing/bonding precautions are necessary for flammable solvents or combustible solutes such as milk powder. Fluidised-bed driers may show similar problems with dusty organic materials, and gas-inerting is desirable.

There are unusual hazards associated with partial desolvation of crystalline solvated oxosalts, notably perchlorates. This may be because desolvation causes the oxygen balance to approach the zero balance point and maximum energy release potential. A similar effect has also been seen with an hydrated salt.

These and other examples may be found in the entries:

METAL-HALOCARBON INCIDENTS, (references 2, 3)

MILK POWDER

MOLECULAR SIEVE INCIDENTS: ethylene

ORGANIC POWDER HANDLING

PEROXIDES IN SOLVENTS

SOLVATED OXOSALT INCIDENTS

Cadmium propionate, 2418

Calcium acetylide: Methanol

Diazomethane: Calcium sulfate, 0406

3,5-Dinitrotoluamide

Lithium tetrahydroaluminate: Dioxane, 0075

Magnesium: Methanol, 4690

Magnesium perchlorate, 4084

Mercury(II) thiocyanate, 0979

Silicon dioxide: Hydrochloric acid

Sodium: Halocarbons (reference 10)

Sodium azide Heavy metals, 4758

Sulfuric acid: Hydrofluoric acid, 4479

Vinyl acetate: Desiccants, 1532

*See* ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

*See also* FLASH POINTS

*See other* UNIT OPERATIONS AND PROCESSES

## DUST EXPLOSION INCIDENTS

1. Dorsett, H. G. *et al.*, *Rept. RI 7132*, Washington, US Bur. Mines, 1968
2. Hartmann, I., *Ind. Eng. Chem.*, 1948, **40**, 752
3. Palmer, K. N., *Dust Explosions and Fires*, London, Chapman & Hall, 1973
4. Nagy, J. *et al.*, *Rept. BM-RI 7208*, Washington, USAEC, 1968
5. Yowell, R. L. *et al.*, *Loss Prev.*, 1968, **2**, 29–53
6. Strizhevskii, I. *et al.*, *Chem. Abs.*, 1975, **82**, 6147
7. Griffiths, W. C., *Ann. Rev. Fluid Mech.*, 1978, **10**, 93–105
8. Cardillo, P. *et al.*, *Dust Explosions & Fires: Guide to Literature*, Milan, Staz. Sperim. Combust., 1979
9. Moore, P., *Chem., & Ind.*, 1979, 430–434
10. Pomeranstsev, V. V. *et al.*, *Chem. Abs.*, 1979, **91**, 7257
11. Field, P., *Handbook of Powder Technol.*, Vol. 4, *Dust Explosions*, Amsterdam, Elsevier, 1981
12. Eckhoff, R. K. *et al.*, *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, F11–20, Rugby, IChE, 1983
13. Fusamura, N. *et al.*, *Chem. Abs.*, 1983, **98**, 5957
14. *Dust Explosions: Combustible Particles and Control*, PB84-878073, Richmond (Va.), USNTIS, 1984
15. Radsziszewska, J. M., *Arch. Combust.*, 1986, **6**, 139–149
16. Enright, R. J., *Chem. Abs.*, 1987, **106**, 125260; **110**, 120443h
17. Sweis, F. K., *J. Haz. Mat.*, 1987, **14**, 241–246
18. Lunn, G., *Inf. Chim.* (Fr.), 1986, **278**, 225–230
19. Moore, P. E., *EuropEx Newsl.*, 1987, (4), 2–4
20. Moore, P. E. *et al.*, *Staub-Reinheit. Luft*, 1987, **47**(7–8), 207–213
21. Weckman, H., *Fire Saf. J.*, 1987, **12**(2), 97–102
22. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62–74
23. *ASTM Spec. Tech. Publ. 958*, Industrial Dust Explosions, Cashdollar, K. L., Hertzberg, M. (eds), Philadelphia, ASTM, 1987, 191–201
24. Lunn, G. A., *J. Haz. Mat.*, 1988, **17**, 207–213
25. Aglan, H., *Part. Sci. Technol.*, 1988, **6**, 43–51
26. Lee, J. H. S. *et al.*, *Arch. Combust.*, 1987, **7**, 279–297
27. Bartknecht, W., *Staub — Reinheit. Luft*, 1988, **48**(10), 354–368; (11), 417–425
28. Dehn, C. J., *Arch. Combust.*, 1987, **7**(3–4), 299–312
29. Amyotte, P. R. *et al.*, *J. Loss Prev. Proc. Ind.*, 1989, **2**, 87–94
30. Radsziszewska, J. M., *Arch. Combust.*, 1987, **7**, 315–320
31. Matsuda, T., *Arch. Combust.*, 1987, **7**, 237–253
32. Jarosinski, J. *et al.*, *Arch. Combust.*, 1987, **7**, 267–278
33. Fangrat, J. *et al.*, *Arch. Combust.*, 1987, **7**, 321–332
34. Abbot, J. A., *EuropEx Newsl.*, 1988, (8), 4–10
35. Eckhoff, R. K., *Dust Explosions in the Process Industries*, Oxford, Butterworth-Heinemann, 1991
36. *Proc. 6th Int. Colloq. Dust Expl.*, Deng, X., Wolanski, P. (Eds.), Shenyang China, Northeast. Univ. Press, 1994.
37. Plewinsky, B. *et al.*, *Prax. Sicherheitstech.*, 1997, **4**, 95

Laboratory dust explosion data were presented for 73 chemical compounds, 29 drugs, 27 dyes and 46 pesticides, including ignition temperatures of clouds and layers, minimum ignition energy, explosion-limiting concentrations and pressures, and rates of rise at various dust concentrations. Explosibility indices were computed where possible and variation of explosibility parameters with chemical composition was discussed. General means of minimising dust explosion hazards were reviewed [1]. Of the 17 dusts investigated earlier, the 4 metals examined — aluminium, magnesium, titanium and zirconium — were among the most hazardous. Aluminium and magnesium show the maximum rates of pressure rise and final pressures, magnesium having a low minimum explosive concentration. Ignition of zirconium dust often occurred spontaneously, apparently owing to static electric discharges, and undispersed layers of the dust could be ignited by less than 1μJ compared with 15μJ for a dispersed dust. All except aluminium ignite in carbon dioxide atmospheres [2]. A comprehensive account of practical and theoretical aspects of laboratory and plant-scale dust explosions and fires includes appended tabulated data for over 300 dusts of industrial significance [3]. Laboratory dust explosion data for 181 miscellaneous hazardous materials and 88 non-hazardous materials are presented [4]. Papers and symposium discussions on several aspects of the topic were presented [5], together with further data on dust-explosivity of several metallic and non-metallic industrial materials [6]. A comprehensive survey of the whole field has recently (1991) been published [35].

A review including fluid mechanical considerations and useful applications among other aspects of dust explosions [7], and a collection of abstracts covering 20 years to 1977 [8] have been published. In a comparative study of laboratory methods available for assessing dust explosibility, the influence of ignition source type and containing vessel size are discussed in detail [9]. Spontaneous combustion and explosion of natural fuel dusts are covered [10], and a new text on the topic is available [11]. The ultimate experiments in dust explosion research in full size 500 m<sup>3</sup> silos using wheat grain, soya meal and maize starch dusts have been described [12]. Explosions of dispersed 200 mesh cellulose dust was inhibited by presence of potassium chloride, lead nitrate and cadmium sulfate, but promoted by barium chloride or potassium nitrate above 1.3% conc. [13]. A new bibliography (163 entries, 1970–84) cites dust generated explosion details in various industrial environments, particularly agricultural, and classifies combustible dusts [14]. An extensive series of papers on many aspects of dust explosions are collected in [36].

The lower explosive limit and minimum explosive concentrations of flax, wool, cotton, jute, hemp and sisal fibres are of the same order of magnitude as those of highly explosive dusts [15]. The explosibility of pyrites dusts with sulfur contents above 20% was evaluated experimentally. Dusts of 30% sulfur content gave explosion pressures of 3 bar at pressure rise rates of 16 bar/sec. Mixtures of 60% pyrites and 40% powdered limestone still showed significant pressure effects, and the proportion of limestone actually needed to suppress explosions was considerably above the values currently accepted by mining industries [16]. Effects of mixtures of particle sizes in combustible dusts upon minimum ignition temperature ( $T_i^m$ ) and upon presence or absence of explosion were studied. Presence of 30% of fines in a coarse dust lowers  $T_i^m$  significantly [17]. Experimental explosions of polyethylene,

phenolic resin, dye, and aspirin powders demonstrated the resistance to explosion of an industrial dust collector fitted with automatic explosion relief panels [18]. The validity of suppressing dust explosions in volumes up to 1000 m<sup>3</sup> using a few large suppressors has been established [19], and the efficacy of the system was proven in an experimental spherical vessel 6.3 m in diameter [20]. The maximum explosion pressures for relatively fine and dry peat dusts may be estimated with a fair degree of accuracy from the moisture content, provided that the mean particle size is below 200µm and that the moisture content is below 35%. For coarser and moister peat dusts, it may only be possible to assess whether it is explosive, and inhomogeneity in peat samples causes further significant problems [21].

In a comprehensive review of dust explosion problems and hazards associated with mechanical handling systems (pneumatic, screw, and belt conveyors, bucket elevators, en masse conveyors) for bulk transfer of a wide variety of solid chemicals and industrial materials, tabulated data for some 400 such materials are presented. The data are given under the headings minimum ignition temperatures, explosible concentrations in air, and ignition energies; and maximum explosion pressures, rates of pressure rise, and oxygen concentrations to prevent ignition. Of these 400 materials, 33 are notable in that the maximum rates of pressure rise observed exceed 680 bar/s (10,000 psi/s). Figures below for these 33 materials are for maximum explosion pressure (bar) and maximum rate of rise (bar/s), respectively, except where noted.

Acetoacet-4-phenetidine, 5.9, 680; atomised aluminium, 5.7, >1.36 kbar/s; aluminium flake, 8.6, >1.36 kbar/s; aluminium-cobalt alloy, 6.25, 748; aluminium-magnesium alloy, 5.85, 680; aluminium-nickel alloy, 6.5, 680; aluminium stearate, 5.85, 680; benzoic acid, 6.85, 700; 2,2-bis(4-hydroxyphenyl) propane, 5.5, 803; calcium silicide, 5.85, 1.36 kbar/s; calcium stearate, 6.6, >680; cellulose nitrate, >17.4, >1.42 kbar/s; 2-chlorobenzylidenemalononitrile, 6.1, >680; coumarone-indene resin, 6.3, 748.

1,4-Diaminobenzene, 6.4, 748; 2,6-di-*tert*-butyl-4-cresol, 5.4, 884; dimethyl terephthalate, 7.1, 816; 3,3'-dimethoxy-4,4'-diaminobiphenyl, 5.6, 680; 3,5-dinitrotoluamide, 10.4, 680; 1,3-diphenyltriazene, 7.75, >680; 2,4-hexadienoic acid, 7.2, >680; hexamethylenetetramine, 6.7, 748; magnesium, 7.9, 884; paraformaldehyde, 9.0, 884; phytosterols, 5.2, >680; poly(acrylonitrile), 6.0, 748; rosin, 5.7, 816; silicon, 6.4, 884; tetraphosphorus decasulfide, 4.35, >680; thorium hydride, 5.5, 816; titanium, 5.8, 816; titanium hydride, 8.2, 816; zinc stearate, 5.4, >680; zirconium, 5.1 bar, 740 bar/s [22]. In the proceedings of the 1986 Pittsburgh conference on dust explosions, many aspects of the occurrence, prevention and protection from the effects of industrial dust explosions involving a wide variety of materials are presented in a series of papers [23].

Lower limits of explosibility of several organic dusts were determined and found to be in general agreement with estimated values [24]. Probabilistic aspects of occurrence of dust explosions were studied experimentally with lycopodium powder in relation to dust and hot surface (or dust) temperature. The probability of explosion increases with dust concentration, then falls off, due to the ballast effect of unburnt dust. Probability also increases continuously with the temperature of the hot surface and/or dust particles. Application of the results to practical plant

installations is discussed [25]. The effect of turbulence (which increases degree of dispersion and reduces the rate of settlement) on closed-volume explosions of dust–air mixtures has been studied [26]. In a 2 part publication, test methods and derived parameters, and preventive and protective measures are reviewed in relation to explosions in combustible dusts and in their mixtures [27]. A method has been described to assess the effect on explosion energy of presence of low concentrations of flammable vapours in dust–air mixtures in a 20 l chamber. Significant increases in rate of pressure rise were observed in corn starch–air mixtures with added refuse-derived fuel vapour [28]. The effect of turbulence on explosion parameters of lycopodium dust in a 1.2 l Hartmann bomb has been studied in two parallel series of experiments. One series in the bomb gave relation between dispersing air pressure, dust concentration, ignition delay time and the maximum rate of pressure rise. A second series in a plexiglass version of the bomb (without ignition) showed the relation between dispersing air pressure and dust velocity (measured by laser Doppler velocimeter) and settling time. The decay of turbulence in the Hartmann bomb is rapid (below 200 ms), and this time frame coincided closely with the rapid fall off in the rate of pressure rise with ignition delays of 40–180 ms. The correlation depends on dust concentration and dispersing air pressure [29]. The explosive behaviour of mixtures of flax dust and fibres with air has been studied [30]. The influence of air velocity upon ignition and flame propagation in dust–air mixtures under pneumatic tube conveyor conditions has been studied [31]. Minimum quenching distances for control of dusts of cornstarch, aluminium and coal have been determined [32], and flame propagation and transition to detonation has been studied in mixtures of organic dusts with oxygen-enriched air [33]. A survey of dust fires and explosions in UK during 1979–84 revealed that dusts most frequently involved were those of grains and cereals, animal feeds and food products, while wood and metal dusts were often involved. Other dusts involved were sulfur, phosphorus trisulfide, zinc phosphide, carbon and rubber. Losses from dust fires were more common than from dust explosions [34].

Mist explosions are, of course, dust explosions in which the particles happen to be liquid. Other less common types of detonation involving gaseous oxidants are reviewed in [37]. These include wick explosions, foam explosions, and surface explosions.

*See* METAL SULFIDES, FLOUR

*See also* GEOMETRY OF VESSELS AND PIPEWORK, DEFLAGRATION TO DETONATION

#### Methane

Reeh, D., *Chem. Abs.*, 1979, **90**, 126799

Tests on the explosive behaviour of combustible dust–methane–air mixtures in a 45 mm pipeline 200 m long showed that presence of a little fuel gas could cause combustible but non-explosive dusts to become unexpectedly hazardous.

*See* CARBONACEOUS DUSTS, DUSTS, METAL DUSTS

Individually indexed incidents include:

Acetoacet-4-phenetidine, 3529

*O*-Acetylsalicylic acid, 3137  
Aluminium, 0048  
Aluminium–cobalt alloy, 0049  
Aluminium–magnesium alloy, 0053  
Aluminium stearate, 3914  
Benzoic acid, 2732  
2,2-Bis(4-hydroxyphenyl)propane, 3686  
Calcium silicide, 3943  
Calcium stearate, 3896  
2-Chlorobenzylidenemalononitrile, 3333  
1,4-Diaminobenzene, 2371  
2,6-Di-*tert*-butyl-4-cresol, 3691  
3,3'-Dimethoxy-4,4'-diaminobiphenyl, 3660  
Dimethyl terephthalate, 3292  
3,5-Dinitro-2-toluamide, 2941  
1,3-Diphenyltriazene, 3506  
2,4-Hexadienoic acid, 2385  
Hexamethylenetetramine, 2477  
Magnesium, 4690  
Magnesium–nickel hydride, 4464  
Paraformaldehyde, 0417  
Poly(ethylene), 0782  
Silicon, 4909  
Sucrose, 3558  
Tetraphosphorus decasulfide, 4878  
Thorium dihydride, 4489  
Titanium, 4919  
Titanium carbide, 0561  
Titanium dihydride, 4490  
Zinc stearate, 3897  
Zirconium, 4928

## DUSTS

1. Taubkin, S. I. *et al.*, *Chem. Abs.*, 1976, **85**, 110611
2. Leuschke, G., *Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 2, 647–656, Basle, SSCI, 1980
3. *NFPA 654*, Quincy (Ma), National Fire Protection Association, 1988  
A new method of classifying hazardous dusts into the 3 groups, highly explosible, explosible and fire-hazardous was proposed, based on lower explosive limits and maximum rate of pressure increase. An extension of the system to classify work-rooms taking account of their volumes was also suggested [1]. The dependency of induction time (time until critical self-heating occurs) upon storage temperature and volume of dusts stored at or above their ignition temperatures has been studied [2]. A new US fire code covers prevention and control of fires and dust explosions in the chemical, dyestuffs, pharmaceutical and plastics industries [3].



## EARTHQUAKE

Pine, S. H., *Chem. Health & Safety*, 1994, **1**(2), 10.

A discussion, based on experience, of the measures needed to protect laboratories and equipment in earthquake zones.

Earthquakes provide the ultimate test of the storage of incompatible chemicals and are sometimes followed by fires in chemical stores. Very few causes of ignition are found: alkali metals; halogen oxysalts in conjunction with strong acids; and sulphuric or nitric acid and cellulose (wood flooring). These usually then ignite vapours of flammable solvents.

*See* STORAGE OF CHEMICALS

## ELECTRIC FIELDS

Kabanov, A. A. *et al.*, *Russ. Chem. Rev.*, 1975, **44**, 538–551

Application of electric fields to various explosive heavy metal derivatives (silver oxalate, barium, copper, lead, silver or thallium azides, or silver acetylide) accelerates the rate of thermal decomposition. Possible mechanisms are discussed.

## ELECTROLYSIS

Mason, J. P., personal communication, 1999

Electrolysis is a means of putting energy into a chemical system. That energy may be stored in the system, to emerge spontaneously later. Apparently innocuous systems can thereby become extremely hazardous. The obvious example is the cleavage of water to produce an explosive mix of hydrogen and oxygen. There are more subtle risks: the performance of an electrode design was being tested over several weeks in a solution of ammonium chloride, topped up daily with ammonia. After about three weeks, the technician who topped up the beaker containing the assembly found its contents flying past his ears. No substantial piece of the beaker was ever found. That was trichloroamine formation, and destruction. Other nitrogenous compounds, in other halide electrolytes, could behave similarly.

*See* Ammonium chloride, Deuterium oxide

*See also* BATTERIES

## ELECTRON BEAM MELTING

Brinza, V. N. *et al.*, *Chem Abs.*, 1987, **106**, 22657

Potential hazards associated with electron beam vacuum melting of metals include the possibility of ignition of metal aerosols or condensate films in the event of sudden loss of vacuum at elevated temperatures.

## ELECTROSTATIC HAZARDS

1. Haase, H., *Electrostatic Hazards: Evaluation and Control*, Weinheim, Verlag Chemie, 1977
2. Anon., *Loss Prev. Bull.*, 1979, (029), 134–138
3. Anon., *CISHC Chem. Safety Summ.*, 1980, **51**, 4–6

4. Anon., *Loss Prev. Bull.*, 1980, (035), 1–5
5. Maksimov, B. K. *et al.*, *Chem. Abs.*, 1982, **96**, 165336
6. Anon., *Jahresber.*, 1985, 70–72
7. Wilson, N., *Chem. Abs.*, 1986, **105**, 138978
8. Jury, E., *Safety aspects and measures in electrostatic gas purification*, DECHEMA Monogr. 107, 1987, 383–388
9. Pay, F. J., *Loss Prev. Bull.*, 1987 (078), 1–8
10. Cartwright, P., *Chem. Engr.* (Rugby), 1988, (454), 49
11. Pratt, T. H., *Process Safety Progr.*, 1993, **12**(4), 203

The comprehensive text contains numerous case studies and quantitative calculations on many aspects of static electrical hazards [1]. Case histories involving leakage of steam or other pressurised fluid, flow to or from storage tanks, dusts and unearthed plant segments are discussed [2]. In a group of 7 incidents involving fire or explosion, the common ignition source was static generated by pouring fine solids from plastic bags or through non-conducting ducts or funnels [3]. Seven further case histories involving fires or explosions in dusts or powders under various circumstances are detailed [4]. Equations for calculating maximum flow rates to avoid static build up during transfer of petroleum products to or from road or rail tanks have been derived [5].

In the preparations during unsettled weather for a large outdoor firework display, the pyrotechnic components, together with the starting fuses, electric igniters and charged batteries were all stored in the same building. The batteries were to be protected from the weather by wrapping in polythene film, and when this was unreeled, static discharge led to ignition of the stored materials, and uncontrolled fires and explosions destroyed the building [6]. Factors affecting incendiary behaviour of static spark discharges from the human body on ignition of methane–and hydrogen–air mixtures are discussed [7]. Safety aspects and precautionary measures to prevent fire and explosion in electrostatic gas purifiers are discussed [8]. A brief survey of the phenomenon, consequences and hazards of electrostatic charging in industrial operations is illustrated by case histories [9]. Accidents originating from static charge generation during the pouring of powder from polythene-lined fibreboard drums, or when digging dry cake from a vacuum filter bed dryer are analysed, and preventive measures proposed [10]. Poorly designed fire extinguishing systems may also lead to static hazards. A specialised mechanism for ignition of oxygen-rich atmospheres by electrostatic effects generated by bursting oxygen bubbles from decomposing hydrogen peroxide is postulated [11].

See Carbon dioxide: Flammable materials

See other IGNITION SOURCES

## ENDOTHERMIC COMPOUNDS

1. Weast, 1979, D61–84
2. Mellor, 1941, Vol. 1, 706–707
3. Stull, 1977, 8–10

Most chemical reactions are exothermic, but indirect or high temperature reactions permit preparation of high energy product(s) which are known as endothermic

(or energy-rich) compounds. Such compounds are thermodynamically unstable, because heat would be released on decomposition to their elements. The majority of endothermic compounds possess a tendency towards instability and possibly to explosive decomposition under various circumstances of initiation. Often, endothermic compounds possess features of multiple bonding ('unsaturation'), as in acetylene, hydrogen cyanide, silver fulminate, mercury azide or chlorine dioxide. Other singly bonded endothermic compounds are hydrazine, diborane, dichlorine monoxide, or nitrogen trichloride.

Many, but not all, endothermic compounds have been involved in violent decompositions, reactions or explosions, and in general, compounds with significantly positive values of standard heat of formation may be considered suspect on stability grounds. Notable exceptions are benzene and toluene ( $\Delta H_f^\circ$  +82.2, 50.0 kJ/mol; 1.04, 0.54 kJ/g, respectively), where there is the resonance stabilising effect of aromaticity. Values of thermodynamic constants for elements and compounds are tabulated conveniently [1], but it should be noted that endothermicity may change to exothermicity with increase in temperature [2]. There is a more extended account of the implications of endothermic compounds and energy release in the context of fire and explosion hazards [3]. Many examples of endothermic compounds will be found in the groups:

*See also* ACETYLENIC COMPOUNDS, ALKYL METALS, ALKYNES, AZIDES, BORANES, CYANO COMPOUNDS, DIENES, HALOACETYLENE DERIVATIVES, HALOGEN OXIDES, METAL ACETYLIDES, METAL FULMINATES, OXIDES OF NITROGEN

The individually indexed endothermic compounds, for most of which heats of formation are given in the text:

- † Acetonitrile, 0758
- \* Ammonium hexacyanoferrate(II), 2577
- † Arsine, 0100
- Azido-2-butyne, 1473
- 3-Azidopropyne, 1114
- cis*-Azobenzene, 3484
- Azoxybenzene, 3485
- Barium azide, 0214
- Benzenediazonium nitrate, 2275
- Benzotriazole, 2269
- Borane, 0135
- Bromine azide, 0256
- † 3-Bromopropyne, 1090
- † 1,2-Butadiene, 1479
- † 1,3-Butadiene, 1480
- † Buten-3-yne, 1423
- † 1-Butyne, 1481
- † 2-Butyne, 1482
- Cadmium azide, 3957
- Cadmium cyanide, 0588
- Cadmium fulminate, 0589
- Cadmium nitride, 3960

Calcium azide, 3936  
 † Carbon disulfide, 0560  
 Chlorine dioxide, 4042  
 Chloroacetylene, 0652  
 Chloryl perchlorate, 4104  
 Copper(I) azide, 4287  
 Cyanamide, 0404  
 Cyanoform, 1383  
 Cyanogen bromide, 0313  
 Cyanogen chloride, 0323  
 Cyanogen fluoride, 0323  
 3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-) oxide, 2630  
 † Cyclopropane, 1197  
 Diazene, 4469  
 2,3-Diazido-1,3-butadiene, 1437  
 Diazomethane, 0406  
 † Diborane(6), 0166  
 Dichlorine oxide, 4095  
 Dichlorine trioxide, 4100  
 † Dicyanoacetylene, 1801  
 1,4-Dicyano-2-butene, 2311  
 Dicyanofurazan, 1803  
 Dicyanofurazan *N*-oxide, 1804  
 † Dicyanogen, 0996  
 Diethylcadmium, 1677  
 Difluorodiazene, 4314  
 Diiodomethane, 0400  
 Dimethylcadmium, 0894  
 Dimethylmercury, 0907  
 Dimethylzinc, 0935  
 Dinitrogen oxide, 4744  
 Dinitrogen tetraoxide, 4747  
 Dioxygen difluoride, 4320  
 \* *trans*-1,2-Diphenylethylene, 3643  
 Fluoroacetylene, 0662  
 Gold(III) oxide, 0115  
 1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine, 4795  
 Hydrogen azide, 4441  
 † Hydrogen selenide, 4486  
 † Hydrogen telluride, 4488  
 Iodoform, 0376  
 Lead(II) azide, 4782  
 Lead(IV) azide, 4790  
 Mercury(II) cyanide, 0976  
 Mercury(II) fulminate, 0978  
 \* Mercury(II) thiocyanate, 0979

- † 2-Methyl-1,3-butadiene, 1893
- † 3-Methyl-1,2-butadiene, 1892
- † 3-Methyl-1-butyne, 1894
- \* Methyl isocyanide, 0759
- Nickel(II) cyanide, 0997
- Nitrogen oxide, 4724
- Nitrogen trichloride, 4143
- Nitrosyl chloride, 4023
- Nitrogen triiodide, 4633
- Nitryl chloride, 4025
- Nitryl hypofluorite, 4304
- Oxygen difluoride, 4317
- † Pentaborane(9), 0188
- † 1,2-Pentadiene, 1895
- † 1,3-Pentadiene, 1896
- † 1,4-Pentadiene, 1897
- † 1-Pentyne, 1898
- † 2-Pentyne, 1899
- Perchloryl perchlorate, 4107
- † Phosphine, 4508
- \* Phosphorus triazide oxide, 4788
- Potassium hexacyanoferrate(III), : Hydrochloric acid, 4242
- † Propadiene, 1124
- Propadienedithione, 1350
- † Propyne, 1125
- Silicon tetraazide, 4791
- Silver azide, 0023
- Silver cyanide, 0299
- Silver fulminate, 0301
- \* Sodium hexaazidophosphate, 4794
- † Stibine, 4510
- Strontium azide, 4785
- Styrene, 2945
- Tetracyanoethylene, 2629
- Tetraethyllead, 3095
- Tetramethyl-2-tetrazene, 1759
- Tetrasulfur tetranitride, 4770
- \* Tetravinyllead, 3016
- Tetrazole, 0411
- \* Thallium(I) tetraazidothallate, 4792
- \* 2,4,6-Trichloro-1,3,5-triazine, 1038
- \* Vinyl isocyanide, 1109
- Zinc cyanide, 1004

## ENERGETIC COMPOUNDS

1. Witucki, E. F. *et al.*, *J. Chem. Eng. Data*, 1983, **28**, 285–286
2. Various, *Mater. Res. Soc. Proc.* (418), 1996

Syntheses of 5 energetic aliphatic azido compounds are described: caution is necessary in handling these because of their impact-sensitivity [1]. A later symposium on energetic materials, here meaning explosives and propellants, is reported [2].

Individual compounds are:

- 6-Azidoethyl 6-azidohexanoate, 3551
- Bis(2-azidoethoxymethyl)nitramine, 2481
- N*-Butyl-*N*-2-azidoethylnitramine, 2528
- 1,12-Diazido-3,10-dioxo-5,8-dinitrazadodecane, 3049
- Tris(2-azidoethyl)amine, 2482

*See also* ENDOTHERMIC COMPOUNDS, FLUORODINITROMETHYL COMPOUNDS (reference 6)

## ENVIRONMENTALISM

1. Kletz, T. A., *Chemical Engineer*, 1992, 527, 38
2. Kletz, T. A., *Process Safety Progr.*, 1993, **12**(3), 147
3. Förster, H. *et al.*, *Ber. Dtsch. Wiss. Ges.; Erdöl, Erdgas, Kohle Forschungsber.*, 1994, 462
4. De Haan, J. D. *et al.*, *Proc. Int. Conf. Fire. Safety*, 1995, **20** 67

Environmentalists react violently to the mere word chemical. Some cases where Green and naive over-reaction has led to environmental damage and accompanying human fatalities from explosion are described and some likely causes of future mishap suggested [1,2]. It is proposed to lower the permitted vapour pressure of gasoline, to reduce environmental release of Volatile Organic Compounds, which will bring the headspace of car fuel tanks below the upper explosive limit on cool mornings [3]. Consideration is given to the increased fire risk of household aerosols associated with use of liquid petroleum gases and dimethyl ether as environmentally friendly propellants [4].

*See* Hydrogen peroxide: Waste treatment

## EPOXIDATION

Swern, 1971, Vol. 2, 428–533

Preparation of epoxides (oxirans) on the commercial scale as resin or polymer components is widely practised. Careful control of conditions is necessary to avoid hazards, and the several factors involved are reviewed.

*See* Peroxyformic acid: Organic materials

Hydrogen peroxide: Unsaturated compounds, 4477

*See related* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## 1,2-EPOXIDES

Pogany, G. A., *Chem. & Ind.*, 1979, 16–21

All factors relevant to the safe use of ethylene oxide and propylene oxide in high pressure bench scale experiments are detailed. Salient points include the need for a well-designed agitated reactor with adequate provision for reaction heat removal and emergency pressure relief; prevention of back-flow from reactor to oxide storage vessels; avoidance of a reaction atmosphere of 100% ethylene oxide vapour and/or presence of air; avoiding an excess of oxide. The 3 lower members of this group of compounds are bulk industrial chemicals, and their high reactivity has been involved in several serious incidents.

#### Dinitrogen pentaoxide

*See* Dinitrogen pentaoxide: Strained-ring heterocycles

#### Nitronium perchlorate

*See* Nitronium perchlorate: 1,2-Epoxides

Individually indexed compounds are:

- 1-Allyloxy-2,3-epoxypropane, 2434
- 1,4-Bis(2,3-epoxypropoxy)butane, 3353
- 2,2-Bis[4(2',3'-epoxypropoxy)phenyl]propane, 3825
- † 1-Chloro-2,3-epoxypropane, 1162
- † Cyclopentene oxide, 1906
- 2,3-Dibromo-5,6-epoxy-7,8-dioxabicyclo[2.2.2]octane, 2298
- † 1,2:3,4-Diepoxybutane, 1507
- † 1,2:3,4-Diepoxybutane, 1507
- 2,3:5,6-Diepoxy-7,8-dioxabicyclo[2.2.2]octane, 2339
- Endrin, 3459
- † 1,2-Epoxybutane, 1609
- † 3,4-Epoxybutene, 1520
- endo*-2,3-Epoxy-7,8-dioxabicyclo[2.2.2]oct-5-ene, 2336
- 2,3-Epoxypropanol (Oxiranemethanol), 1229
- 2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone, 3130
- 2,3-Epoxypropionaldehyde oxime (Oxiranecarboxaldehyde oxime), 1182
- 4(2,3-Epoxypropoxy)butanol, 2866
- \* 2,3-Epoxypropyl nitrate, 1186
- 3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2403
- † Ethylene oxide, 0829
- † 1-Fluoro-2,3-epoxypropane, 1171
- Glycidyl azide, 1191
- Nitrilotris(oxiranemethane), 3181
- † Propylene oxide, 4831
- Tetrafluorooxirane, 0632
- † Thiirane, 0840
- 1,3,5-Tris(2,3-epoxypropyl)triazine-2,4,6-trione, 3533

*See other* STRAINED-RING COMPOUNDS

## EQUATIONS

Editor's comments

Balance them! The editor has frequently found chemists fresh from university blithely ignoring evolution of gaseous byproducts, such as carbon monoxide and methyl halides, capable of rupturing vessels and killing operators. Write them step by step too, this may reveal mechanistic and catalytic effects harmful to chemist, cost or yield.

*See also* NITRATION INCIDENTS

## ETHERS

1. Jackson, H. L. *et al.*, *J. Chem. Educ.*, 1970, **47**, A175
2. Davies, A. G., *J. R. Inst. Chem.*, 1956, **80**, 386–389
3. Dasler, W. A. *et al.*, *Ind. Eng. Chem. (Anal. Ed.)*, 1946, **18**, 52
4. Hazardous Chemicals: Information and Disposal Guide, 1984, 87, 91, 98, 265
5. Robertson, R., *Chem. & Ind.*, 1933, **52**, 274
6. Morgan, G. T. *et al.*, *Chem. & Ind.*, 1936, **55**, 421–422
7. Williams, E. C., *Chem. & Ind.*, 1936, **55**, 58–581
8. Karnojitsky, V. J., *Chim. et Ind. (Paris)*, 1962, **88**, 233–238
9. Unpublished observations, 1973
10. Schwartz, A. M., *Chem. Eng. News*, 1978, **56**(24), 88

There is a long history of laboratory and plant fires and explosions involving the very high flammability and/or tendency to peroxide formation in these widely used solvents, diisopropyl ether being the most notorious. Methods of controlling peroxide hazards in the use of ethers have been reviewed [1], and information on storage, handling, purification [2,3] and disposal [4] have been detailed.

Three violent explosions of diisopropyl ether had been reported [5,6] and a general warning on the hazards of peroxidised ethers had been given by 1936 [7]. The latter reference mentions diethyl, ethyl *tert*-butyl, ethyl *tert*-pentyl and diisopropyl ethers as very hazardous, while methyl *tert*-alkyl ethers, lacking non-methyl hydrogen atoms adjacent to the ether link, are relatively safe. Bis(2-methyl-2-propen-1-yl) ether ('dimethyl ether') is unusual in that although it forms peroxides with extreme rapidity, these are thermolabile and are progressively destroyed without danger during distillation [7]. For like reasons, the slower distillation enforced by industrial scale partly explains why peroxidation induced explosions are essentially laboratory accidents only. The mechanism of peroxidation of ethers has been reviewed [8].

When solvents have been freed from peroxides by percolation through a column of activated alumina, the adsorbed peroxides must promptly be desorbed by treatment with the polar solvents methanol or water, which should be discarded safely. Small columns used to deperoxidise diethyl ether or tetrahydrofuran were allowed to dry out by evaporation. When moved several days later, the peroxide concentrated on the alumina at the top of the columns exploded mildly and cracked the glass columns [9]. A procedure for preparation of dry oxygen- and peroxide-free low boiling ethers (diethyl ether, THF, dioxane, glyme etc.) is described which involves distillation from sodium diphenylketyl.



See Nitrogen oxide: Sodium diphenylketyl for care in disposal of the sodium–ketyl residues.

Individually indexed compounds include:

- † Allyl ethyl ether, 1955
  - 1-Allyloxy-2,3-epoxypropane, 2434
- † Bis(2-ethoxyethyl) ether, 3076
  - Bis-(2-methoxyethyl) ether, 2549
- † Butyl ethyl ether, 2540
  - 1-(1,1-Dimethylethoxy)-2-methylpropane, 3072
- † Butyl methyl ether, 2010
- † *tert*-Butyl methyl ether, 2011
- † Butyl vinyl ether, 2484
- † Cyclopropyl methyl ether, 1608
- † Diallyl ether, 2431
  - Dibenzyl ether, 3655
- † Dibutyl ether, 3071
- † 1,1-Diethoxyethane, 2545
- † 1,2-Diethoxyethane, 2546
- † 3,3-Diethoxypropene, 2858
- † 2,3-Dihydrofuran, 1517
- † Diisopropyl ether, 2542
- † 1,1-Dimethoxyethane, 1700
- † 1,2-Dimethoxyethane, 1701
- † Dimethoxymethane, 1281
- † 3,3-Dimethoxypropene, 1968
  - 1-(1,1-Dimethylethoxy)-2-methylpropane, 3072
- † 1,3-Dioxane, 1616
- † 1,4-Dioxane, 1617
- † Dipropyl ether, 2543
  - Di(2-propynyl) ether, 2327
- † Divinyl ether, 1519
  - 2-Ethoxyethanol, 1702
    - 1-Ethoxy-2-propyne, 1909
- † Ethyl isopropyl ether, 2012
- † Ethyl propenyl ether, 1956
- † Ethyl vinyl ether, 1610
- † Furan, 1439
- † Isopropyl vinyl ether, 1957
- \* Methoxy-1,3,5,7-cyclooctatetraene, 3149
  - 2-Methoxyethanol, 1284
- † 2-Methoxyethyl vinyl ether, 1973
- † 2-Methyltetrahydrofuran, 1961
- † Methyl vinyl ether, 1221
- † Tetrahydrofuran, 1612
- † Tetrahydropyran, 1965

See *other* PEROXIDISABLE COMPOUNDS

## ETHOXYETHYNYL ALCOHOLS



1. Arens, J. F., *Adv. Org. Chem.*, 1960, **2**, 126
2. Brandsma, 1971, 12, 78

Vigorous decompositions or violent explosions have been observed on several occasions during careless handling (usually overheating) of ethoxyethynyl alcohols (structures not stated) [1]. The explosions noted when magnesium sulfate was used to dry their ethereal solutions were attributed to the slight acidity of the salt causing exothermic rearrangement of the alcohols to acrylic esters and subsequent explosive reactions (or polymerisation). Glassware used for distillation must be pretreated with ammonia to remove traces of acid [2].

See 4-Ethoxy-2-methyl-3-butyn-2-ol

See other ACETYLENIC COMPOUNDS

## EXOTHERMIC DECOMPOSITION REACTIONS

1. Grewer, T., *Proc. 2nd Int. Symp. Loss Prev. Safety Prom. Process Ind.*, III-105–113, 539, Frankfurt, Dechema, 1978
2. Grewer, T., *Chem. Ing. Tech.*, 1979, **51**, 928–933
3. Grewer, T., *Runaway Reactions*, 1981, Paper 2/E, 1–18

Problems in relating chemical structure to the type and course of exothermic decomposition are discussed, with an outline of some general methods useful in following the course of such reactions. Comparative figures for the temperature of onset of decomposition for typical molecular groupings which confer instability are tabulated and the mutual effects of the presence of two such groupings are discussed [1]. The role played by undesired or unexpected reactions in leading to the development of hazards in chemical processing operations is discussed. Typical decomposition energies are assigned to 'unstable' molecular groupings. The results of DTA examination are compared with warm storage tests, and the effects of various substituents and of other substances on the stability of particular compounds are studied [2]. The use of relatively simple tests, either at atmospheric or elevated pressures, to assess the hazards of exothermic decomposition reactions by determining the quasi-adiabatic self-heating curves and induction times are described in detail [3].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

## EXOTHERMICITY

Craven, A. D., *Hazards from Pressure*, IChE Symp. Ser. No. 102, Oxford, Pergamon, 1987

A simplified method for near-quantitative estimation of the exothermicity (energy of exothermic decomposition /unit mass) of products or reaction mixtures, which is suitable for a hand-calculator, is presented. It is based on the difference between the total energies of atomization of all the bonds in the starting material(s) and of those in the likely products of decomposition or reaction, rather than on the group contribution methods used with computer programs, which are more accurate but

more complex. Examples are given which show the accuracy of the method to be sufficient for preliminary assessment of potential hazards, together with tabulated values of average bond energies suitable for the purpose.

*See also* COMPUTATION OF REACTIVE CHEMICAL HAZARDS, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

## EXOTHERMIC REACTION MIXTURES IN STEEL MAKING

Babaitsev, I. V. *et al.*, *Chem. Abs.*, 1987, **107**, 138866

Minimum impact energies to initiate the explosion of various exothermic mixtures, used for the continuous casting of steel, were determined. Components used included sodium nitrate, aluminium-iron scale, silicocalcium, ferrosilicon; fluorspar, borax, etc. Hazardous mixtures were defined, and improved safety controls were derived.

## EXPLOSIBILITY

1. Lothrop, W. C. *et al.*, *Chem. Rev.*, 1949, **44**, 419–445
2. Tomlinson, W. R. *et al.*, *J. Chem. Educ.*, 1950, **27**, 606–609
3. Coffee, R. D., *J. Chem. Educ.*, 1972, **49**, A343–349; *Chemical Stability*, Chapter 17 in *Safety & Accident Prevention in Chemical Operations*, Fawcett, H. H. & Wood, W. S. (Eds.), New York, Wiley, 2nd edn., 1982
4. Van Dolah, R. W., *Ind. Eng. Chem.*, 1961, **53**(7), 50A–53A
5. Stull, D. R., *Chem. Eng. Progr.*, 1973, **7**, 67–73; reprinted *J. Chem. Educ.*, 1974, **51**(1), A21–25
6. Spear, R. J. *et al.*, *Rept. MLR-R-850, AR-003-031*, Richmond (Va.) USNTIS, 1982
7. Chahine, G., *Inform. Chim. (Paris)*, 1987, (283), 141–143
8. Melhem, G. A. *et al.*, *Process Safety Progr.*, 1996, **15**(3), 168

Explosibility may be defined as the tendency of a chemical system (involving one or more compounds) to undergo violent or explosive decomposition under appropriate conditions of reaction or initiation. It is obviously of great practical interest to be able to predict which compound or reaction systems are likely to exhibit explosibility (and the degree exhibited), and much work has been devoted to this end. Early work [1] on the relationship between structure and performance of 176 organic explosives (mainly nitro compounds or nitrate esters) was summarised and extended in general terms to multi-component systems [2]. The contribution of various structural factors (bond-groupings) was discussed in terms of heats of decomposition and oxygen balance of the compound or compounds involved in the system. Materials or systems approaching stoichiometric composition (zero oxygen balance) are the most powerfully explosive, giving the maximum heat energy release. Bond groupings (see below) known to confer explosibility were classed as ‘plosophores’, and explosibility-enhancing groups as ‘auxoploses’ by analogy with dyestuffs terminology. The latter groups (ether, nitrile or oximino) tend to increase the proportion of nitrogen and/or oxygen in the molecule towards (or past) zero oxygen balance.

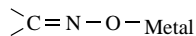
Although the semi-empirical approach outlined above is of some value in assessing potential explosibility hazards, much more fundamental work has been done in recent years to institute a more quantitative basis for such assessment. A combination of thermodynamical calculations with laboratory thermal stability and impact-sensitivity determinations has allowed a system to be developed which indicates the relative potential of a given compound or reaction system for sudden energy release, and the relative magnitude of the latter [3]. A similar treatment, specifically for compounds designed or expected to be explosives, was developed earlier [4]. A further computational technique which took account of both thermodynamic and kinetic considerations permitted the development of a system which provides a numerical Reaction Hazard Index (RHI) for each compound, which is a real, rather than a potential, indication of hazard. The RHI's calculated for 80 compounds are in fairly close agreement with the relative hazard values (assessed on the basis of experience) assigned on the NFPA Reactivity Rating scale for these same compounds [5]. In the context of the preparation of highly energetic materials, recent developments in methods of prediction of explosive properties are discussed briefly [6]. Recent information on methods of predicting explosive instability in organic and organometallic compounds is included in a general survey of this topic [7]. It is suggested that the Calculated Adiabatic Reaction Temperature, CART, the temperature the reaction products would attain under adiabatic containment is generally a better predictor of explosive risk than is the simple heat of reaction since it allows for the variable thermal capacities of the products. It is not too good for organic peroxides. Both techniques depend upon selecting the right decomposition reaction [8].

*See* ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, COMPUTATION OF REACTIVE CHEMICAL HAZARDS, EXOTHERMIC DECOMPOSITION, OXYGEN BALANCE, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

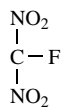
<i>BOND GROUPINGS</i>	<i>as in</i>	<i>CLASS ENTRY</i>
$-\text{C}=\text{C}-$		ACETYLENIC COMPOUNDS
$-\text{C}=\text{C}-\text{Metal}$		METAL ACETYLIDES
$-\text{C}=\text{C}-\text{X}$		HALOACETYLENE DERIVATIVES DIAZIRINES
$\text{>CN}_2$		DIAZO COMPOUNDS
$\text{>C}-\text{N}=\text{O}$		NITROSO COMPOUNDS
$\text{>C}-\text{NO}_2$		NITROALKANES, C-NITRO and POLYNITROARYL COMPOUNDS POLYNITROALKYL COMPOUNDS TRINITROETHYL ORTHOESTERS
$\text{>C}-\text{O}-\text{N}=\text{O}$		ACYL OR ALKYL NITRITES
$\text{>C}-\text{O}-\text{NO}_2$		ACYL OR ALKYL NITRATES



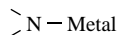
1,2 EPOXIDES



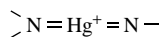
METAL FULMINATES or  
*aci*-NITRO SALTS, OXIMATES



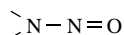
FLUORODINITROMETHYL COMPOUNDS



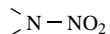
*N*-METAL DERIVATIVES



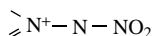
POLY(DIMERCURYIMMONIUM SALTS)



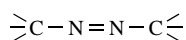
NITROSO COMPOUNDS



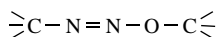
*N*-NITRO COMPOUNDS



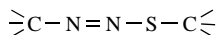
*N*-AZOLIUM NITROIMIDATES



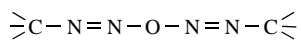
AZO COMPOUNDS



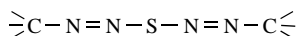
ARENEDIAZOATES



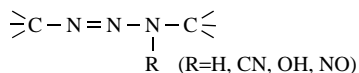
ARENEDIAZO ARYL SULPHIDES



BIS-ARENEDIAZO OXIDES



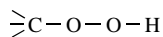
BIS-ARENEDIAZO SULPHIDES



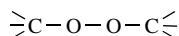
TRIAZENES



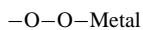
HIGH-NITROGEN COMPOUNDS  
TETRAZOLES



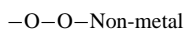
ALKYLHYDROPEROXIDES, PEROXYACIDS



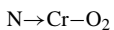
PEROXIDES (CYCLIC, DIACYL,  
DIALKYL), PEROXYESTERS



METAL PEROXIDES, PEROXOACID SALTS



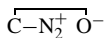
PEROXOACIDS, PEROXYESTERS



AMMINECHROMIUM PEROXOCOMPLEXES



AZIDES (ACYL, HALOGEN, NON-METAL,  
ORGANIC)



ARENEDIAZONIUM OXIDES

$\text{>C-N}_2^+\text{S}^-$	DIAZONIUM SULPHIDES AND DERIVATIVES, 'XANTHATES'
$\text{N}^+-\text{H Z}^-$	HYDRAZINIUM SALTS, OXOSALTS OF NITROGENOUS BASES
$-\text{N}^+-\text{OH Z}^-$	HYDROXYLAMINIUM SALTS
$\text{>C-N}_2^+\text{Z}^-$	DIAZONIUM CARBOXYLATES or SALTS
$[\text{N}\rightarrow\text{Metal}]^+ \text{Z}^-$	AMMINOMETAL OXOSALTS
$\left. \begin{array}{l} \text{Ar-Metal-X} \\ \text{X-Ar-Metal} \end{array} \right\}$	HALO-ARYLMETALS HALOARENOMETAL $\pi$ -COMPLEXES
$\text{N-X}$	HALOGEN AZIDES <i>N</i> -HALOGEN COMPOUNDS <i>N</i> -HALOIMIDES
$-\text{NF}_2$	DIFLUOROAMINO COMPOUNDS <i>N,N,N</i> -TRIFLUOROALKYLAMIDINES
$\text{N-O-}$	<i>N</i> -O COMPOUNDS
$-\text{O-X}$	ALKYL PERCHLORATES AMINIUM PERCHLORATES CHLORITE SALTS HALOGEN OXIDES HYPOHALITES PERCHLORYL COMPOUNDS

---

## EXPLOSIONS

Stull, 1977

Fundamental factors which contribute to the occurrence of fire and explosions in chemical processing operations have been collected and reviewed in this 120-page book, which serves as an extremely informative guide to the whole and complex subject, subdivided into 12 chapters. These are: Introduction; Thermochemistry; Kinetochemistry; Ignition; Flames; Dust Explosions; Thermal Explosions; Gas Phase Detonations; Condensed Phase Detonations; Evaluating Reactivity Hazard Potential; Blast Effects, Fragments, Craters; Protection Against Explosions. There are also 3 Appendices, 153 references and a Glossary of Technical Terms.

## EXPLOSIVE BOILING

1. Vogel 1957, 4
2. Weston, F. E., *Chem. News*, 1908, 27

The hazards associated with the addition of nucleating agents (charcoal, porous pot, pumice, anti-bumping granules, etc.) to liquids at or above their boiling points have been adequately described [1]. The violent or near-explosive boiling which ensues is enhanced by gases adsorbed onto such solids of high surface area. Incidents involving sudden boiling of salt solutions being concentrated for crystallisation in vacuum desiccators have also been described. The heat liberated by rapid crystallisation probably caused violent local boiling to occur, and the crystallising dishes (soda glass) were fractured [2].

## EXPLOSIVE COMBUSTION

1. Lafitte, P. *et al.*, *Hautes Temp., Leurs Util. Phys. Chim.*, 1973, **1**, 1–40
2. Gardner, G., *Chemical Engineer*, 1994, (563), 153.

A comprehensive review includes autoignition of gas mixtures, explosions at low and high temperatures, properties of flames and combustion of metals [1]. A review of explosion suppression techniques for dust, mist or vapour deflagrations, as an alternative to venting industrial plant [2].

## EXPLOSIVES

1. Federoff, 1960–1987
2. *Explosives, Propellants and Pyrotechnic Safety Covering Laboratory, Pilot Plant and Production Operations: Manual AD-272-424*, Washington, US Naval Ordnance Laboratory, 1962
3. Kirk-Othmer, 1980, Vol. 9, 561–671
4. Ullmann, 1990, A10, 143
5. Urbanski, 1964–1984, Vols. 1–4.
6. *Explosives* Köhler, J. & Meyer, R., Weinheim, VCH, (4th Edn), 1993

Explosive materials intended as such are outside the scope of this work and many, even of those in widespread use, do not have an entry. Several specialist reference works on them contain much information relevant to their properties and safety practices for unstable materials.

## FERROALLOY POWDERS

### Fe–Mn, Fe–Si, Fe–Ti

Barbaitsev, I. V. *et al.*, *Chem. Abs.*, 1983, **99**, 161983

Explosion parameters have been measured for ferromanganese, ferrosilicon and ferrotitanium powders in a 1 m<sup>3</sup> chamber. Maximum pressures of 2.8–3.9 bar, at maximum rates of rise of 8.9–21.8 bar/s were determined. Individual entries are:

Ferromanganese, 4389

Ferrosilicon, 4390

Ferrotitanium, 4391

*See other ALLOYS*

## FERTILISER

1. Bacarani, C., *et al.*, *Chem. Abs.*, 1992, **117**, 177392
2. Laing, M., *J. Chem. Educ.*, 1993, **70**(5), 392

Self-sustaining thermal decomposition of NPK fertilisers is apparently possible if crystalline potassium nitrate is present from an exchange reaction of ammonium nitrate [1]. Almost pure fertiliser grades of ammonium nitrate are legally restricted in some countries because of its instability [2].

*See Ammonium nitrate*

## FINELY DIVIDED METALS

1. Manuev, N. V. *et al.*, *Chem. Abs.*, 1979, **90**, 111642
2. Murdock, T. O., *Diss. Abs. Int. B*, 1978, (9), 1291

Requirements for safe storage of powdered Al, Hf, Mg, Ti, Zn and Zr are outlined. Fires are best extinguished with various fluxes, trimethyl boroxine, asbestos fines (!), talc, graphite, sodium chloride, soda ash, lithium chloride or powdered dolomite [1]. Slurries of Al, Cd, Cu, Ge, In, Ni, Pb, Sn or Zn produced by metal atom-solvent cocondensation at  $-196^{\circ}\text{C}$  are extremely active chemically [2], and would be pyrophoric on exposure to air.

See Aluminium: Diethyl ether *See other* METAL DUSTS

## **FIRE**

1. *Fire Protection Handbook*, Quincy (Ma.), National Fire Protection Association, 16th edn., 1986
2. Fire Service Abstracts, (quarterly since 1981), Boreham Wood., Fire Research Station
3. Bahme, 1972
4. Meidl, 1972
5. *Fire and Related Properties of Industrial Chemicals*, London, Fire Protection Association, 4th edn., revised 1974
6. *Fire-Hazard Properties of Flammable Liquids, Gases and Volatile Solids*, 325M, Quincy (Ma.), NFPA, 1984
7. *Matrix of Electrical and Fire Hazard Properties and Classification of Chemicals*, AD-A027 181/7GA, Richmond (Va.), USNTIS, 1975
8. *Fire Precautions in Chemical Plant: A Code of Practice*, BS 5908: 1980
9. *DH-HLH-88*, 1988; *NFPA 45*, 1986, Quincy (Ma), National Fire Protection Association

The handbook covers all aspects of fire protection and remedial measures, including those for involvement of chemicals in storage or in process operations [1]. The compilation of references to the scientific literature on fire has been renamed [2] and is now a quarterly publication subdivided and classified as previously. Further aspects, with examples of the special extinguishing problems arising from involvement of reactive chemicals in fires, are detailed [3,4]. The tabulated list of the physical and fire-hazardous properties of some 800 industrially significant chemicals [5] has a US counterpart covering 1300 materials [6]. A matrix relates fire hazardous properties of 226 commercial chemicals to the classification groups of the US National Electrical Code [7]. A UK Code of Practice is applicable to all chemical industry [8], and two recent US fire codes cover electrical installations in hazardous locations, and requirements for chemical-using laboratories, respectively [9].

## **FIRE EXTINGUISHERS**

1. *Fire Safety Data Sheets 6001-6003*, London, Fire Protection Association
2. Hirst, R., *Chem. Engr.*, 1974, 627-628, 636
3. Anon., *Loss Prev. Bull.*, 1978, (022), 107-113
4. Webster, J. M., *Fire Surveyor*, 1984, **13**(2), 5-7
5. Hird, D., *Fire Prev.*, 1987, (202), 20-26

Three illustrated data sheets cover the choice; siting, care and maintenance; and use of portable fire extinguishers [1]. Detailed accounts of modern extinguishing



agents and their use in chemical environments are available [2,3]. Of 3 types of multipurpose hand extinguishers tested comparatively (multipurpose powder, halon, and spray foam), the latter provides higher efficiency for a lower level of skill [4]. In a review of foam applications, a list of flammable liquids which destroy the blanketing effect is given. The most adverse effects are shown by ethylamine and isopropylamine, while several esters, ketones, alcohols and glycols have but slight effects on foam stability [5].

## FLAMMABILITY

1. Coward, H. F. *et al.*, *Limits of Flammability of Gases and Vapours*, Bull. 503, Washington, US Bur. Mines, 1952
2. Zabetakis, M. G., *Flammability Characteristics of Combustible Gases and Vapours*, Bull. 627, Washington, US Bur. Mines, 1965
3. Shimy, A. A., *Fire Technol.*, 1970, **6**(2), 135–130
4. Hilado, C. J., *J. Fire Flamm.*, 1975, **6**, 130–139
5. Hilado, C. J., *Fire Technol.*, 1977, **13**(3), 195–198
6. Glikin, M. A. *et al.*, *Chem. Abs.*, 1978, **88**, 39541
7. Mullayanov, F. I. *et al.*, *Chem. Abs.*, 1978, **89**, 91976
8. Ducros, M. *et al.*, *Thermochim. Acta*, 1981, **48**, 351–359
9. Khramov, V. V. *et al.*, *Chem. Abs.*, 1982, **96**, 183907
10. Roberts, P. *et al.*, *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, E1–E10, Rugby, IChE, 1983
11. Kishore, K. *et al.*, *J. Haz. Mat.*, 1980, **3**, 349–356
12. High, M. S. *et al.*, *Ind. Eng. Chem. Res.*, 1987, **26**, 1395–1399
13. Mitsui, T. *et al.*, *Chem. Abs.*, 1987, **107**, 182611
14. Hodo, H. *et al.*, *Int. Chem. Eng.*, 1987, **27**(4), 709–715
15. Zetsepin, V. M., *Chem. Abs.*, 1988, **109**, 98069
16. Ducros, M. *et al.*, *J. Haz. Mat.*, 1988, **19**, 33–49
17. Mulzyczuk, J., *Chem. Abs.*, 1989, **110**, 12860
18. Lihou, D., *J. Loss Prevention*, 1993, **6**(4), 266
19. Barfuss, S. *et al.*, *Arch. Combust.*, 1993, **13**(1–2), 33
20. Melhem, G. A., *Process Safety Progr.*, 1997, **16**(4), 203

The hazards associated with flammability characteristics of combustible gases and vapours are excluded from detailed consideration in this Handbook, since the topic is adequately covered in standard reference works on combustion, including the 2 sources of much of the data on flammability limits [1,2].

However, to reinforce the constant need to consider flammability problems in laboratory and plant operations, the flammability (or explosive) limits have been included (where known) for those individual substances with flash points below 25°C. With the few noted exceptions, explosive limits quoted are those at ambient temperature and are expressed as % by volume in air in Appendix 2.

Semi-empirical formulae, based only on molecular structure, have been derived which allow flammability limits to be calculated for hydrocarbons and alcohols. Flash points, autoignition temperatures and boiling points may also be calculated from molecular structure for these classes. Quoted examples indicate the methods

to be reasonably accurate in most cases [3]. Equations are given for calculating upper and lower flammability limits of 102 organic compounds (hydrocarbons, alcohols, ethers, esters, aldehydes, ketones, epoxides, amines and halides) from structure and stoichiometry in air [4]. The HC value (Hazardous Concentration, the ratio of the concentration of a substance to its lower flammable limit in the same units) is useful in estimating flammable limits of mixtures of combustible gases [5]. Equations have been derived to calculate the LEL for an organic compound as a function of the number of carbon atoms, the heats of formation of the compound and of an alkane of the same carbon number, state of aggregation, etc., [6], and for petroleum products and their components [7].

The criteria defined by the CHETAH program (*See* COMPUTATION OF HAZARDS) were used to predict lower and upper flammable limits for various organic (C,H,O,N) compounds, results generally being in good agreement with experimental values [8]. A method for predicting upper flammable limits for C<sub>1</sub>–C<sub>8</sub> hydrocarbons has been developed [9]. Determination of flammability limits in a spherical container, rather than in the traditional vertical tubes tends to show rather wider values than the tube method for methane to pentane, and for ethylene. It is proposed that these wider limits are more realistic in practice, and especially for purging purposes in significant volumes [10]. The recent concept of relevance in the context of flammability and extinguishment is that of the minimum oxygen content necessary to support combustion. The Oxygen Index is a quantified measure of this, and is becoming of widespread use for non-volatile flammable solids of many types [11].

A group contribution method has been developed to predict upper flammability limits for pure organic compounds. It is applicable to many homologous series which can be constructed from the groups included, and a procedure is given for calculating the confidence limits of the predictions [12]. The use of a microcomputer to estimate flammability limits for organic compounds is described, based on MW and functional groups present. Estimated LELs agreed well with published data, but there was some deviation in UELs [13]. Factors affecting propagation and quenching of flames in cylindrical pipes were investigated experimentally to establish design criteria for flame arresters. Critical velocity to assure flame quenching was below 5 m/s for an open-sided (venting) arrester, or rather higher when the arrester is inside a pipe [14]. Equations relating upper flammability limits to lower limits have been derived for hydrocarbons. From an experimental or calculated lower limit, the upper limit can be predicted with good accuracy [15]. Use of the CHETAH program to determine the flammability of organic oxygen compounds and to estimate their lower flammability limits has been described [16]. A method of calculating lower and upper flammability limits for complex gas mixtures, based on Le Chatelier's law, is described [17]. A procedure for calculating flammable limits of vapour/air mixes under reduced pressure and with nitrogen enrichment, for safe industrial drying operations, is reported [18]. Prediction of flammable limits, for both pure materials and mixtures in air or oxygen, is attainable by way of theoretical flame temperatures. If these are below 1000–1500 C, the mixture should be non-flammable [20]. It is reported that bubbles of air or oxygen in

flammable liquids can be ignited even at pressures too high for the bubble to be within conventional explosive limits 19].

See OXYGEN INDEX (reference 5)

See also OXYGEN ENRICHMENT

## FLASH POINTS

1. *Flash Points*, Poole, BDH Ltd., 1962
2. 'Catalogue KL4', Colnbrook, Koch-Light Laboratories, Ltd., 1973
3. *Flash Point Index of Trade Name Liquids*, 325A, Quincy (Ma.), NFPA, 1972
4. *Properties of Flammable Liquids*, 325M, Quincy (Ma.), NFPA, 1969
5. Prugh, R. W., *J. Chem. Educ.*, 1973, **50**, A85–89
6. Shimy, A. A., *Fire Technol.*, 1970, **6**(2), 135–139
7. Thorne, P. F., *Fire Mater.*, 1976, **1**, 134–140
8. Magdanz, H., *Plaste Kautsch.*, 1977, **24**, 774–777
9. Li, C. C. *et al.*, *J. Fire Flamm.*, 1977, **8**, 38–40
10. Tiedtke, K. H., *Ger. Offen.*, 2 723 157, 1978
11. Saborowska-Szpyrkowa, I. *et al.*, *Chem. Abs.*, 1979, **90**, 189290; 1981, **95**, 64598
12. Gmehling, J. *et al.*, *Ind. Eng. Chem. Fundam.*, 1982, **21**, 186–188
13. Shebeko, Yu. N. *et al.*, *Chem. Abs.*, 1983, **98**, 184837
14. Gooding, C. H., *Chem. Eng. (Intern. Ed.)*, 1983, **90**(25), 88
15. Bodinelli, L., *Chem. Eng. News*, 1982, **60**(28), 4
16. MacDermott, P. E., *Chem. Brit.*, 1974, **10**, 228
17. Mitsui, T., *Chem. Abs.*, 1987, **107**, 222429
18. *Flash points of organic and organometallic compounds*, Stevenson, R. M., New York, Elsevier, 1987
19. Bretherick, L., *Chem. Eng. News*, 1988, **66**(50), 2
20. Hasegawa, K. *et al.*, *J. Loss Prev. Process Ind.*, 1991, **4**(3), 176
21. Kohlbrand, H. T., *Plant/Oper. Progr.*, 1991, **10**(1), 52
22. Anon., *Jahresbericht*, 1991, 73

Flash point is defined as the minimum temperature at which a flammable liquid or volatile solid gives off sufficient vapour to form a flammable mixture with air.

There is usually a fair correlation between flash point and probability of involvement in fire if an ignition source is present in the vicinity of the source of the vapour; materials with low flash points being more likely to be involved than those with higher flash points. While no attempt has been made to include in this Handbook details of all known combustible materials, it has been thought worthwhile to include substances with flash points below 25°C, a likely maximum ambient temperature in many laboratories in warm temperate zones. These materials have been included to draw attention to the high probability of fire if such flammable or highly flammable materials are handled with insufficient care to prevent contact with their vapours with an ignition source (stirrer motor, hot-plate, energy controller, flame, etc.). The figures for flash points quoted in Appendix 2 are closed cup values except where indicated by (o), and most are reproduced by permission of the two Companies concerned. A comprehensive listing of flash points for commercial liquids and formulated mixtures is also available [3,4].

A method for estimating approximate flash point temperatures based upon the boiling point and molecular structure was published. This involved calculation of the stoichiometric concentration in air, followed by reference to a nomograph to give the flash point to within 11°C [5]. Many alternative methods of achieving the same ends have now been published, including one for hydrocarbons and alcohols [6], for mixtures of flammable and non-flammable liquids [7], and for partially miscible liquids (when activity coefficients must be known) [8]. Methods based on relative boiling points [9], or using a flame ionisation detector [10] have been described, and equations for use with multicomponent systems [11], or an additive group contribution method [12] are available among others [13,14]. Although chlorinated solvents are sometimes added to hydrocarbon solvents to raise the flash point, addition of inhibitor-containing 1,1,1-trichloroethane to a petroleum solvent actually reduced the flash point. This was attributed to the effect of the inhibitor [15], but this halogenated solvent, which has no flash point, will in fact burn and other haloalkanes have been shown to catalyse combustion.

The commonly accepted fallacy that liquids at temperatures below their flash points cannot give rise to flammable mixtures in air is dispelled with some examples of process operations with solvents at sub-atmospheric pressures. Under such conditions, flammable atmospheres may be generated at temperatures below the flash point. Thus, the real criterion should be whether flammable atmospheres can exist under given process conditions, rather than a flammable liquid being at a temperature below its flash point [16]. The use of a BASIC microcomputer program to calculate the flash points of organic compounds is described, based on the MW and functional groups present, and constants are given for 20 functional groups. Calculated values are satisfactory for monofunctional compounds, but not always for multifunctional compounds [17]. A new 296 page compilation of flash points is available [18]. There are a few halogenated hydrocarbons for which a flash point cannot be determined by standard tests, and these unfortunately are often described as non-flammable, though they will burn if the ignition source is sufficiently intense. Bromomethane, dichloromethane, trichloroethylene and 1,1,1-trichloroethane are compounds of this type [19].

The Japanese have started to measure the temperature corresponding to a composition of the upper explosive limit of a vapour in air under the name: Upper Flash Point. Some examples are given [20].

Liquids can form explosive atmospheres at temperatures below the flash point appropriate to the pressure in question if agitation is sufficient to form a mist. A destructive instance is reported [21].

Explosion of a reactor consequent upon taking a flash point (which refers to air) as indicating safety limits in pure oxygen is reported [22].

## **FLASH POWDER**

1. Partington, 1967, 364
2. Bentzinger, von R. *et al.*, *Praxis Naturwiss., Chem.*, 1987, **36**, 38
3. Young, J. A., *CHAS Notes*, 1991, **IX**(6), 2

Small portions of mixtures of magnesium powder with aluminium powder, with various oxidants (barium peroxide, barium nitrate, potassium chlorate, or even dry

silica powder) were formerly used for flash photography [1]. During a classroom demonstration, several attempts were necessary before a large amount (20 g) of an old sample of flash powder could be ignited, but when ignition eventually occurred, a 20 cm fireball was produced, which caused severe burns [2]. Larger (20 kg) portions of similar mixtures may ignite more easily, and unexpectedly, with serious blast effects [3].

*See* Barium peroxide: Metals

Potassium chlorate: Metals, 4017

Magnesium: Silicon dioxide, 4690

## **FLOUR**

Bond, 1991, 48

A common fuel for dust explosions, with the distinction of causing the first such event investigated and recorded (in 1795).

*See* DUST EXPLOSION INCIDENTS

## **FLUORINATED COMPOUNDS**

**RF**

*See* Lithium tetrahydroaluminate: Fluoroamides

Sodium: Fluorinated compounds, or: Halocarbons (reference 6), 4796

## **FLUORINATED CYCLOPROPENYL METHYL ETHERS**

Methanol, or Water

Smart, B. E., *J. Org. Chem.*, 1976, **41**, 2377–2378

There are hazards involved both during the preparation and after isolation of these materials. Addition of sodium methoxide powder to perfluoropropene in diglyme at  $-60^{\circ}\text{C}$  led to ignition in some cases, and the products, 1,3,3-trifluoro-2-methoxycyclopropene (very volatile and flammable), or 3,3-difluoro-1,2-dimethoxycyclopropene, react violently with water or methanol, as does 1-chloro-3,3-difluoro-2-methoxycyclopropane.

There are hazards involved both during the preparation and after isolation of these materials. Addition of sodium methoxide powder to perfluoropropene in diglyme at  $-60^{\circ}\text{C}$  led to ignition in some cases, and the products, 1,3,3-trifluoro-2-methoxycyclopropene (very volatile and flammable), or 3,3-difluoro-1,2-dimethoxycyclopropene, react violently with water or methanol, as does 1-chloro-3,3-difluoro-2-methoxycyclopropane.

The individual compounds are:

1-Chloro-3,3-difluoro-2-methoxycyclopropene, 1411

3,3-Difluoro-1,2-dimethoxycyclopropene, 1866

1,3,3-Trifluoro-2-methoxycyclopropene, 1414

## **FLUORINATED ORGANOLITHIUM COMPOUNDS**

Anon., *Jahresber.*, 1981, 79

An unspecified partially fluorinated unsaturated ether was converted to the lithium salt with methyllithium in ether. A 70 g preparation exploded violently towards

the end of the preparation, possibly owing to ingress of air down the stirrer guide when vacuum was applied to the flask. The hazardous nature of such compounds is stressed.

See Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide

See other ORGANOLITHIUM REAGENTS

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

#### FLUORINATED PEROXIDES AND SALTS HOC(CF<sub>3</sub>)<sub>2</sub>OOM, F<sub>5</sub>SOO-

Anderson, L. R. *et al.*, *J. Fluorine Chem.*, 1976, **7**, 481–500

Five derivatives, including the O–O lithium or sodium salts of the hydrogen peroxide adduct of hexafluoroacetone (2-hydroxyhexafluoro-2-propyl hydroperoxide), and their reaction products with acyl halides, are less flammable or explosive than their hydrocarbon analogues, though less stable than the parent hydroperoxides. Relevant entries are:

\* Pentafluorosulfur peroxyacetate, 0755

\* Pentafluorosulfur peroxyhypochlorite, : Haloalkenes, 3990

#### FLUORINATION

1. Grakauskas, V., *J. Org. Chem.*, 1970, **35**, 723; 1969, **34**, 2835

2. Sharts, C. M. *et al.*, *Org. React.*, 1974, **21**, 125–265

3. Brekhovskikh, M. N. *et al.*, *Mater. Res. Bull.*, 1988, **23**, 1417–1421

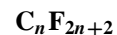
Safety precautions applicable to direct liquid phase fluorination of aromatic compounds are discussed [1]. Attention is drawn to the hazards attached to the use of many newer fluorinating agents [2]. In a study of fluorination reactions of hafnium and zirconium oxides by the fluoroxidisers xenon difluoride, chlorine trifluoride and bromine trifluoride, reactivity decreased in the order given [3].

For further references, *see* Fluorine

See \*Pentafluorosulfur peroxyacetate,

See related UNIT PROCESS OR OPERATION INCIDENTS

#### FLUOROCARBONS



Oxygen

1. Dawe, B. *et al.*, *Chem. Eng. News*, 1991, **69**(23), 2

2. Taylor, J. E., *ibid.*, **69**(38), 2

3. Larsen, E. R., *ibid.*, 1992, **70**(7), 2

4. Christe, K. O., *ibid.*, 1991, **69**(40), 2

A liquid perfluorocarbon was being used as solvent in an oxidation by oxygen under pressure; more energy was released than expected [1]. It is cautioned that fluorocarbons are not inert to oxidation, presumably to carbonyl fluoride. An explosion has been experienced with perfluorotoluene in like circumstances [2]. A correspondent reports that perfluorotoluene is flammable in air, more saturated perfluorocarbons in pure oxygen [3]. Another detailed the combustion performance of polytetrafluoroethylene: 148 kcal/mole; ignition temperature not below 465°C at 7000 psi of oxygen [4], the product is mostly carbonyl fluoride. Other oxidants may also present a risk in extreme circumstances.

See Oxygen: Polymers

Oxygen: Polytetrafluoroethylene, Stainless steel, 4831

Poly(tetrafluoroethylene): Oxygen, 0629

## FLUORODINITRO COMPOUNDS

## FC(NO<sub>2</sub>)<sub>2</sub>–, FCH<sub>2</sub>C(NO<sub>2</sub>)<sub>2</sub>–

1. Peters, H. M. *et al.*, *J. Chem. Eng. Data*, 1975, **20**(1), 113–117
2. Snaeberger, D. F., *Rept. UCID-16141*, Lawrence Livermore Lab., Univ. Calif., 1972

Several fluorodinitro compounds of methane (1,1,1-) and ethane (1,2,2-) are described as explosive, sensitive to initiation by impact, shock, friction or other means [1]. Procedures for safe handling of fluorine and explosive fluoronitro compounds are detailed [2].

## FLUORODINITROMETHYL COMPOUNDS

## F(O<sub>2</sub>N)<sub>2</sub>C–

1. Kamlet, M. J. *et al.*, *J. Org. Chem.*, 1968, **33**, 3073
2. Witucki, E. F. *et al.*, *J. Org. Chem.*, 1972, **37**, 152
3. Adolph, H. J., *J. Org. Chem.*, 1972, **37**, 749
4. Gilligan, W. H., *J. Org. Chem.*, 1972, **37**, 3947
5. Coon, C. L. *et al.*, *Synthesis*, 1973, (10), 605–607
6. Gilligan, W. H. *et al.*, *J. Chem. Eng. Data*, 1982, **27**, 94–99

Several of this group are explosives of moderate to considerable sensitivity to impact or friction and need careful handling. Fluorodinitromethane and fluorodinitroethanol are also vesicant [1]–[4]. 1-Fluoro-1,1-dinitro derivatives of ethane, butane, 2-butene and 2-phenylethane are explosive [5]. Among the preparations of a series of energetic and explosive compounds, that of *N,N,N',N'*-tetrakis(2-fluoro-2,2-dinitroethyl)oxamide is especially hazardous, as it involves heating an undiluted explosive to a high temperature [6].

Individually indexed compounds are:

Bis(2-fluoro-2,2-dinitroethoxy)dimethylsilane, 2421

Bis(2-fluoro-2,2-dinitroethyl)amine, 1459

2,2-Dinitro-2-fluoroethoxycarbonyl chloride, 1072

1-Fluoro-1,1-dinitrobutane, 1562

4-Fluoro-4,4-dinitrobutene, 1458

1-Fluoro-1,1-dinitroethane, 0748

\* 2(?) -Fluoro-1,1-dinitroethane, 0749

2-Fluoro-2,2-dinitroethanol, 0750

2-Fluoro-2,2-dinitroethylamine, 0800

Fluorodinitromethane, 0374

Fluorodinitromethyl azide, 0341

1-Fluoro-1,1-dinitro-2-phenylethane, 2934

See also ENERGETIC COMPOUNDS

## FOAM BLANKETING FOR SPILL CONTROL

1. DiMaio, L. R. *et al.*, *Plant/Oper. Progr.*, 1988, **7**, 195–198
2. Norman, E. C., *Vapour suppression by aqueous foams*, Chapter 2 in *Hazardous and toxic materials*, Fawcett, H. H. (ed.), New York, Wiley, 2nd edn., 1988

The use of aqueous foams to control fume or vapour release from reactive chemicals is discussed. An acid-resistant foam NF2 controlled fume emission from 35% and 65% oleum, and from titanium tetrachloride, but was not effective for sulfur trioxide and chlorosulfuric acid. An alcohol-resistant foam NF1 suppressed ammonia vapour emission by 80%, and Universal fire foam reduced evaporation of ethylene oxide, vinyl chloride and methanethiol, and reduced vapour emission of 1,3-butadiene by 60%. Safety aspects of foam blanketing are discussed [1]. Equipment and application techniques are covered in some detail [2].

## FOAM RUBBER

1. Woolley, W. D. *et al.*, *BRE CP 36/75*, Garston, Building Res. Est., 1975
2. Smith, E. E., *Consum. Prod. Flammability*, 1975, **2**, 589–69

A fire involving foam rubber mattresses in a storeroom led to an unexpected and serious explosion. Subsequent investigation showed that an explosion risk may exist when the flammable smoke and vapour from smouldering of large amounts of foam rubber are confined in an enclosed space. Suitable strict precautions are recommended [1]. Methods of quantitatively evaluating potential fire hazards from release rates of heat, smoke and toxic gases from heated foam rubber and plastics materials were developed, and their application to real situations discussed [2].

Oxygen

*See* Oxygen (Gas): Polymers

## FREEZE DRYING

*See* Sodium azide: Heavy metals (references 4,5)

## FRICTIONAL IGNITION OF GASES AND VAPOURS

1. Powell, F., *Ind. Eng. Chem.*, 1969, **61**(12), 29
2. Desy, D. H. *et al.*, *Rept. RI 8005*, Washington, US Bur. Mines, 1975
3. Uchida, S. *et al.*, *Chem. Abs.*, 1984, **101**, 154290
4. van Laar, G. F. M., *EuropEx Newsl.*, 1986, (2), 9
5. Ihara, H. *et al.*, *Chem. Abs.*, 1987, **107**, 80558
6. Krasnayanskii, M. M. *et al.*, *Chem. Abs.*, 1987, **107**, 204305
7. Bartknecht, J., *Plant/Oper. Progr.*, 1988, **7**(2), 114–121.

The ignition of flammable gases and vapours by sparks from friction or impact was reviewed [1]. Ignition of methane by frictional impact of aluminium alloys and rusted steel has been investigated [2]. The effect of presence of beryllium in light alloys on the ignition of methane by sparks derived from their impact with rusted or corroded steel has been studied in a mining context [3]. Recent findings



on initiation of gases by mechanically derived sparks are discussed, including relationships between ignition sensitivity and minimum ignition temperatures and energies [4]. Ignition of methane by sparks produced by continuous contact of various metals with a rotating disc of the same or another metal has been studied [5]. From a study of a wide range of flammable organic vapours and gases by frictional sparks, it was concluded that only mixtures containing acetylene, carbon disulfide, carbon monoxide, hydrogen or methane could be so ignited. However, this conclusion is stated to be irrelevant if the temperature of the frictional surfaces exceeds the autoignition temperatures of the mixtures, or reaches 50–70°C [6]. The ignition capability of mechanically generated sparks or hot surfaces for gas and dust–air mixtures have been studied experimentally. A previous analysis of 357 industrial dust explosions had concluded that 30% were caused by mechanical sparks, and 5% by hot surfaces, but the results of the present work show that the converse is likely to be true [7].

See FRICTIONAL INITIATION OF DUST CLOUDS

See IGNITION SOURCES, THERMITE REACTIONS

## FRICTIONAL INITIATION INCIDENTS

1. Cartwright, R. V., *Chem. Eng. News*, 1983, **61**(6), 4
2. Négyesi, G., *Process Safety Progress*, 1996, **15**(1), 42
3. Négyesi, G., *Process Safety Progress*, 1997, **16**(4), 237

Following the explosion of a perchlorate salt during filtration on a sintered funnel which caused severe injuries, the advantages of using plastic sintered funnels were stressed. Frictional heating will be much less on plastic sinters, and if explosive decomposition is initiated on a plastic funnel, fragmentation and resulting injuries should be much less with, for example, high-density polythene. (If the use of perchlorate salts cannot be avoided, fully appropriate measures for personal protection in addition to the use of plastic sinters seem essential [1].) Many non-explosive organic compounds, usually containing N or S heteroatoms, show decomposition, charring or sparks when subjected to friction or, less often, impact tests. This may be important as a source of ignition during grinding. Of 167 compounds tested, mostly pharmaceuticals and intermediates, 36 (listed) showed friction sensitivity. Testing of suspect compounds prior to industrial milling is suggested, with inerting or explosion protection measures for those proving positive [2]. Investigation of friction sensitivity of various pharmaceutical intermediates suggested that nitrogen-heterocycle carbothionamides may be sensitive to frictional ignition, apparently because of decomposition to give carbon disulphide and hydrogen sulphide, which have very low auto-ignition temperatures [3]. Other instances of frictional initiation are indexed under:

Barium: Halocarbons, 0200

Barium peroxide, 0216

1,2-Bis(azidocarbonyl)cyclopropane, 1835

\* Calcium hypochlorite, 3924

Chromium trioxide: Potassium hexacyanoferrate(3–), 4242

Diazidodimethylsilane, 0918

Diazoacetonitrile, 0675  
 \* Dimercury dicyanide oxide, 0983  
 Dimethylketene, 1518  
 Dysprosium perchlorate, 4131  
 Erbium perchlorate, 4132  
 Hexaamminechromium(III) perchlorate, 4129  
 † Phosphorus, 4874  
 Potassium chlorate: Metal phosphinates, 4017  
 Potassium perchlorate, 4018  
 Sodium 5-azidotetrazolide, 0551  
 Sodium chlorate : Paper, Static electricity, 4039  
 Sodium chlorate: Wood, 4039  
 Succinoyl diazide, 1438  
 Tetrakis(chloroethynyl)silane, 2879  
 Thianthrenium perchlorate, 3455  
 Triferrocenylcyclopropenium perchlorate, 3885  
*See other* IGNITION SOURCES

#### FRICIONAL INITIATION OF DUST CLOUDS

1. Pederson, G. H. *et al.*, *Arch. Combust.*, 1987, **7**(1–2), 59–83
2. Dahn, C. J. *et al.*, *ASTM Spec. Tech. Publ. 958*, (Ind. Dust Explos.), 1987, 324–332

At net impact energies below 20 J (approach velocities of 10–25 m/s), the heat generated by single impacts between various steels, between steel and rusty steel or concrete was insufficient to ignite dust clouds of corn starch, grain, feedstuffs or flour, even if dry. Dry dusts of titanium or zirconium may ignite, but not if 10% moisture is present in the cloud. Turbulence from a moving object in a dust cloud reduced the ignitability in the vicinity of the object. Impacts against a coarse surface (gravel) produced more sparking than against a smooth (cement-covered concrete) surface [1]. Six alloys, 2 of aluminium, a mild steel and 3 stainless were assessed for their ability to produce frictional sparks and to ignite dust clouds of various propellants and corn starch. The aluminium alloys showed the least hazard potential, and the ferrous alloys a greater tendency to cause ignition, particularly above frictional speeds of 9.2 m/s, and especially for long contact times [2].

*See also* FRICTIONAL IGNITION OF GASES AND VAPOURS

#### FRICION DUST

Unpublished information, 1979

This is used in manufacture of brake linings and is a polymer based on cashew nutshell liquid admixed with formaldehyde or furfuraldehyde and other ingredients. The polymerised resin mixture is cast into 8 cm thick slabs and then ground finely to produce the friction dust. Several fires have been experienced during bulk storage of the dust, attributed to autoxidation of the still partially unsaturated resin compound. Previously, linseed oil was used in place of the nutshell liquid, but fires were then more frequent.

## FULLER'S EARTH

Turpentine

See TURPENTINE: diatomaceous earth

## FULMINATING GOLD

Ephraim, 1939, 462–463

This appears not to be one specific compound or mixture, but is of variable composition, depending on the method of preparation. Prepared from gold chloride and aqueous ammonia, the explosive precipitate is largely  $(\text{ClAuNH}_2)_2\text{NH}$ , but on washing with ammonia hydrolysis to the more explosive  $(\text{HOAuNH}_2)_2\text{NH}$  occurs, and the equilibrium is reversed by washing with chloride.

See Gold(III) chloride (and the entries following).

## FULMINATING METALS

1. Tan, K. G., *Can. Inst. Metals Bull.*, 1987, **80**(903), 96–97

2. Bretherick, L., *Chem. Haz. Ind.*, 1988, (8), item 1595

3. Wilhelm, S. M., *Plant/Oper. Progr.*, 1991, **10**(4), 192

The fallacy that the 'fulminating silver' and 'fulminating gold' produced by reaction of ammonia with silver or gold salts are silver fulminate or gold fulminate is perpetuated in a recent publication [1]. In fact, 'fulminating silver' is largely silver nitride,  $\text{Ag}_3\text{N}$ , and 'fulminating gold', while of less certain constitution, contains several Au–N bonds. In contrast, the true fulminates, salts of hydrogen cyanide *N*-oxide, contain C–metal bonds [2].

Although the description 'fulminating' is not used and thus confusion with the fulminate not caused, mercury also forms explosive compounds of similar nature. The nitride (*ibid.*) is the most common and can be formed from the metal and ammonia in some circumstances, causing accidents where mercury manometers are used with ammonia. Halo-hydroxy- and oxy-nitrides can also be involved [3]. See METAL FULMINATES, GOLD COMPOUNDS, *N*-METAL DERIVATIVES, PRECIOUS METAL DERIVATIVES, SILVER COMPOUNDS

## FULMINATING SILVER

Ephraim, 1939, 462

Fulminating silver is the most violently explosive compound among the nitrogen derivatives of the noble metals. Formed from action of ammonia on silver oxide, or on addition of potassium hydroxide to an ammoniacal solution of a silver salt, it is a black powder which explodes violently in the liquid in which it is formed if the slightest stirring is used. It probably contains aminesilver hydroxides,  $[\text{Ag}(\text{NH}_3)_x]\text{OH}$ .

See Silver chloride: Ammonia

Silver nitrate: Ammonia (4 items), 0022

## FUMES

1. Smith-Hansen, L. *et al.*, *J. Loss Prevention*, 1993, **6**(4), 227; *ibid.*, 1995, **8**(2), 127
2. Christiansen, V., *J. Loss Prevention*, 1994, **7**(1), 39
3. Smith-Hansen, L., *Risoe Natl. Lab.*, [Rep] *Risoe-R*, 1994; *Chem. Abs.*, 1995, **122**, 247076u
4. Smith-Hansen, L. *et al.*, *Risoe Natl. Lab.*, [Rep] *Risoe-R*, 1995; *Chem. Abs.*, 1996, **124**, 65180g

Readers have indicated that they regard information on toxic fumes emitted in fires as important. This is not a simple subject and little is definitely known. Other reference works are packed with improbable products of 'heating to decomposition' (which is seldom distinguished from combustion). These appear to be the product of simplistic extrapolations from the empirical formulae. They also commonly list species which can have no existence under any conditions the human frame can tolerate, although they may, indeed, be present at 1000°C. What little experimental study has been reported indicates that in reality, as one would expect, the off-gases depend greatly on the fire conditions. Some Scandinavian studies have looked at pesticides, which contain an unusual wealth of hetero-atoms [1,2,3,4]. There are always fumes of water, carbon monoxide and carbon dioxide. Nitrogen may appear as the element, as ammonia, as hydrogen cyanide or as NOx; sulphur as the element, as hydrogen sulphide and as sulphur dioxide. Phosphorus will emerge mostly as the pentoxide, (which will have picked up water before it gets near the lungs) and may possibly sometimes appear as phosphine. Chlorine usually appears as hydrogen chloride, but partially as the element and sometimes as phosgene. Bromine and iodine are more likely to appear as the element. Most of these materials seldom reach the levels of a 30 minute LC<sub>50</sub>.

Genuine acute dangers appear to be heat (the lungs cannot take air much above 60°C), oxygen depletion and carbon monoxide. These are found in all fires, even those involving no "chemicals" as the environmentalist considers them. The obstruction to the lungs' function caused by deposition of solid carbon particles (soot) is also not chemical but none the less deleterious for that. Sulphur dioxide and hydrogen chloride (both readily detected irritants) may reach dangerous levels; hydrogen cyanide probably never does (except under conditions where CO is the greater danger) and nitrogen oxides only when the NO bond was already present in the starting material. Some NOx, the product of heating air, is always formed by hot fires anyway. Certain materials, such as fats, may produce irritant, if not actually toxic, fumes of propenal but poisonous organic fumes seem rare. However, pyrolysis is an excellent way of producing high energy species such as may induce chronic effects by interaction with nucleic acids, whether the starting material be tobacco, cannabis, dried banana-skin or whatever. It is not healthy to inhale more smoke than can be helped.

Readers are warned that the literature includes some incident reports originating from the emergency services which are undoubtedly in error. An example is the claimed production of hydrogen cyanide by fuels containing no nitrogen, but much chlorine (the ordinary gas detection tubes for cyanide actually generate and then

measure hydrogen chloride; for which they have very limited absorption capacity in the pre-layer).

### FURAZAN *N*-OXIDES

1. Barnes, J. F. *et al.*, *J. Chem. Soc., Perkin Trans.*, 1983, 294–295
  2. Barnes, J. F. *et al.*, *J. Chem. Soc., Chem. Comm.*, 1978, 113–114
  3. Naixing, W. *et al.*, *Propellants, Explos., Pyrotech.*, 1994, **19**(3), 145
- Low MW strained-ring furazan *N*-oxides (furoxans) and some of their precursors are highly energetic compounds and should be handled carefully with due caution [1], and preferably in solution [2]. Benzofuroxans are reviewed, especially in relation to their explosive properties, which may be superior to corresponding nitrocompounds in energy, speed of detonation and bulk density [3].

Individually indexed compounds are:

- 4-(2'-Ammonio-2'-carboxyethylthio)-5,7-dinitro-4,5-dihydrobenzofurazanide *N*-oxide, 3146
- Benzotri(furazan *N*-oxide), 2631
- 3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-) oxide, 2630
- 4,5-Cyclopentanofurazan-*N*-oxide, 1871
- Dicyanofurazan *N*-oxide, 1804
- 4,6-Dinitrobenzofurazan *N*-oxide, 2089
- \* 3-Ethyl-4-hydroxy-1,2,5-oxadiazole, 1504
- 4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2357
- Potassium 4-hydroxyamino-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2176
- Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2114
- Potassium 3-methylfurazan-4-carboxylate 2-oxide, 1415
- 4a,5,7a,8-Tetrahydro-4,8-methano-4*H*-indeno[5,6-*c*]-1,2,5-oxadiazole 1- and 3-oxide, 3282

See other *N*-OXIDES

### GAS CYLINDERS

1. *The Safe Filling, Handling, Storage and Distribution of Gases in Transportable Containers*, Code of Practice CP9, London, Brit. Comp. Gases Assoc., 1982
2. *Properties of Gases*, Wall Chart 57012, Poole, BDH Chemicals Ltd., 3rd edn., 1981
3. Braker, W. *et al.*, *Matheson Gas Data Book*, E. Rutherford (NJ), Matheson Gas Products, 6th edn., 1981
4. *Guide to Safe Handling of Compressed Gases*, Lyndhurst (NJ), Matheson, 1982
5. *Handbook of compressed gases*, Compressed Gas Association Inc., New York, Van Nostrand-Reinhold, 2nd ed., 1981

The *Code of Practice* covers UK legislation, containers, identification and marking, valves, handling and storage, transportation, emergency procedures and personnel training. Data sheets for 114 gases are included [1]. An inexpensive wall chart summarises the important properties of 116 gases and volatile liquids [2]. The

*Gas Data Book* gives comprehensive details of handling techniques and cylinder equipment necessary for 120 gases [3], and the newer guide covers the design of gas systems, premises, cylinder handling and storage, and air-monitoring techniques for a range of gases [4]. Another volume covers all aspects of handling gases in gas, liquid and solid states [5].

## GAS EVOLUTION INCIDENTS

1. Lubernau, J. O., *Health Phys.*, 1986, **51**(1), 147
2. Lambert, P. G. *et al.*, *Chem. & Ind.*, 1987, 490–491
3. Carson, P. J. *et al.*, *Loss Prev. Bull.*, 1992, (102), 15
4. Lambert, P. G. *et al.*, *Chem. Eng. Progress*, 1992, **88**(10), 53

Several incidents of pressure build-up in sealed containers of solutions of radioactive materials are noted for the period 1906–1985. The cause is radiolysis of the solvent, usually water, with evolution of hydrogen [1]. A method for evaluating gas evolution hazards in batch processing has been described. Based upon the use of a corrosion-resistant thermal mass flowmeter in conjunction with normal laboratory glassware, the electrical output can be fed either to a recorder/integrator, or to a data-logger/computer system. To exemplify the method, the rates of evolution of hydrogen chloride during the addition of carbon tetrachloride to a cold mixture of benzene and aluminium chloride (to form trityl chloride) are shown diagrammatically [2]. A list of combinations which may evolve toxic gases is given [3].

Although gas evolution is usually endothermic in open systems, and seldom a problem on laboratory scale, industrial batch reactors combine relatively far smaller vents with lower rupture pressures. This can give dangers with even endothermic evolutions. Exothermic gas evolving reactions readily become uncontrollable. A further hazard is nucleation and heating of saturated and supersaturated gas solutions when crystallisation of products occurs; this is the cause of many reactions jumping from flasks even in the lab. Details of combined calorimetric and gas flow safety-evaluation procedures are given [4]. A danger unremarked by the authors, but present in one of several examples, is autocatalysis of a slow step of the reaction by a non-gaseous product.

Elsewhere in the text, a number of incidents have involved evolution of gas(es) arising from slow decomposition or hydrolysis in storage, progressive thermal decomposition, or from other miscellaneous reactions or processing faults. Individual incidents may be found under:

- Aluminium chloride, : Water, 0062
- Aluminium hydride, : Carbon dioxide, or Sodium hydrogen carbonate, 0070
- Aluminium phosphide, : Mineral acids, 0083
- Americium trichloride, 0090
- 2-Ammoniothiazole nitrate, 1194
- Argon, : Liquid nitrogen, 0091
- Azidoiodoiodonium hexafluoroantimonate, 4361
- Benzenesulfinyl chloride, 2234
- Benzenesulfonyl chloride, 2235

Benzyl bromide, : Molecular sieve, 2735  
 Benzyl chloride, : Catalytic impurities, 2738  
 1,2-Bis(chloromethyl)benzene, 2946  
 Bis(2-cyanoethyl)amine, 2397  
 Bis(trimethylsilyl) peroxomonosulfate, 2602  
 Borane–tetrahydrofuran, 0138  
 Butylmagnesium chloride, 1641  
 Calcium acetylide, : Methanol, 0585  
 Calcium chloride, 3923  
 Cerium, : Water, 3961  
 Chlorine, : Chlorinated pyridine, Iron powder, 4047  
 Chlorine, : Dichloro(methyl)arsine, 4047  
 \* 2-Chloro-*N*-hydroxyacetamide, 0849  
 \* 2-Chloro-*N*-(2-hydroxyethyl)aniline, 2975  
 2-Chloromethylthiophene, 1842  
 Chlorosulfuric acid, : Hydrocarbons, 3997  
 Chlorosulfuric acid, : Sulfuric acid, 3997  
 Chromic acid, 4229  
 Chromium(II) chloride, 4052  
 Cyclohexanone oxime, 2452  
 1,4-Dicyano-2-butene, 2311  
 Diethyl dicarbonate, 2444  
 Diethyl sulfate, : Iron, Water, 1710  
 (Difluoroamino)difluoroacetonitrile, : Hydrazine, 0630  
 Difluoroammonium hexafluoroarsenate, 0098  
 1,1-Difluorourea, 0398  
 Dihydroxymaleic acid, 1447  
 † Diketene, : Acids, or Bases, or Sodium acetate, 1441  
   *N,N*-Dimethylacetamide, 1656  
   Dimethylmethylenesulfanickel(0) diethylene complex, 2856  
 † Dimethyl sulfoxide, : Sodium hydride, 0921  
 \* 1,3-Dioxol-4-en-2-one, 1087  
   Disulfur dichloride, 4114  
 † Ethylene oxide, : Polyhydric alcohol, Propylene oxide, 0829  
   Ethylmagnesium bromide, : Water, 0847  
   Ethyl oxalyl chloride, 1456  
   *N*-Ethyl-*N*-propylcarbamoyl chloride, 2468  
 † Formaldehyde, : Magnesium carbonate hydroxide, 0416  
   Formamide, : Iodine, Pyridine, Sulfur trioxide, 0453  
   Formic acid, 0418  
   Formic acid, : Palladium–carbon catalyst, 0418  
   Formic acid, : Phosphorus pentoxide, 0418  
   Furan-2-amidoxime, 1872  
   Hydrogen chloride, : Chlorine, Dinitroanilines, 3993  
   Hydrogen chloride, : Sulfuric acid, 3993  
   Hydrogen peroxide, : Catalyst (unspecified), 4477

Hydrogen peroxide, : Copper(II) chloride, 4477  
 Hydrogen peroxide, : Iron(III) chloride, Hydrocarbons, 4477  
 Hydrogen peroxide, : Methanol, Copper sulfate, Cyanide residues, 4477  
 Hydrogen peroxide, : Polymer residues, 4477  
 Hydrogen peroxide, : 2-Propanol, 4477  
 Iron, : Water, 4388  
 Lithium, : 1,2-Diaminoethane, Tetralin, 4680  
 Lithium tetrahydroaluminate, : Fluoroamides, 0075  
 Lithium tetrahydroaluminate, : Water, 0075  
 Magnesium, : Barium carbonate, Water, 4690  
 Maleic anhydride, : Bases, or Cations, 1404  
 Mercaptoacetonitrile, 0767  
 † Methanol, : Hydrogen, Raney nickel catalyst, 0484  
 Methoxyacetyl chloride, 1165  
 4-Methoxy-3-nitrobenzoyl chloride, 2916  
 † Methyl formate, : Methanol, Sodium methoxide, 0834  
 3-Methyl-2-penten-4-yn-1-ol, 2384  
 Nitric acid, 4436  
 Nitric acid, : Acrylonitrile–methacrylate copolymer, 4436  
 Nitric acid, : Alcohols, 4436  
 Nitric acid, : 1,4-Bis(methoxymethyl)2,3,5,6-tetramethylbenzene, 4436  
 Nitric acid, : Formaldehyde, 4436  
 Nitric acid, : Formic acid, 4436  
 Nitric acid, : Organic materials, 4436  
 Nitric acid, : Sulfur halides, 4436  
 Nitrobenzene, : Tin(IV) chloride, 2262  
 2-Nitrobenzoyl chloride, 2653  
 2-Nitrobenzyl bromide, 2710  
 Orthophosphoric acid, : Chlorides, Stainless steel, 4505  
 Oxalic acid, : Urea, 0725  
 Peroxyacetic acid, : Metal chlorides, 0837  
 Phosphorus tribromide, : Phenylpropanol, 0293  
 Phosphorus trichloride, : Water, 4153  
 Phosphoryl chloride, : Water, 4149  
 Potassium bromate, : Aluminium, Dinitrotoluene, 0255  
 Pyrimidine-2,4,5,6-(1*H*,3*H*)-tetrone, 1398  
 Pyruvic acid, 1150  
 Sodium carbonate, 0552  
 Sodium chlorate, : or Non-metals, or Sulfides, 4039  
 Sodium dihydrobis(2-methoxyethoxy)aluminate, 2575  
 Sodium hydride, : Water, 4444  
 Sodium hydrogen carbonate, : Carbon, Water, 0390  
 Sodium hypochlorite, : Sodium ethylenediaminetetracetate, Sodium hydroxide, 4037  
 Sodium tetrahydroborate, 0147  
 Sodium tetrahydroborate, : Dimethyl formamide, 0147



Sodium triamine, 4581  
 Sulfinyl bromide, 0274  
 Sulfinyl chloride, : Dimethylformamide, 4096  
 Sulfinyl chloride, : Tetrahydrofuran, 4096  
 † Sulfur, : Limonene, 4897  
 Terephthaloyl chloride, 2889  
 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent, 2079  
 Tetrachloroethylene carbonate, : Tributylamine, 1042  
 Tetrachlorosilane, : Ethanol, Water, 4173  
 Titanium, : Water, 4919  
 2-Toluenediazonium bromide, 2736  
 Trichloroacetaldehyde oxime, 0698  
 Trichloroperoxyacetic acid, 0659  
 Trifluoromethanesulfonic acid, : Acyl chlorides, Aromatic hydrocarbons, 0375  
 Trimethylsulfonium chloride, 1303  
 Trimethylsulfoxonium bromide, 1299  
 Uronium nitrate, 0494  
 SUGARS  
 ALKYL NITRATES: lewis acids  
 CYANIDES: hypochlorites  
 DEVARDA'S ALLOY  
 DIAZONIUM TETRAHALOBORATES  
 ISOXAZOLES  
 NITROBENZALDEHYDES  
 NITROBENZYL COMPOUNDS  
 PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

## GAS HANDLING

1. O'Hanlon, J. F. *et al.*, *J. Vac. Sci. Technol. A*, 1988, **6**(3, part 1), 1226–1254
  2. *Photovoltaic safety*, Proc. Amer. Inst. Phys. Conf., 1988, 166
- The American Vacuum Society's recommended procedures for handling hazardous gases include consideration of pump types, pump fluids, system design, effluent control, and storage of gases used for etching and deposition work. Examples of processes discussed in detail are aluminium plasma etching; silicon nitride, tungsten silicide, boron phosphosilicate-glass, silicon and gallium arsenide deposition; and ion implantation [1]. The conference dealt with various aspects of safety in gas handling systems in photovoltaic production processes, including a practical evaluation of wet gas-scrubbing systems, and a review of controlled combustion or oxidation of waste process gas streams. Gases discussed include arsine, diborane, disilane, hydrogen, hydrogen selenide, hydrogen telluride, phosphine, silane, trimethylaluminium and trimethylgallium [2].
- See also* CHEMICAL VAPOUR DEPOSITION

## GEOMETRY OF VESSELS AND PIPEWORK

1. Phylaktou, H. *et al.*, *J. Loss Prevention*, 1993, **6**(1), 15 & 21
2. Chatrathi, K. *et al.*, *Process Safety Progr.*, 1996, **15**(4), 237
3. Singh, *Process Safety Environ. Protect.*, 1994, **72**(B4), 220

The geometry of a detonable or deflagrating charge has a strong influence upon its performance. Pressure rise on ignition of gas/air mixtures in pipework was studied. In general, departures from the straight and narrow accelerated pressure rise and, presumably, transition to detonation [1]. A study of deflagration to detonation transition in pipes, for gas/air and dust mixtures has subsequently been published [2]. Gas explosions in interconnected vessels generate much higher pressures in the second, due to 'pressure piling'. A mathematical technique for prediction of hazard is given [3].

*See also* VAPOUR CLOUD EXPLOSIONS, DUST EXPLOSION INCIDENTS

## GLASS INCIDENTS

1. Craig, T., *New Scientist*, 1995, **145**(1968), 33

Toughened glass used in fume cupboard windows can occasionally shatter explosively when edge defects are present. Although a physical hazard, it is possible to imagine it triggered by a small chemical explosion, which could even amplify the hazards of flying fragments. Application of polyester film to the outside of such windows is recommended [1].

There are several incidents in the text where glass has been involved as a direct cause, either because of its chemical properties (alkalinity, corrosive attack), or its physical properties (actinic transparency, or mechanical limitations under stress). Some of these incidents may be found under the entries:

- Acrylic acid, : Initiator, Water, 1148
- Aluminium chloride, : Water, 0062
- Barium peroxide, : Propane, 0216
- 1,3-Benzodithiolium perchlorate, 2677
- 1,1-Bis(fluorooxy)tetrafluoroethane, 0641
- Borane-tetrahydrofuran, 0138
- Boron tribromide, : Water, 0122
- Bromine, : Aluminium, Dichloromethane, 0261
- Bromine, : Tungsten, Tungsten trioxide, 0261
- † 1,3-Butadiene, 1480
- Calcium oxide, : Water, 3937
- Chlorine trifluoride, : Refractory materials, 3981
- Chromium trioxide, : Acetic acid, 4242
- Copper(II) oxide, : Boron, 4281
- Diazoacetonitrile, 0675
- Dihydroxymaleic acid, 1447
- Ethyl azide, 0872
- Ethylmagnesium bromide, : Water, 0847
- Formic acid, 4436
- † Hydrogen cyanide, 0380

- Hydrogen hexafluorophosphate, : Borosilicate glass, 4360
- Hydrogen peroxide, : Diethyl ether, 4477
- Imidazoline-2,4-dithione, 1141
- Lithium nitride, : Silicon tetrafluoride, 4688
- Magnesium, : Metal oxides, 4690
- Manganese trifluoride, 4335
- † Methyl acrylate, 1531
- Nitric acid, : Glassware, 4436
- Oxalic acid, : Urea, 0725
- † Pentaborane(9), : Pentacarbonyliron, Pyrex glass, 0188
- † Pentaborane(9), : Reactive solvents, 0188
- Potassium hydroxide, : Glass, 4428
- Potassium–sodium alloy, : Fluoropolymers, 4646
- † Propene, : Lithium nitrate, Sulfur dioxide, 1198
- Propionaldehyde, 1085
- Silicon dioxide, : Hydrochloric acid, 4839
- Sodium sulfide, : Glass, 4811
- Sodium tetrahydroborate, 0147
- Succinic anhydride, : Sodium hydroxide, 1443
- Sulfuric acid, : Hydrofluoric acid, 4479
- Trifluoromethyl hypofluorite, : Lithium, 0353
- 2,4,6-Trimethylpyrilium perchlorate, 2992
- Trimethylsulfonium chloride, 1303
- Trimethylsulfoxonium bromide, 1299
- Urea hydrogen peroxidate, 0476

## **GOLD CATALYSTS**

Cusumano, J. A., *Nature*, 1974, **247**, 456

Supported metal catalysts containing gold should never be prepared by impregnation of a support with solutions containing both gold and ammonia. Dried catalysts so prepared contain extremely sensitive gold–nitrogen compounds which may explode at a light touch.

*See* FULMINATING GOLD, GOLD COMPOUNDS

## **GOLD COMPOUNDS**

Many gold compounds exhibit a tendency to decompose violently with separation of the metal. Individually indexed compounds are:

- Bis(dihydroxygold)imide, 0114
- Chloromercuriodiphenylgold, 3473
- Cyclopentadienylgold(I), 1839
- \* 1,2-Diaminoethanebis(trimethylgold), 3105
- Diethylgold bromide, 1672
- Digold(I) ketenide, 0574
- Dimethylgold selenocyanate, 1200

Gold(I) acetylide, 0573  
Gold(III) chloride, 0111  
Gold(I) cyanide, 0308  
Gold(III) hydroxide–ammonia, 0112  
Gold(I) nitride–ammonia, 0117  
Gold(III) nitride trihydrate, 0118  
Gold(III) oxide, 0115  
Gold(III) sulfide, 0116  
Phenylgold, 2221  
Sodium triazidoaurate(?), 0113  
Tetracyanooctaethyltetragold, 3814  
\* Tetramethylbis(trimethylsilanoxy)digold, 3382  
Tetramethyldigold diazide, 1739  
Triethylphosphinegold nitrate, 2558  
*See also* PLATINUM COMPOUNDS, SILVER COMPOUNDS

### GRAPHITE OXIDE

Boehm, H. P. *et al.*, *Z. Anorg. Chem.*, 1965, **335**, 74–79  
The oxide (an intercalated laminar material) is thermally unstable and on rapid heating it will deflagrate at a temperature dependent on the method of preparation. This temperature is lowered by the presence of impurities, and dried samples of iron(III) chloride-impregnated oxide explode on heating.  
*See related* NON-METAL OXIDES

### GRAVEL

Forell, B. *et al.*, *Müll. Abfall*, 1998, **30**(5), 327  
Falling gravel is found to be an especial risk of ignition in boreholes containing flammable atmospheres. Flint, and some other forms of silica, are, of course, mechanical igniters of some antiquity. This observation brings into question use of gravel as a surface covering near where spills may be expected in chemical plants.

### GRIGNARD REAGENTS

**RMgX, ArMgX**

1. Kharasch and Reinmuth, 1954
2. Bondarenko, V. G. *et al.*, *Chem. Abs.*, 1975, **82**, 89690
3. Brogli, F. *et al.*, *Runaway Reactions*, Paper 3/M, 4, 7, Rugby, IChE, 1981
4. *See entry* SELF-ACCELERATING REACTIONS
5. Eckert, T. S., *J. Chem. Educ.*, 1987, **64**(2), 179
6. Sharkey, J. J. *et al.* *J. Loss Prevention*, 1994, **7**(5), 413.

Preparation of Grignard reagents is frequently beset by practical difficulties in establishing the reaction (i.e. is usually subject to an induction period). Improved equipment and control methods for safer preparations have been described [2]. Initiation of the Grignard reaction has been studied in a heat flow calorimeter [3].

Addition of part of a previous reaction mass may effect a smooth initiation [4]. An improved preparation of Grignard reagents (e.g. phenylmagnesium bromide) is described which involves the flame drying of assembled glassware in presence of iodine and magnesium to activate the latter [5]. Ether must be excluded from the vicinity during this procedure! Vent sizing calculations are given for industrial Grignard reactions [6].

Individually indexed compounds are:

- \* Bromomethane, : Metals, 0429  
Butylmagnesium chloride, 1641
- \* Ethyl acetoacetate, : 2,2,2-Tris(bromomethyl)ethanol, Zinc, 2440  
Ethylmagnesium bromide, 0847  
Ethylmagnesium iodide, 0859  
Methylmagnesium iodide, 0446  
Phenylmagnesium bromide, 2225  
2-Trifluoromethylphenylmagnesium bromide, 2643  
3-Trifluoromethylphenylmagnesium bromide, 2643  
4-Trifluoromethylphenylmagnesium bromide, 2643

*See related* UNIT OPERATION OR PROCESS INCIDENTS

*See other* HALO-ARYLMETALS

## HALOACETYLENE DERIVATIVES



1. Whiting, M. C., *Chem. Eng. News*, 1972, **50**(23), 86
2. Brandsma, 1971, 99
3. Kloster-Jensen, E. *et al.*, *Chem. Eng. News*, 1978, **56**(19), 38

The tendency towards explosive decomposition noted for dihalo-2,4-hexadiyne derivatives appears to be associated more with the co-existence of halo- and acetylene functions in the same molecule, than with its being a polyacetylene. Haloacetylenes should be used with exceptional precautions [1]. Explosions may occur during distillation of bromoacetylenes when bath temperatures are too high, or if air is admitted to a hot vacuum-distillation residue [2]. Precautions necessary in isolating and handling such compounds on the small (1 g) scale are detailed [3]. Individually indexed compounds are:

- Bromoacetylene, 0651
- Bromochloroacetylene, 0578
- 1-Bromo-1,2-cyclotridecadien-4,8,10-triyne, 3599
- † 3-Bromopropyne, 1090
- \* Calcium hypochlorite, : Acetylene, 3924
- Chloroacetylene, 0652
- 4-Chloro-2-butynol, 1455
- Chlorocyanoacetylene, 1036
- Chloroiodoacetylene, 0598
- 3-Chloro-1-iodopropyne, 1073
- 1-Chloro-3-phenylpent-1-en-4-yn-3-ol, 4680
- † 3-Chloropropyne, 1092

- Copper(I) chloroacetylide, 1354
- \* 3-Cyanopropyne, 1416
- Dibromoacetylene, 0582
- 1,4-Dibromo-1,3-butadiyne, 1351
- Dichloroacetylene, 0602
- 1,4-Dichloro-1,3-butadiyne, 1353
- 1,4-Dichloro-2-butyne, 1428
- 1,6-Dichloro-2,4-hexadiyne, 2157
- † Dicyanoacetylene, 1801
- Diffluoroacetylene, 0623
- Diiodoacetylene, 0985
- 1,4-Diiodo-1,3-butadiyne, 1799
- 1,6-Diiodo-2,4-hexadiyne, 2173
- Fluoroacetylene, 0662
- Iodoacetylene, 0670
- 1-Iodo-1,3-butadiyne, 1381
- 1-Iodo-3-penten-1-yne, 1845
- 3-Iodo-1-phenylpropyne, 3120
- 3-Iodopropyne, 1105
- Lithium bromoacetylide, 0580
- Lithium chloroacetylide, 0599
- \* Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide, 1820
- Lithium trifluoropropynide, 1046
- Mercury bis(chloroacetylide), 1356
- \* Silver chloroacetylide, 0566
- Silver trifluoropropynide, 1030
- Sodium bromoacetylide, 0581
- Sodium chloroacetylide, 0601
- Tetrakis(chloroethynyl)silane, 2879
- Thallium(I) iodacetylide, 0984
- 3,3,3-Trifluoropropyne, 1066

## HALOALKANES

## RX

### Azides

1. Suzuki, A. *et al.*, *Bull. Chem. Soc. Jap.*, 1991, **64**(11), 3345
  2. Nzeyimana, E. *et al.*, *Progr. Aeronaut. Astronaut.* 1991, (133), 77
  3. Bretherick, L., *Chem. & Ind.*, 1986, 729; *Chem. Eng. News*, 1986, **64**(51), 2
- Of the lower members of this reactive group of compounds, the more lightly substituted are of high flammability like the haloalkenes. The more highly substituted find use as fire suppressants, not always with the anticipated results: Bromotrifluoromethane can promote ignition of mixtures of air and methane (but not ethane) [1]; up to 5% tetrafluoromethane accelerates detonation of hydrogen oxygen mixtures [2]. Reaction with the lighter divalent metals may give much more reactive materials analogous to Grignard reagents. Individually indexed compounds are:

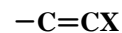
Potential hazards arising from slow formation of explosive azides from prolonged contact of halogenated solvents with metallic or other azides are outlined.

*See* Dichloromethane: Sodium azide

- \* 1,4-Bis(1,2-dibromoethyl)benzene, 3268
- \* 1,3-Bis(trichloromethyl)benzene, 2891
- \* 1,3-Bis(trifluoromethyl)benzene, 2894
- † 1-Bromobutane, 1631
- † 2-Bromobutane, 1632
- † Bromoethane, 0846
  - Bromoform, 0368
- † Bromomethane, 0429
- † 1-Bromo-3-methylbutane, 1984
- † 1-Bromo-2-methylpropane, 1633
- † 2-Bromo-2-methylpropane, 1634
- † 2-Bromopentane, 1985
- † 1-Bromopropane, 1241
- † 2-Bromopropane, 1242
  - Bromotrichloromethane, 0310
  - 3-Bromo-1,1,1-trichloropropane, 1126
  - Bromotrifluoromethane, 0311
- \* 2-Bromo-2,5,5-trimethylcyclopentanone, 3018
  - Carbon tetrabromide, 0315
  - Carbon tetrachloride, 0322
  - Carbon tetrafluoride, 0349
  - Carbon tetraiodide, 0525
- † 1-Chlorobutane, 1637
- † 2-Chlorobutane, 1638
- † Chlorocyclopentane, 1923
- † 1-Chloro-1,1-difluoroethane, 0731
  - Chlorodifluoromethane, 0369
- † Chloroethane, 0848
  - Chloroform, 0372
- † Chloromethane, 0432
- † 1-Chloro-3-methylbutane, 1986
- † 2-Chloro-2-methylbutane, 1987
- † Chloromethyl ethyl ether, 1246
- † Chloromethyl methyl ether, 0850
- † 1-Chloro-2-methylpropane, 1639
- † 2-Chloro-2-methylpropane, 1640
- † 1-Chloropentane, 1988
- † 1-Chloropropane, 1243
- † 2-Chloropropane, 1244
- † 1-Chloro-3,3,3-trifluoropropane, 1127
  - 1,2-Dibromoethane, 0785
  - Dibromomethane, 0395

- Dichlordifluoromethane, 0326
- † *miso*-Dichlorobutane, 1587
- 2,2-Dichloro-3,3-dimethylbutane, 2469
- † 1,1-Dichloroethane, 0790
- † 1,2-Dichloroethane, 0791
- 1,1-Dichloro-1-fluoroethane, 0738
- † Dichloromethane, 0397
- † 1,1-Dichloropropane, 1203
- † 1,2-Dichloropropane, 1204
- 2,2-Dichloropropane, 1205
- 1,2-Dichlorotetrafluoroethane, 0604
- † 1,1-Difluoroethane, 0801
- Diiodomethane, 0400
- Fluorodiiodomethane, 0373
- † Fluoroethane, 0855
- † Fluoromethane, 0441
- Hexabromoethane, 0584
- \* 1,2,3,4,5,6-Hexachlorocyclohexane, 2306
- Hexachloroethane, 0611
- † 2-Iodobutane, 1647
- Iodoethane, 0858
- \* 2-Iodoethanol, 0860
- Iodoform, 0376
- Iodomethane, 0445
- † 1-Iodo-2-methylpropane, 1648
- † 2-Iodo-2-methylpropane, 1649
- † 2-Iodopentane, 1990
- † 2-Iodopropane, 1252
- Pentachloroethane, 0660
- \* Poly(carbon monofluoride), 0337
- \* Poly(chlorotrifluoroethylene), 0592
- \* Poly(tetrafluoroethylene), 0629
- \* Tetracarbon monofluoride, 1362
- 1,1,2,2-Tetrachloroethane, 0699
- † 1,1,1-Trichloroethane, 0740
- 1,1,2-Trichloroethane, 0741
- \* 2,2,2-Trichloroethanol, 0744
- Trichlorofluoromethane, 0330
- 1,1,2-Trichlorotrifluoroethane, 0606
- † 1,1,1-Trifluoroethane, 0754

## HALOALKENES



Of the lower members of this reactive group of compounds, the more lightly substituted are of high flammability and many are classed as peroxidisable and as polymerisable compounds. Individually indexed compounds are:



- † Acrylonitrile, 1107
- † 1-Bromo-2-butene, 1548
- † 4-Bromo-1-butene, 1549
- 4-Bromocyclopentene, 1884
- † Bromoethylene, 0727
- † 3-Bromo-1-propene, 1153
- † Bromotrifluoroethylene, 0579
- † 2-Chloroacrylonitrile, 1074
- † 2-Chloro-1,3-butadiene, 1451
- † 2-Chloro-2-butene, 1551
- † 3-Chloro-1-butene, 1552
- 3-Chlorocyclopentene, 1885
- † Chloroethylene, 0730
- † 3-Chloro-2-methyl-1-propene, 1553
- † 1-Chloro-1-propene, 1156
- † 2-Chloropropene, 1157
- † 3-Chloropropene, 1158
- † Chlorotrifluoroethylene, 0591
- 3,5-Dibromocyclopentene, 1860
- † 1,1-Dichloroethylene, 0695
- † *cis*-1,2-Dichloroethylene, 0696
- † *trans*-1,2-Dichloroethylene, 0697
- \* (2,2-Dichloro-1-fluorovinyl)ferrocene, 3470
- † 2,3-Dichloropropene, 1132
- † 1,1-Difluoroethylene, 0700
- \* 2-Ethoxy-1-iodo-3-butene, 2449
- † Fluoroethylene, 0747
- Hexachlorocyclopentadiene, 1808
- † Hexafluoropropene, 1051
- 1-Iodohepta-2,4-diene, 2393
- † 3-Iodopropene, 1174
- \* Methyl trifluorovinyl ether, 1101
- 1,2,3,-4,5-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2069
- 1,2,3,-5,6-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2070
- Perfluorobutadiene, 1364
- \* Poly(1-pentafluorothio-1,2-butadiyne), 1379
- 1,1,2,3-Tetrachloro-1,3-butadiene, 1389
- 1,1,4,4-Tetrachlorobutatriene, 1360
- Tetrachloroethylene, 0609
- Tetrachloropropadiene, 1041
- 1,1,4,4-Tetrafluorobutatriene, 1363
- † Tetrafluoroethylene, 0628
- Tetraiodoethylene, 0986
- † Trichloroethylene, 0656

† Trifluoroethylene, 0663  
† 3,3,3-Trifluoropropene, 1099  
See other PEROXIDISABLE COMPOUNDS

## HALOANILINES



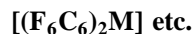
Kotoyori, T., *Proc. 6th Int. Sympos. Loss Prev. Safety Prom, Proc. Ind.*, 38-1–38-16, Oslo, Norweg. Soc. Chartered Engrs., 1989

Available information on the thermal instability of halogenated anilines during vacuum distillation is presented and analysed, and the roles of dehydrohalogenation, polymerisation, salt formation and dissociation, aerobic oxidation, corrosion and metal-catalysed decomposition are discussed. Experimental work on these topics is presented, and preventive measures proposed.

Some halo-substituted anilines are of limited thermal stability, tending to eliminate hydrogen halide which may catalyse further decomposition. To avoid decomposition during distillation, this should be conducted in the presence of solid alkali or magnesium oxide at minimum temperature (under relatively high vacuum) and/or with exclusion of air by inert gas. Individually indexed compounds are:

- 4-Bromoaniline, 2296
- \* 4-Bromo-1,2-diaminobenzene, 2345
- 2-Bromo-3,5-dimethoxyaniline, 2974
- 4-Bromodimethylaniline, 2973
- 4-Chloro-2-aminophenol, 2303
- 2-Chloroaniline, 2300
- 3-Chloroaniline, 2301
- 4-Chloroaniline, 2302
- 2-Chloro-1,4-benzenediamine, 2349
- \* 4-Chloro-1,2-benzenediamine, 2347
- \* 4-Chloro-1,3-benzenediamine, 2348
- 4-Chloro-2,6-diamino-*N*-methylaniline, 2822
- \* 2-Chloro-*N*-(2-hydroxyethyl)aniline, 2975
- 3-Chloro-4-methoxyaniline, 2795
- 4-Chloro-2-methylaniline, 2794
- 2,4-Dibromoaniline, 2226
- 2,4-Dichloroaniline, 2238
- 2,5-Dichloroaniline, 2239
- 3,4-Dichloroaniline, 2241
- 2,3,4-Trichloroaniline, 2163

## HALOARENEMETAL $\pi$ -COMPLEXES



1. Klabunde, K. *et al.*, *Inorg. Chem.*, 1975, **14**, 790–791
2. Klabunde, K. *et al.*, *Angew. Chem. (Intern. Ed.)*, 1975, **14**, 288
3. Klabunde, K. *et al.*, *J. Fluorine Chem.*, 1974, **4**, 11
4. Graves, V. *et al.*, *Inorg. Chem.*, 1976, **15**, 578

The  $\pi$ -complexes formed between chromium(0), vanadium(0) or other transition metals, and mono- or poly-fluorobenzene show extreme sensitivity to heat and are

explosive [1,2]. Hexafluorobenzenenickel(0) exploded at 70°C [3], and presence of two or more fluorine substituents leads to unstable, very explosive chromium(0) complexes [1]. Apparently, the aryl fluorine atoms are quite labile, and on decomposition M–F bonds are formed very exothermically. Laboratory workers should be wary of such behaviour in any haloarenemetal  $\pi$ -complex of this type [1]. However, in later work, no indications of explosivity, or indeed of any complex formation, were seen [4]. Individually indexed compounds are:

Bis(1,n-difluorobenzene)chromium(0) isomers

Bis(fluorobenzene)chromium(0)

Bis(fluorobenzene)vanadium(0)

Bis(hexafluorobenzene)chromium(0)

Bis(hexafluorobenzene)cobalt(0)

Bis(hexafluorobenzene)iron(0)

Bis(hexafluorobenzene)nickel(0)

Bis(hexafluorobenzene)titanium(0)

Bis(hexafluorobenzene)vanadium(0)

*See other* HALO-ARYLMETALS

## HALOARYL COMPOUNDS

ArX

Though normally not very reactive, a few haloaryl compounds if sufficiently activated by other substituents or by specific reaction conditions, may undergo violent reactions. Individually indexed compounds are:

Bis(4-chlorobenzenediazo) oxide, 3456

Bis(2,4,5-trichlorobenzenediazo) oxide, 3431

\* 1,3-Bis(trichloromethyl)benzene, 2891

\* 1,3-Bis(trifluoromethyl)benzene, 2894

Bromobenzene, 2224

Chlorobenzene, 2228

4-Chloro-2,5-diethoxynitrobenzene, 3301

1-Chloro-2,4-dinitrobenzene, 2098

† 2-Chlorofluorobenzene, 2134

† 3-Chlorofluorobenzene, 2135

† 4-Chlorofluorobenzene, 2136

4-Chloro-2-methylphenol, 2741

2-Chloronitrobenzene, 2141

4-Chloronitrobenzene, 2142

2-Chloro-5-nitrobenzenesulfonic acid, 2144

4-Chlorotrifluoromethylbenzene, 2646

1,2-Dichlorobenzene, 2156

1,5-Dichloro-2,4-dinitrobenzene, 2077

2,4-Dichloronitrobenzene, 2104

3,4-Dichloronitrobenzene, 2105

Dichlorophenol mixed isomers, 2161

† 1,3-Difluorobenzene, 2168

† 1,4-Difluorobenzene, 2169

- 1,5-Difluoro-2,4-dinitrobenzene, 2080
- 1,2-Diodobenzene, 2172
- † Fluorobenzene, 2248
- \* 1-Fluoro-2,4-dinitrobenzene, 2108
- † 2-Fluorotoluene, 2747
- † 3-Fluorotoluene, 2748
- † 4-Fluorotoluene, 2749
- Iodobenzene, 2249
- 2-Iodo-3,5-dinitrobiphenyl, 3450
- 4-Iodotoluene, 2750
- 1,2,4,5-Tetrachlorobenzene, 2079
- † 1,2,4,5-Tetrafluorobenzene, 2081
- 2,4,5-Trichlorophenol, 2107
- † 1,2,4-Trifluorobenzene, 2110

## HALO-ARYLMETALS

## ArMX, XArM

The name adopted for this group of highly reactive (and in some circumstances intramolecularly self-reactive) compounds is intended to cover both arylmetal halides (halogen bonded to the metal) and haloaryl metals (halogen attached to the aryl nucleus). Individually indexed compounds are:

- Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium, 3830
- \* Bis(cyclopentadienyl)pentafluorophenylzirconium hydroxide, 3703
- Bis(pentafluorophenyl)aluminium bromide, 3418
- \* Bis(trimethylphosphine)di(3,5-dibromo-2,6-dimethoxyphenyl)nickel, 3837
- 3-Bromophenyllithium, 2129
- 4-Bromophenyllithium, 2130
- 3-Chlorophenyllithium, 2138
- 4-Chlorophenyllithium, 2139
- 4-Fluorophenyllithium, 2166
- Pentafluorophenylaluminium dibromide, 2053
- Pentafluorophenyllithium, 2059
- Tetrakis(pentafluorophenyl)titanium, 3842
- 2-Trifluoromethylphenyllithium, 2655
- 3-Trifluoromethylphenyllithium, 2656
- 4-Trifluoromethylphenyllithium, 2657
- 2-Trifluoromethylphenylmagnesium bromide
- 3-Trifluoromethylphenylmagnesium bromide
- 4-Trifluoromethylphenylmagnesium bromide

See GRIGNARD REAGENTS

HALOARENEMETAL  $\pi$ -COMPLEXES

ORGANOLITHIUM REAGENTS

## HALOBORANES

–BHX, –BX<sub>2</sub>

The degree of reactivity to air or to water depends on the degree of substitution of hydrogen by halogen. This highly reactive group includes the individually indexed compounds:

- Bromodiborane, 0159
- 1-Bromopentaborane(9), 0186
- Chlorodiborane, 0160
- \* B-Chlorodimethylaminodiborane, 0962
- Diboron tetrachloride, 0161
- Diboron tetrafluoride, 0162
- 1,2-Dibromopentaborane(9), 0187
- Iododiborane, 0165
- Tetraboron tetrachloride, 0179

*See related* NON-METAL HALIDES, NON-METAL HYDRIDES

## HALOCARBONS

RX, ArX

This generic name often to be found in the text is used in the sense of halogen-substituted hydrocarbons which may also contain hydrogen, i.e. substitution may not necessarily be complete. It represents a range of halogenated aliphatic or aromatic compounds widely used in research and industry, often as solvents or diluents. None are completely inert chemically, but in general, reactivity decreases with increasing substitution of hydrogen by halogen (particularly with fluorine), in both saturated and unsaturated hydrocarbons.

Several lower partially halogenated hydrocarbons (dichloromethane, bromomethane, trichloroethylene, 1,1,1-trichloroethane) have no measurable flash point, but are nonetheless capable of forming flammable and explosive mixtures with air, and several such accidents are recorded.

*See entry* FLASH POINTS (reference 19)

- CHLOROFLUOROCARBONS
- FLUOROCARBONS
- HALOALKANES
- HALOALKENES
- HALOARYL COMPOUNDS

*See* METAL–HALOCARBON INCIDENTS

- Pentaborane(9), : Reactive solvents, 0188
- Calcium disilicide, : Carbon tetrachloride, 3944
- Fluorine, : Halocarbons, 4310
- Disilane, : Non-metal halides, 4569
- Dinitrogen tetraoxide, : Halocarbons, 4747
- Oxygen (Liquid), : Halocarbons, 4832

## HALOGENATION INCIDENTS

Examples of incidents involving halogenation reactions are:

- Bromine, : Alcohols, 0261
- Bromine, : Aluminium, Dichloromethane, 0261

Bromine, : Isobutyrophenone, 0261  
*N*-Bromosuccinimide, : Dibenzoyl peroxide, 4-Toluic acid, 1425  
Chlorine, 4047  
Chlorine, : Antimony trichloride, Tetramethylsilane, 4047  
Chlorine, : 2-Chloroalkyl aryl sulfides, Lithium perchlorate, 4047  
Sulfur tetrafluoride, : 2-(Hydroxymethyl)furan, Triethylamine, 4350  
Titanium, : Halogens, 4919  
Trifluoromethanesulfonyl chloride, : Chlorine fluorides, 0322  
    ALKYLALUMINIUM DERIVATIVES: Halocarbons  
    BORANES: Carbon tetrachloride  
    *N*-HALOIMIDES: Xylene  
    SILANES: Chloroform  
*See other* UNIT PROCESS INCIDENTS

## HALOGEN AZIDES

**XN<sub>3</sub>**

Metals, or Phosphorus

Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 240

A comprehensive review covers stability relationships and reactions of these explosive compounds and their derivatives. Bromine, chlorine and iodine azides all explode violently in contact with magnesium, zinc or white phosphorus.

Individually indexed compounds are:

Bromine azide, 0256

Chlorine azide, 4030

\* Cyanogen azide, 0544

Fluorine azide, 4307

Iodine azide, 4621

*See* METAL Pnictides

*See other* *N*-HALOGEN COMPOUNDS, NON-METAL AZIDES

## *N* -HALOGEN COMPOUNDS

**-NX**

1. Kovacic, P. *et al.*, *Chem. Rev.*, 1970, **70**, 640

2. Petry, R. C. *et al.*, *J. Org. Chem.*, 1967, **32**, 4034

3. Freeman, J. P. *et al.*, *J. Amer. Chem. Soc.*, 1969, **91**, 4778

4. Guillamin, J. C. *et al.*, *Synthesis*, 1985, (12), 1131–1133

5. Guillamin, J. C. *et al.*, *Tetrahedron*, 1988, **44**, 4431–4446; 4447–4455

6. Kirk-Othmer, 1993, (4th Edn) Vol IV, 917, 921

Many compounds containing one or more N–X bonds show unstable or explosive properties (and are also oxidants), and this topic has been reviewed [1]. Difluoroamino compounds, ranging from difluoramine and tetrafluorohydrazine to polydifluoroamino compounds, are notably explosive and suitable precautions have been detailed [2,3]. Preparative scale *N*-chlorination of 1y and 2y amines by passing them over *N*-chlorosuccinimide is described. In presence of alumina, 1y amines give the *N,N*-dichloro derivatives. The products must be handled with

great caution, and collection and storage at  $-30^{\circ}\text{C}$  is recommended, as some of the products exploded at ambient temperature [4]. The range of compounds so prepared has been further extended [5]. *N*-Halosulfinylamines ( $\text{O}=\text{S}=\text{NHal}$ ) are stable at room temperature but react explosively with water. Dialkyldichlorosulfurdiimides [ $\text{R}_2\text{S}(\text{=NCl})_2$ ] explode violently when heated [6].

Within this class fall the separate groups:

*N*-CHLORONITROAMINES  
DIFLUOROAMINO COMPOUNDS  
HALOGEN AZIDES  
*N*-HALOIMIDES  
*N,N,N'*-TRIFLUOROALKYLAMIDINES

Individually indexed compounds are:

Azidoiodoiodonium hexafluoroantimonate, 4361  
Azo-*N*-chloroformamidine, 0792  
Benzoquinone 1,4-bis(chloroimine), 2159  
1,4-Benzoquinone-4-chloroimine, 2140  
4,4-Bis(difluoroamino)-3-fluoroimino-1-pentene, 1867  
Bromamine, 0249  
*N*-Bromoacetamide, 0784  
1-Bromoaziridine, 0783  
3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2645  
*N*-Bromo-3-nitrophthalimide, 2884  
*N*-Bromosuccinimide, 1425  
*N*-Bromotetramethylguanidine, 2002  
*N*-Bromotrimethylammonium bromide(?), 1300  
Chloramine, 4000  
\* Chloriminovanadium trichloride, 4165  
*N*-Chloroacetamide, 0789  
*N*-Chloroallylamine, 1202  
*N*-Chloro-3-aminopropyne, 1129  
*N*-Chloro-3-aminopropyne, 1129  
1-Chloroaziridine, 0786  
1-Chlorobenzotriazole, 2150  
*N*-Chloro-bis(2-chloroethyl)amine, 1590  
*N*-Chlorobis(trifluoromethanesulfonyl)imide, 0596  
*N*-Chlorocinnamaldimine, 3126  
*N*-Chlorodimethylamine, 0895  
*N*-Chloro-4,5-dimethyltriazole, 1490  
*N*-Chloro-4-methyl-2-imidazolinone, 1554  
*N*-Chloro-5-methyl-2-oxazolidinone, 1488  
*N*-Chloro-3-morpholinone, 1489  
*N*-Chloro-4-nitroaniline, 2231  
*N*-Chloro-5-phenyltetrazole, 2674  
*N*-Chloropiperidine, 1948  
*N*-Chloropyrrolidine, 1584

*N*-Chlorosuccinimide, 1427  
*N*-Chlorotetramethylguanidine, 2004  
 Diamminedichloroamidotrithloroplatinum(IV), 4179  
 2,6-Dibromobenzoquinone-4-chloroimide, 2076  
 Dichloramine, 4063  
*N,N*-Dichloro- $\beta$ -alanine, 1168  
 1-Dichloroaminotetrazole, 0371  
*N,N*-Dichloroaniline, 2242  
 2,6-Dichlorobenzoquinone-4-chloroimide, 2078  
*N,N'*-dichlorobis(2,4,6-trichlorophenyl)urea, 3596  
 Dichlorofluoramine, 4059  
*N,N*-Dichloroglycine, 0739  
*N,N*-Dichloromethylamine, 0437  
*N,N*-Dichloropentafluorosulfanylamine, 4060  
 Difluoramine, 4311  
 3-Difluoroamino-1,2,3-trifluorodiaziridine, 0358  
 \* Difluoroammonium hexafluoroantimonate, 4380  
 Difluoroammonium hexafluoroarsenate, 0098  
 Difluorodiazene, 4314  
 Difluoro-*N*-fluoromethanimine, 0344  
 Diiodamine, 4426  
 Dimethyl *N,N*-dichlorophosphoramidate, 0901  
 1,1-Dimethylethyldibromamine, 1636  
 Ethyl *N*-chloro-*N*-sodiocarbamate, 1159  
 Fluoramine, 4296  
 1-Fluoroiminohexafluoropropane, 1058  
 2-Fluoroiminohexafluoropropane, 1059  
*N*-Fluoroiminosulfur tetrafluoride, 4357  
*N*-Fluoro-*N*-nitrobutylamine, 1645  
 3-Fluoro-3-(trifluoromethyl)-3*H*-diazirine, 0631  
 \* Iodine isocyanate, 0524  
 Nitrogen chloride difluoride, 3978  
 Nitrogen tribromide hexaammoniate, 0290  
 Nitrogen trichloride, 4724  
 Nitrogen trifluoride, 4336  
 Nitrogen triiodide, 4633  
 Nitrogen triiodide–silver amide, 4634  
 Nitrogen triiodide–ammonia, 4635  
 Nitrosyl chloride, 4023  
 Nitrosyl fluoride, 4302  
 Nitryl chloride, 4025  
 Nitryl fluoride, 4303  
 \* Pentafluoroguanidine, 0359  
 Sodium *N*-chlorobenzenesulfonamide, 2229  
 Sodium *N*-chloro-4-toluenesulfonamide, 2739  
*N,N,N'',N''*-Tetrachloroadipamide, 2370



Tetrafluoroammonium hexafluoromanganate, 4384  
 Tetrafluoroammonium hexafluoronickelate, 4385  
 Tetrafluoroammonium octafluoroxenate, 4386  
 Tetrafluoroammonium perbromate, 0242  
 Tetrafluoroammonium perchlorate, 3986  
 Tetrafluoroammonium tetrafluoroborate, 0133  
 Tetrafluorodiaziridine, 0351  
 † Tetrafluorohydrazine, 4345  
 Tetrakis(*N,N*-dichloroaminomethyl)methane, 1900  
 Tribromamine oxide, 0291  
 1,3,5-Trichloro-2,4,6-trifluoroborazine, 0173  
 1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine, 4145  
 1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum, 4142  
 Trifluoroacetylminoiodobenzene, 2903  
 2,4,6-Tris(bromoamino)-1,3,5-triazine, 1091  
 2,4,6-Tris(dichloroamino)-1,3,5-triazine, 1043

## HALOGEN OXIDES

## XO<sub>n</sub>

Of the various compounds arising from union of oxygen with one or more halogens, many are endothermic and all are generally unstable but powerful oxidants.

Individually indexed compounds are:

Bromine bromate, 0276  
 Bromine dioxide, 0258  
 Bromine perchlorate, 0235  
 Bromine trioxide, 0259  
 Bromyl fluoride, 0239  
 Chlorine dioxide, 4042  
 Chlorine perchlorate, 4101  
 Chlorine trifluoride oxide, 3982  
 Chlorine trioxide, 4044  
 Chloryl hypofluorite, 3973  
 Chloryl perchlorate, 4104  
 Dichlorine oxide, 4095  
 Dichlorine trioxide, 4100  
 \* Dicyanogen *N,N'*-dioxide, 0998  
 Dioxygen difluoride, 4320  
 Fluorine perchlorate, 3976  
 Hexaoxygen difluoride, 4327  
 Iodine dioxide trifluoride, 4334  
 Iodine(V) oxide, 4627  
 Iodine(VII) oxide, 4628  
 Oxygen difluoride, 4317  
 Perbromyl fluoride, 0240  
 Perchloryl fluoride, 3974

Perchloryl perchlorate, 4107  
Tetrafluoroiodosyl hypofluorite, 4356  
'Trioxxygen difluoride', 4323

## HALOGENS

X<sub>2</sub>

The reactivity hazards of this well defined group of oxidants towards other materials decrease progressively from fluorine, which reacts violently with most materials (except for those metals on which resistant fluoride films form), through chlorine and bromine to iodine. Astatine may be expected to continue this trend. The individual entries are:

Bromine, 0261  
Chlorine, 4047  
Fluorine, 4310  
Iodine, 4625

## N-HALOIMIDES

—CO.N(X)CO.—

Alcohols, or Amines, or Diallyl sulfide, or Hydrazine, or Xylene

Martin, R. H., *Nature*, 1951, **168**, 32

Many of the reactions of *N*-chloro- and *N*-bromo-imides are extremely violent or explosive. Those observed include *N*-chlorosuccinimide with aliphatic alcohols or benzylamine or hydrazine hydrate; *N*-bromosuccinimide with aniline, diallyl sulfide, or hydrazine hydrate; or 3-nitro-*N*-bromophthalimide with tetrahydrofurfuryl alcohol; 1,3-dichloro-5,5-dimethyl-2,4-imidazolidindione with xylene (violent explosion). Individually indexed compounds are:

*N*-Bromosuccinimide, 1425  
Chloriminovanadium trichloride, 4165  
*N*-Chlorosuccinimide, 1427  
1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione, 1865  
Potassium 1,3-dibromo-1,3,5-triazine-2,4-dione-6-oxide, 0132  
Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide, 1037  
1,3,5-Trichloro-1,3,5-triazinetrione, 1039

See other N-HALOGEN COMPOUNDS

## 2-HALOMETHYL-FURANS OR -THIOPHENES

Heterocyclic Compounds, Vol. 1, 207, Elderfield, R. C. (Ed.), New York, Wiley, 1950

The great instability of 2-bromomethyl- and 2-chloromethyl-furans, often manifest as violent or explosive decomposition on attempted distillation, is reviewed. The furan nucleus is sensitive to traces of halogen acids, and decomposition becomes autocatalytic. Individually indexed compounds are:

2,5-Bis(chloromethyl)thiophene, 2305  
2-Bromomethylfuran, 1840  
2-Bromomethyl-5-methylfuran, 2346

2-Chloro-5-chloromethylthiophene, 1830

2-Chloromethylfuran, 1841

2-Chloromethyl-5-methylfuran, 2352

2-Chloromethylthiophene, 1842

*See also* BENZYL COMPOUNDS

## HALOPHOSPHINES

—PHX, —PX<sub>2</sub>

The degree of reactivity towards air or to water depends upon the degree of substitution of hydrogen by halogen. Individually indexed compound are:

\* Phosphorus azide difluoride, 4315

Phosphorus trifluoride, 4339

Phosphorus triiodide, 4636

Tetrachlorodiphosphane, 4171

Tetraiododiphosphane, 4637

*See related* NON-METAL HALIDES, NON-METAL HYDRIDES

## HALOSILANES

Si<sub>m</sub>X<sub>n</sub>

1. Schumb, W. C. *et al.*, *Inorg. Synth.*, 1939, **1**, 46

2. Halvorsen, F. *et al.*, *Proc. 29th Annu. Loss Prev. Symp.*, 1995, paper 6B (Amer. Inst. Chem. Engineers)

When heated, the vapours of the higher chlorosilanes (hexachlorodisilane to dodecachloropentasilane) ignite in air. Other halo- and haloalkyl-silanes ignite without heating or have low flash points: some react violently with water [1]. An account has been given of cleaning and dismantling a plant contaminated with shock sensitive and polymeric 'oil silanes' arising as byproducts from trichlorosilane handling [2]. Individually indexed compounds are:

† Bromosilane, 0250

Decachlorotetrasilane, 4197

† Dichlorosilane, 4066

Dodecachloropentasilane, 4198

Fluorosilane, 4298

Hexachlorodisilane, 4191

Iododisilane, 4543

Octachlorotrisilane, 4194

\* Poly(difluorosilylene), 4330

Tetrachlorosilane, 4173

† Tribromosilane, 0287

† Trichlorosilane, 4136

† Trifluorosilane, 4333

*See related* NON-METAL HALIDES, NON-METAL HYDRIDES

## HAZARDOUS MATERIALS

1. Cloyd, D. R. *et al.*, *Handling Hazardous Materials*, NASA Tech. Survey SP-5032, Washington, NASA, 1965

2. *Fire Protection Guide on Hazardous Materials*, SPP-1C, Boston (Ma.), NFPA, 6th edn., 1975

The survey of hazards and safety procedures involved in handling rocket fuels and oxidisers includes liquid hydrogen, pentaborane, fluorine, chlorine trifluoride, ozone, dinitrogen tetroxide, hydrazine, methyl hydrazine and 1,1-dimethyl hydrazine [1]. The later volume [2] is a bargain compendium of five NFPA publications:

- 325A, *Flashpoint Index of Tradename Liquids* (8800 items), 1972
- 325M, *Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids* (1300 items), 1969
- 49, *Hazardous Chemicals Data* (416 items), 1975
- 491M, *Manual of Hazardous Chemical Reactions* (3550 items), 1975
- 704M, *Recommended System for Identification of Fire Hazards of Materials*, 1975

## HAZARDS FROM PRESSURE

*Hazards from Pressure: Exothermic Reactions, Unstable Substances, Pressure Relief and Accidental Discharge*, Gibson, N. (ed.), IChE Symp. Ser. No. 102, Oxford, Pergamon, 1987

The 1986 UK Symposium covered hazards from pressure effects originating in various ways from exothermic runaway reactions and unstable substances, and the measures necessary to mitigate these effects. Some of the reactive hazards involved may be found under the entries:

- Copper(II) acetylide(reference 2), 0615
- 2-Hydroxyethylamine: Carbon dioxide, etc., 0943
- Sodium dithionite (reference 2), 4807
- BLOWING AGENTS (reference 2)
- HEAT FLOW CALORIMETRY (reference 5)

See PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

## HEAT FLOW CALORIMETRY

1. Hub, L., *Proc. 6th Symp. Chem. Proc. Hazards*, Symp. Ser. No. 49, 39–46, Rugby, IChE, 1977
2. Brogli, F. *et al.*, *Runaway Reactions*, Paper 3/M, 1–10
3. Fierz, H. *et al.*, *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, A12–A21, Rugby, IChE, 1983
4. Stockton, G. W. *et al.*, Euro-pat. Appl. EP 170713, 1986
5. Wright, T. K. *et al.*, *Hazards from Pressure*, IChE Symp. Ser. No. 102, 85–96, Oxford, Pergamon, 1987
6. Burke, P. E. *Spec. Publ. -R. Soc. Chem., 195(Pilot Plants and Scale-up of Chemical Processes)*, 1997, 52
7. Cardillo, P. *et al.*, *Afinidad*, 1998, **55**(474), 115

As an alternative and complementary technique to the study of chemical materials by DTA, DSC, or ARC, the study of chemical processes in miniature reactors has been developed. Equipment which is sufficiently instrumented to permit full

analysis of processing heat flows arising from reaction exotherms or process deviations is available, in two variants. Both have accurately controlled heating and cooling systems which are used separately or simultaneously to maintain the stirred reactor temperature at the desired level as reaction proceeds, and to indicate the heat flows from the liquid phase to the jacket and from the vapour phase to the reflux condenser etc. The first variant uses a glass flask reactor of 2 l capacity fitted with stirrer, doser and reflux condenser and can operate between  $-30^{\circ}$  to  $+200^{\circ}\text{C}$  under vacuum or at atmospheric pressure. Further details of the reaction safety calorimeter (RSC) and of its application to various processing problems are published [1]. The second variant has interchangeable glass vessels of 0.5 to 2.5 l operable between  $-20$  to  $+200^{\circ}\text{C}$  at up to 3 bar internal pressure, and operation and application of the bench scale calorimeter (BSC) to several different processing problems and investigations has been discussed [2,3]. Improved design features claimed include use of a zirconium reaction vessel rather than glass ( $10^3$  increase in thermal conductivity), thermostatted feed streams and adiabatic shield [4]. The design and use of an isothermal heat flow calorimeter to assess cooling and other processing requirements for safe operation of (semi-)batch processes are discussed. Use of this simpler type of calorimeter is complementary to that of the more expensive variable heat flow calorimeters [5].

In the 1990s, reaction calorimetry has found extensive use in industrial scale-up operations. The editor's limited exposure to it suggests that the commercially available equipment has indifferent agitation and may in consequence handle multiphase reactions poorly: anathema though they be to academic kineticists, industry finds slurries attractive. However it is a simple technique by which to acquire data on the kinetics of heat production. Publications have become very numerous, mostly publicity from testing houses offering the service. Some very recent work is found in [6], [7].

See CALORIMETRY

## HEAT TRANSFER

1. Bourne, J. R. *et al.*, *Chem. Eng. Sci.*, 1987, **42**, 2183–2192
2. Bourne, J. R. *et al.*, *Chem. Eng. Sci.*, 1987, **42**, 2193–2196

The factors which affect heat transfer from an exothermic fluid reaction system are important in determining whether a runaway reaction (thermal explosion) will ensue. Agitation reduces local heat accumulation and applied cooling affects overall heat retention and temperature of the reactor contents. Studies in unstirred vertical cylinder reactors showed the effects of convection in modifying the temperature- and flow-fields existing in a conduction-only system. An analogy between the temperature profiles in active (exothermally reacting) systems and passive (cooling without reaction) systems at equal heat-removal rates was established, offering the possibility of simpler and safer experimental assessments [1]. Correlations in a freely conducting active system show that the maximum temperature occurs just below the liquid surface, and to avoid thermal runaway, the temperature must not exceed a critical value, which depends on the heat generation rate, the liquid physical properties and the vessel size [2].

See 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, etc. (references 10, 11)

## HEAVY METAL DERIVATIVES

This class of compounds showing explosive instability deals with heavy metals bonded to elements other than nitrogen and contains the separately treated groups:

GOLD COMPOUNDS  
LEAD SALTS OF NITRO COMPOUNDS  
LITHIUM PERALKYLURANATES  
MERCURY COMPOUNDS  
METAL ACETYLIDES  
METAL FULMINATES  
METAL OXALATES  
PLATINUM COMPOUNDS  
PRECIOUS METAL DERIVATIVES  
SILVER COMPOUNDS

as well as the individually indexed compounds:

Barium acetate, 1486  
Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt, 3868  
Cadmium propionate, 2418  
\* Cobalt(II) picramate, 3460  
Copper(I) chloroacetylide, 1354  
Diacetatotetraaquocobalt, 1780  
Dicopper(I) ketenide, 0621  
\* Diethyllead dinitrate, 1692  
Dimethylmethylenoxosulfanenickel(0) diethylene complex, 2856  
Dinitrosylnickel, 4741  
\* Hydroxycopper(II) glyoximate, 0799  
Iron(II) maleate, 1393  
Iron(III) maleate, 3447  
Lanthanum 2-nitrobenzoate, 3815  
Lead 2-amino-4,6-dinitrophenoxide, 3469  
Lead bromate, 0278  
Lead hyponitrite, 4745  
Lead(II) nitrate phosphinate, 4468  
Lead oleate, 3895  
Lead(II) phosphinate, 4531  
Lead(II) phosphite, 4535  
Lead(II) picrate, 3436  
\* Lead(II) thiocyanate, 1000  
Lead 2,4,6-trinitroresorcinoxide, 2071  
Lead(II) trinitrosobenzene-1,3,5-trioxide, 3594  
Manganese(II) phosphinate, 4519  
Manganese picrate hydroxide, 3742  
Nickel 2,4-dinitrophenoxide hydroxide, 3745  
Nickel 2-nitrophenoxide, 3464  
Nickel picrate, 3435

- \* 5-Nitrosalicylhydrazide, 2778
- Scandium 3-nitrobenzoate, 3816
- Silver osmate, 0034
- Thallium bromate, 0260
- Thallium(I) methanediazoate, 0458
- Thallium(I) 2- or 4-nitrophenoxide, 2187
- Thallium *aci*-phenylnitromethanide, 2723

*See also* METAL AZIDES, METAL CYANIDES (AND CYANO COMPLEXES), *N*-METAL DERIVATIVES

#### HETEROCYCLIC *N*-SULFINYLAMINES

Het-N=S=O

Butler, R. N. *et al.*, *Chem. & Ind.*, 1986, 750; *J. Chem. Soc., Perk. Trans. 2*, 1989, 1855

A range of the title compounds were prepared by treating the amines with sulfinyl chloride in benzene. Purification by vacuum distillation led to violent explosions of some of those with 5 membered rings containing two or more heteroatoms on a number of occasions. It is essential to keep the distillation temperature below 60°C.

*See other* N-S COMPOUNDS

#### HEXAFLUOROCHLORONIUM SALTS

[ClF<sub>6</sub>]<sup>+</sup> Z<sup>-</sup>

1. Christe, K. O., *Inorg. Chem.*, 1973, **12**, 1582
2. Roberts, F. Q., *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 737

These are very powerful oxidants and react explosively with organic materials or water [1]. They are not in themselves explosive, contrary to an earlier report [2].

*See other* OXIDANTS

#### HEXAMETHYLNITRATODIALUMINATE SALTS

M<sup>+</sup> [Al<sub>2</sub>(Me)<sub>6</sub>NO<sub>3</sub>]<sup>-</sup>

Atwood, J. L. *et al.*, *J. Organomet. Chem.*, 1978, **155**, 2

In the series of air-sensitive title salts, the potassium, rubidium or caesium salts ignite on exposure to air, and the tetramethyl- or tetraethyl-ammonium salts ignite with violence.

*See other* PYROPHORIC MATERIALS

#### HIGH-NITROGEN COMPOUNDS

Benson, F. R., *The High-Nitrogen Compounds*, New York, Wiley-Interscience, 1984

The major portion of the book (Ch. 2, pp 2–262) deals with the thermal stability of groups of these compounds in a series of tables.

This class heading is intended to include not only those compounds containing a high total proportion of nitrogen (up to ~90%) but also those containing high local concentrations in substituent groups (notably azide, diazo and diazonium) within the molecule. Many organic molecular structures containing several chain-linked

atoms of nitrogen are unstable or explosive and the tendency is exaggerated by attachment of azide or diazonium groups, or a high-nitrogen heterocyclic nucleus. Closely related but separately treated classes and groups include:

AZIDES (in several groups)  
DIAZOAZOLES  
DIAZO COMPOUNDS  
DIAZONIUM SALTS (in several groups)  
HYDRAZINIUM SALTS  
*N*-NITRO COMPOUNDS  
TETRAZOLES  
TETRAZENES  
TRIAZENES  
TRIAZOLES

Individually indexed compounds are:

1-Acetyl-4-(4'-sulfophenyl)-3-tetrazene, 2982  
Aluminium azide, 0082  
Aluminium tetraazidoborate, 0059  
Aminoguanidine, 0507  
1-Amino-3-nitroguanidine, 0495  
5-Aminotetrazole, 0461  
5-Amino-1,2,3,4-thiatriazole, 0413  
4-Amino-4*H*-1,2,4-triazole, 0812  
Ammonium azide, 4526  
Azidoacetonitrile, 0714  
Azido-2-butyne, 1473  
2,2'-Azobis(2-amidiniopropane) peroxodisulfate  
3,3'-Azo-(1-nitro-1,2,4-triazole), 1401  
Benzotriazole, 2269  
1,3-Bis(5-amino-1,3,4-triazol-2-yl)triazene, 1576  
Bis(1-benzo[*d*]triazolyl) carbonate, 3598  
Bis(1-benzo[*d*]triazolyl) oxalate, 3629  
Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt, 3868  
1,6-Bis(5-tetrazolyl)hexaaza-1,5-diene, 0827  
3,4-Bis(1,2,3,4-thiatriazol-5-ylthio)maleimide, 2073  
5-*tert*-Butyl-3-diazo-3*H*-pyrazole, 2831  
Carbonic dihydrazide, 0508  
Cyanodiazaoacetyl azide, 1346  
Copper(II) 1,3-di(5-tetrazolyl)triazene, 1429  
5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1345  
Cyanoguanidine, 0813  
Cyanohydrazonoacetyl azide, 1083  
2,3-Diazido-1,3-butadiene, 1437  
1,2-Diazidocarbonylhydrazine, 0720  
Diazidomethyleneazine, 1021



Diazidomethylenecyanamide, 1017  
 2,3-Diazidopropionitrile, 1121  
 2,6-Diazidopyrazine, 1400  
 2-Diazo-2H-imidazole, 1082  
 2-Diazonio-4,5-dicyanoimidazolide, 2050  
 3-Diazoniopyrazolide-4-carboxamide, 1399  
 3-Diazo-5-phenyl-3*H*-pyrazole, 3118  
 4-Diazo-5-phenyl-1,2,3-triazole, 2910  
 3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2909  
 4-Diazo-1,2,3-triazole, 0678  
 3-Diazo-3*H*-1,2,4-triazole, 0677  
 1,5-Diphenylpentaazadiene, 3507  
 5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3677  
 Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1853  
 1-Ethyl-1,1,3,3-tetramethyltetrazenium tetrafluoroborate, 2586  
 Formylhydrazine, 0473  
 1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1.3.5-triphosphorine, 4795  
 Hydrazinium azide, 4550  
 Hydrazinium chloride, 4007  
 5-Hydrazino-1,2,3,4-thiatriazole, 0462  
 5,5'-Hydrazotetrazole, 0826  
 1-Hydroxybenzotriazole, 2272  
 1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0817  
 \* Lithium hexaazidocuprate(4-), 4278  
 \* Lithium tetraazidoaluminate, 0081  
 \* Lithium tetraazidoborate, 0151  
 Methyl 3,3-diazido-2-cyanoacrylate, 1824  
 Methylenebis(3-nitramino-4-methylfurazan), 2805  
 1-Methyl-1,2,3-triazole, 1189  
 Nitrosyl azide, 4766  
 3-Nitro-1,2,4-triazolone, 0716  
 Pentazole, 4443  
 3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2804  
*N*-Phenyl-1,2,3,4-thiatriazolamine, 2729  
 Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide  
 Sodium 5-azidotetrazolide, 0551  
 \* Sodium hexaazidophosphate, 4794  
 Tetraallyl-2-tetrazene, 3545  
 \* *trans*-Tetraamminediazidocobalt(III) *trans*-diamminetetraazido-  
 cobaltate(1-)

Tetraazido-1,4-benzoquinone, 2633  
 Tetraimide, 4527  
 1,3,4,6-Tetrakis(2-methyltetrazol-5-yl)-hexaaza-1,5-diene, 3013  
 Tetramethyl-2-tetrazene, 1759  
 1,3,6,8-Tetraphenyloctaazatriene, 3849  
 1,2,4,5-Tetrazine, 0715

2,4,6-Triazido-1,3,5-triazine, 1348  
1,2,4-Triazole-3-diazonium nitrate, 0680  
1,3,5-Triphenyl-1,4-pentaazadiene, 3754

## HIGH PRESSURE REACTION TECHNIQUES

1. Rooymans, C. J. M. in *Preparative Methods in Solid State Chemistry*, Hagenmuller, P. (Ed.), New York, Academic Press, 1972
2. *High Pressure Safety Code*, London, High Pressure Association, 1975
3. Paauwe, J., *High Press. Technol.*, 1977, **1**, 13–28
4. Jercinovic, L. M., *Plant/Oper. Progr.*, 1984, **3**, 34–37
5. Mehne, P. H., *Plant/Oper. Progr.*, 1984, **3**, 37–39
6. Franko-Filipasic, B. R. *et al.*, *Chem. Eng. Progr.*, 1984, **80**(3), 65–69
7. Livingston, E. H., *Chem. Eng. Progr.*, 1984, **80**(3), 70–75
8. Sherman, W. F., *Experimental Techniques in High-pressure Research*, New York, Wiley, 1987

The chapter which reviews high-pressure (HP) techniques in liquid and gas systems for preparative purposes also includes safety considerations [1]. The Code deals mainly with mechanical hazards, but attention is drawn to the fact that application of HP to chemical systems may influence stability adversely [2]. The forces and energy involved in HP systems, and the causes and elimination of accidents in HP operations are reviewed [3]. Design procedures and checklists [4] and training methods [5] relevant to safety in HP operations are discussed. The design features of two HP research laboratories are detailed, including use of remote manipulation for hazardous reaction studies [6]. Operational factors to minimise hazards in HP facilities, including operator training, equipment inspection and maintenance, are presented [7]. A new handbook deals with the design, construction and safe operation of equipment for research at high pressures [8].

## HIGH RATE DECOMPOSITION

Gibson, N. *et al.*, *Runaway Reactions*, 1981, Paper 3/R, 1–14

Some compounds not classified as deflagrating or detonating explosives can decompose violently (deflagrate), and account of this must be taken in designing powder handling plant, which is now usually totally confined. Compounds of this type, often with an oxygen balance around –200, usually decompose when heated with a high rate of decomposition. Those compounds below were examined for ease of initiation when exposed to friction or localised heating, in both open or closed systems. Individually indexed compounds are:

2-Acetylamino-3,5-dinitrothiophene, 2280  
2-Amino-3,5-dinitrothiophene, 1421  
1,5-(or 1,8-)Bis(dinitrophenoxy)-4,8-(or 4,5-)dinitroanthraquinone, 3860  
2-Bromo-4,6-dinitroaniline, 2132  
4-Bromo-2,6-dinitroaniline, 2133  
2-Chloro-4,6-dinitroaniline, 2153  
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1954

2-Formylamino-3,5-dinitrothiophene, 1823  
2-Hydroxy-6-nitro-1-naphthalenediazonium-4-sulfonate, 3240  
2-Methoxyanilinium nitrate, 2829

*See entries* CRITICAL IGNITION TEMPERATURE, DEFLAGRATION INCIDENTS

### HIGH SURFACE-AREA SOLIDS

Smith, E. A., *Processing*, 1977, (11), 35–37

The reactivity of solids may change dramatically as they are ground to sub-micron sizes. Graphite becomes pyrophoric at 400 m<sup>3</sup>/g, and if ground under nitrogen to 600 m<sup>3</sup>/g, cyanogen is produced by direct combination of the elements. Sulfur becomes highly reactive at lower micron sizes, and iron becomes liable to explosive oxidation when ground to below 1 μ. Theoretical aspects of the great increase in surface energy are discussed.

### HIGH VALENCY METAL FLUORIDES

Dukat, W. W., *et al.*, *J. Chem. Soc., Chem. Comm.*, 1993, (18), 1429

High valency transition metal fluorides may react violently with organic materials, not only by fluorinating, C-H bonds but also by exchange reactions with organochlorine compounds. Thus osmium and iridium hexafluorides reacted explosively with a fewfold excess of dichloromethane, unless judiciously cooled with liquid nitrogen, even at sub-gram scale. Such compounds usually also react vigorously with water and other nucleophiles (Editor's comment).

### HOPCALITE

Kirk-Othmer, 1996, Vol. 17, 216

An oxidation catalyst containing cobalt, copper, manganese and silver species. It adsorbs nitroalkanes strongly, which may then ignite. Respirator cartridges containing it should not be used in high concentrations of nitroalkanes.

*See* NITROALKANES

### HYDRAZINE METAL MALONATES AND SUCCINATES

1. Sivasankar, B. N. *et al.*, *Synth. React. Inorg. Met.-Org. Chem.*, 1994, **24**(9), 1573

2. Sivasankar, B. N. *et al.*, *Mater. Res. Bull.*, 1996, **31**(1), 47

Several octahedral dihydrazine metal (II) salts of this class were prepared and thermally decomposed. The succinates and malonates of nickel and cadmium decomposed explosively [1]. A later paper on mixed metal bis-hydrazine malonates of cobalt with magnesium, manganese, nickel, zinc or cadmium recommends that decomposition, in a pre-heated crucible at 500°C, be of small quantities only. The same workers have reported exothermic decomposition of similar hydrazine complexed salts of other small organic acids.

Individual Compounds are:

Dihydrazinecadmium(II) malonate, 1324

Dihydrazinecadmium(II) succinate, 1741

Dihydrazinenickel(II) malonate, 1328

Dihydrazinenickel(II) succinate, 1760

See also AMMINOMETAL OXOSALTS

## HYDRAZINOMETAL NITRATES



1. Médard, L. *et al.*, *Mém. Poudres*, 1952, **34**, 159–166

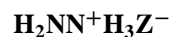
2. Patel, K. C. *et al.*, *Synth. React. Inorg. Met.-Org. Chem.*, 1982, **12**(4), 383

Hydrazine complexes of cadmium, cobalt, manganese, nickel and zinc nitrates were prepared as possible initiator materials. Dihydrazinemanganese(II) nitrate ignites at 150°C but is not shock-sensitive, while trihydrazinecobalt(II) nitrate, which decomposes violently at 206–211°C or in contact with conc. acids, and trihydrazinenickel(II) nitrate (deflagrates at 212–215°C) are fairly shock-sensitive. Trihydrazinecadmium nitrate (defl. 212–245°C) and trihydrazinezinc nitrate are of moderate and low sensitivity, respectively [1]. A later study covers the same ground, adding trihydrazineiron(II) nitrate and dihydrazinecadmium(II) nitrates to the list of potential primary explosives, but reporting the dihydrazinemagnesium salt as not shock-sensitive. This work also covered some dihydrazinemetals azides and perchlorates, those of Mg were not shock sensitive but the azides of Co, Ni, and Zn were [2]. The combination of an endothermic fuel, an oxidant and catalytic metals—mostly having 1 electron transitions capable of initiating radical reactions—might be predicted to be sensitive.

See Trihydrazinenickel(II) nitrate

See other AMMINOMETAL OXOSALTS

## HYDRAZINIUM SALTS



1. Mellor, 1940, Vol. 8, Suppl. 2.2, 84–86

2. Salvadori, R., *Gazz. Chim. Ital.* [2], 1907, **37**, 32

3. Levi, G. R., *Gazz. Chim. Ital.* [2], 1923, **53**, 105

Several salts are explosively unstable, including hydrazinium azide (explodes on rapid heating or on initiation by a detonator, even when damp), chlorate (explodes at m.p., 80°C), chlorite (also highly flammable when dry), hydrogen selenate, hydrogen sulfate (explodes when melted), nitrate, nitrite, and the highly explosive perchlorate and diperchlorate used as propellants [1,2,3].

Some examples are:

1,1-Diphenylhydrazinium chloride, 3519

Hydrazinium azide, 4550

Hydrazinium chlorate, 4010

Hydrazinium chloride, 4007

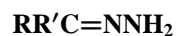
Hydrazinium chlorite, 4008

Hydrazinium dinitrate, 4561

Hydrazinium diperchlorate, 4068

Hydrazinium hydrogen selenate, 4558  
Hydrazinium nitrate, 4549  
Hydrazinium nitrite, 4548  
Hydrazinium perchlorate, 4011  
Hydrazinium salts, 4546  
*See* PROPELLANTS, REDOX COMPOUNDS

## HYDRAZONES



Glycols, Alkali hydroxides

1. Todd, D., *Org. React.*, 1948, **IV**, 8

This mixture is the Huang Minlon modification of the Wolff Kishner reaction. In the editor's experience it often leaps from the flask with sudden gas evolution. In addition to the expected nitrogen, at the operating temperature of around 200°C it is uncomfortably near the temperature of hydrogen evolution from glycol decomposition. The reduction proceeds much cooler in dimethyl sulfoxide or some of the alkoxyethanols as solvent.

*See* Sodium hydroxide: Glycols

## HYDROGENATION CATALYSTS

1. Augustine, R. L., *Catalytic Hydrogenation*, 23, 28, London, Arnold, 1965
2. Anon., *Chem. Brit.*, 1974, **10**, 367
3. Poles, T., private comm., 1973
4. Freifelder, 1971, 74, 78, 81–83, 168, 175, 262, 263
5. Jimenez, M. H., *Org. Prep. Proced. Int.*, 1978, **10**, 295–297

Many hydrogenation catalysts are sufficiently active to effect rapid interaction of hydrogen and/or solvent vapour with air, causing ignition or explosion. This is particularly so where hydrogen is adsorbed on the catalyst, either before a hydrogenation (Raney cobalt, nickel, etc.), or after a hydrogenation during separation of catalyst from the reaction mixture. Exposure to air of such a catalyst should be avoided until complete purging of hydrogen with an inert gas, such as nitrogen, has been effected. With catalysts of high activity and readily reducible substrates, control of the exotherm may be required to prevent runaway reactions, particularly at high pressures [1]. A proprietary form of Raney nickel catalyst in which the finely divided metal particles are coated with a fatty amine is claimed to be free of pyrophoric hazards if it dries out [2].

Platinum-metal catalysts are preferably introduced to the reactor or hydrogenation system in the form of a water-wet paste or slurry. The latter is charged to the empty reactor: air is removed by purging with nitrogen or by several evacuations alternating with nitrogen filling: the reaction mixture is charged, after which hydrogen is admitted. The same procedure applies where it is mandatory to charge the catalyst in the dry state, but in this case the *complete* removal of air before introduction of the reaction mixture and/or hydrogen is of vital importance.

Platinum, palladium and rhodium catalysts are non-pyrophoric as normally manufactured. Iridium and, more particularly, ruthenium catalysts may exhibit

pyrophoricity in their fully reduced form, and for this reason are usually manufactured in the unreduced form and reduced in situ. Spent catalysts should be purged from hydrogen and washed free from organics with water before storage in the water-wet condition. Under no circumstances should any attempt be made to dry a spent catalyst [3].

Specialist advice on safety and other problems in the use of catalysts and associated equipment is freely available from Engelhard Industries Ltd. at Cinderford in Gloucester, where a model high-pressure hydrogenation laboratory with full safety facilities is maintained.

In a volume devoted to hydrogenation techniques and applications, there are several references to safety aspects of catalytic hydrogenation. For noble metal and nickel catalysts, low boiling solvents should be avoided to reduce the risk of ignition when catalysts are added. Risks are highest with carbon-supported catalysts, which tend to float at the air interface of the solvent. The need for dilute solutions of nitro- and polynitro-aromatics or oximes, and for relatively low concentrations of catalysts to minimise the relatively large exotherms, are stressed [4]. A simple syringe-filter apparatus is described, which permits hazard-free rinsing, near-drying and transfer of palladium black catalysts [5].

Individually indexed catalysts are:

Iridium, 4643

Lanthanum–nickel alloy, 4678

Nickel, 4820

Palladium, 4885

Platinum, 4887

Rhodium, 4892

Ruthenium, 4894

*See* CATALYTIC NITRO REDUCTION PROCESSES, COPPER CHROMITE CATALYST

## HYDROGENATION INCIDENTS

Harak, J., *Stud. Sur. Sci. Catal.*, 1986, **27** (Catal. Hydrog.), 579–511

A comprehensive discussion of parameters and methods necessary for effective control of laboratory and industrial scale hydrogenation autoclaves, and the need for early recognition of hazardous situations is available.

For hazardous incidents involving hydrogenation,

*See* CATALYTIC NITRO REDUCTION PROCESSES

and the individual entries:

† Benzene, : Hydrogen, Raney nickel, 2288

Formic acid, : Palladium–carbon catalyst, 0418

† Hydrogen (Gas), : Acetylene, Ethylene, 4453

† Hydrogen (Gas), : Catalysts, Vegetable oils, 4453

† Hydrogen (Gas), : Ethylene, Nickel catalyst, 4453

† Hydrogen (Gas), : Palladium, 2-Propanol, 4453

Hydrogen peroxide, : Hydrogen, Palladium catalyst, 4477

3-Methyl-2-penten-4-yn-1-ol, 2384

1,1,1-Tris(azidomethyl)ethane, 1937

Tris(hydroxymethyl)nitromethane, 1664

*See other* UNIT OPERATION OR UNIT PROCESS INCIDENTS

*See also* CATALYTIC HYDROGENATION AUTOCLAVES

### HYDROXOOXODIPEROXOCHROMATE SALTS

**M[HO<sub>2</sub>Cr(O<sub>2</sub>)<sub>2</sub>O]**

Bailar, 1973, Vol. 3, 699

The ammonium, potassium, and thallium salts are all violently explosive. The entries are:

Ammonium hydroxooxodiperoxochromate(1-), 4230

Potassium hydroxooxodiperoxochromate(1-), 4227

Thallium hydroxooxodiperoxochromate(1-), 4228

*See other* PEROXOACID SALTS

### HYDROXYLAMINIUM SALTS

**HON<sup>+</sup>H<sub>3</sub> Z<sup>-</sup>**

Anon., *Chem. Processing (Chicago)*, 1963, **26**(24), 30

Some decompositions of salts of hydroxylamine are discussed, including violent decomposition of crude chloride solutions at 140° and exothermic decomposition of the solid sulfate at 170°C. The phosphinate and nitrate decompose violently above 92 and 100°C, respectively.

Some examples are:

Hydroxylaminium chloride, 4002

Hydroxylaminium nitrate, 4524

Hydroxylaminium perchlorate, 4005

Hydroxylaminium phosphinate, 4555

Hydroxylaminium sulfate, 4575

\* *N*-(Methylphenylphosphinoyl)hydroxylamine, 2823

*See other* N-O COMPOUNDS, OXOSALTS OF NITROGENOUS BASES

*See* Sodium nitrite

### 3-HYDROXYTRIAZENES

**N=N-NOH**

Houben-Weyl, 1965, Vol. 10.3, 717

Many of the 3-hydroxytriazene derivatives produced by diazo-coupling onto *N*-alkyl or *N*-aryl hydroxylamines decompose explosively above their m.p.s. However, the heavy metal derivatives are stable and used in analytical chemistry.

*See other* TRIAZENES

### HYPOHALITES

**ROX**

1. Sidgwick, 1950, 1218

2. Chattaway, F. D., *J. Chem. Soc.*, 1923, **12** 3, 2999

3. Anbar, M. *et al.*, *Chem. Rev.*, 1954, **54**, 927

4. Lewis, D. J., private comm., 1983

This class of organic oxidant compounds, all containing O–X bonds, includes widely differing types and many compounds of limited stability. Alkyl hypochlorites, readily formed from alcohols and chlorinating agents, will explode on ignition, irradiation or contact with copper powder [1,2]. Of the many alkyl hypochlorites described, only ethyl, *tert*-butyl and *tert*-pentyl are stable enough to isolate, purify and handle [3], though care is needed. Some of the lower alkyl hypochlorites are not as unstable or hazardous as was formerly thought [4]. There are the separately treated groups:

*See also* ACYL HYPOHALITES, BIS(FLUOROOXY)PERHALOALKANES

and the individually indexed compounds:

- \* Bromine(I) trifluoromethanesulfonate, 0312
- \* Chlorine fluorosulfate, 3975
- \* Chlorine(I) trifluoromethanesulfonate, 0320
- \* Chloroperoxytrifluoromethane, 0319
- Chloryl hypofluorite, 3973
- Difluoromethylene dihypofluorite
- Ethyl hypochlorite, 0851
- Fluorine perchlorate, 3976
- Heptafluoroisopropyl hypofluorite, 1035
- Heptafluoropropyl hypofluorite, 1060
- Hypochlorous acid, 3995
- Isopropyl hypochlorite, 1247
- Methyl hypochlorite, 0434
- Methyl hypofluorite, 0433
- Nitryl hypochlorite, 4026
- Pentafluoroselenium hypofluorite, 4368
- Pentafluorosulfur hypofluorite, 4367
- \* Pentafluorosulfur peroxyhypochlorite, 3990
- Pentafluorotellurium hypofluorite, 4369
- \* Perfluoro-*tert*-butyl peroxyhypofluorite, 1373
- Tetrafluoroiodosyl hypofluorite, 4356
- Trifluoromethyl hypofluorite, 0353

## IGNITION SOURCES

1. Howard, W. B., *Chem. Eng. Progr.*, 1970, **66**(9), 59–65
2. Enstad, G., *Reconsideration of the Concept of Minimum Ignition Energy*, Euro. Fed. Chem. Engrs. Wkg. Party, March 16th 1975
3. Kashiwagi, T., *Combustion Sci. Technol.*, 1980, **21**(3–4), 131–139
4. *Guidance on RF Ignition Hazards*, GS21, HMSO, 1983
5. Anon., *Fire Prev.*, 1983, **165**, 27–31
6. Baev, V. K. *et al.*, *Chem. Abs.*, 1984, **100**, 54018
7. McMillan, A. J., *Meas. Control*, 1986, **19**(7), 41–45
8. Anon., *Fire Prev.*, 1986, (194), 45
9. Bernard, F., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 683–704, Heidelberg, ISSA, 1987



10. *Ignition of Solids*, Vlyanov, V. L., Zarko, V. E., Amsterdam, Elsevier, 1989
  11. *Sources of Ignition*, Bond, J., Oxford, Butterworth-Heinemann, 1991
  12. Carson, P. A. *et al.*, *Loss Prev. Bull.*, 1992, 108
  13. Carleton, F. B. *et al.*, *Proc. Roy. Soc. London, Ser. A.*, 1994, **447**(1931), 513
- Some plant incidents involving unexplained ignition sources are detailed [1]. The reason why less energetic sparks will ignite a dust cloud while more energetic sparks will not is that the latter expel dust particles from the ignition zone, while the former do not [2]. The ignition of liquid decane under high intensity CO<sub>2</sub> laser irradiation (1–5 kW/cm<sup>2</sup>) was studied [3], as was ignition of flammable atmospheres by laser beams emergent from optical fibres for various wavelengths and targets [13]. A guide outlining the risks of RF radiation as ignition sources was published [4]. In a discussion of the principles affecting spark ignition of flammable gases and vapours, minimum ignition energies for 60 such materials are included [5]. Under certain conditions involving shock waves, hydrogen or methane released from cylinders at 20–200 bar into an air-filled chamber at 15°C/1 bar may ignite spontaneously [6].

BS 6656:1986, dealing with hazards of ignition by sparks induced by electromagnetic transmissions (radio, television, radar), is discussed in relation to the chemical, petrochemical and oil industries. For hydrogen, any transmission above 2 W radiated power is a potential ignition source [7]. An explosion in a spray drier producing powdered milk was initiated by mechanical failure of the atomiser head, rotating at 7,500 rpm and causing frictional sparks [8]. Causes of 2 cases of ignition at LPG filling stations were analysed. In one, ignition of propane occurred when filling clamps were applied to the cylinder, and in the second, ignition of butane occurred when a connecting hose burst [9]. Various aspects of the ignition of solids are covered in a recent book [10]. For an excellent summary of known causes of ignition in industry, with numerous case histories and some tables of properties [11].

A study of mechanisms and circumstances of spontaneous combustion with incidents and a list of susceptible materials [12]. Water is often involved.

Unexpected sources of ignition have led to many fires and explosions, usually in cases of leakage or spillage of flammable materials. Some examples are:

- FRictional Ignition of Gases and Vapours
- FRictional Initiation of Dust Clouds
- GRAVEL
- IRRADIATION DECOMPOSITION INCIDENTS
- SELF HEATING AND IGNITION INCIDENTS
- Aluminium–magnesium alloy: Iron(III) oxide, Water, 0053
- Aluminium–magnesium–zinc alloy, : Rusted steel, 0054
- Carbon dioxide, Flammable materials, 0557
- Carbon dioxide, Metals, 0557
- † Ethylene, Steel-braced tyres, 0781
- Oxygen (Liquid), Asphalt, 4832
- † Sulfur, Static discharges, 4897

## INCINERATOR DUST

See Diprotium monoxide: Incinerator dust

## INDIGESTION

1. Kimura, I. *et al.*, *Chem. Abs.*, 1993, **119**, 85759c
2. Sidebotham, G., *Chem. Phys. Processes Combust.*, 1995, 463

The afflatus of the human gut consists of carbon dioxide and hydrogen (not methane). A Japanese study of hydrogen generation as a hazard of bowel lavage solutions and a laxative is abstracted. Most produced hydrogen, especially the laxative, when incubated with dog faeces [1]. Use of nitrous oxide as an anaesthetic generates flammable gas mixtures in the intestines. Surgery with potential sources of ignition is to be avoided [2].

See Hydrogen (Gas), 4453

See also BATS

## INDUCTION PERIOD INCIDENTS

In the absence of anything to prevent it, a chemical reaction will begin when the components and any necessary energy of activation are present in the reaction system. If an inhibitor (negative catalyst or chain-breaker) is present in the system, it will prevent the onset of normal reaction until the concentration of the inhibitor has been reduced by decomposition or side reactions to a sufficiently low level for reaction to begin. This delay in onset of reaction is termed the induction period.

The existence of an induction period can interfere significantly with the course of a reaction where this involves either control of the rate of reaction by regulating the rate of addition of one of the reagents, or of the reaction temperature. In the absence of reaction, the concentration of the added reagent (or the temperature) may be increased to a level at which, once reaction does begin, it may accelerate out of control and become hazardous. It is essential, therefore, in the early stages of a reaction to ensure that the desired transformation has begun, particularly if large quantities of material are involved. This may be achieved by watching for a change in colour or appearance in the reaction mixture, for an increase in the rate of heat evolution (as judged from reflux rate, need for cooling, etc.), or by removal of a sample for chemical or instrumental testing.

Grignard reagents are notorious for the existence of induction periods, and an extensive account of methods for their elimination by various activation procedures is given at the beginning of the treatise on Grignard reactions by Kharasch and Reinmuth (1954). Another long-used method of promoting the onset of reaction in on-going processes is the addition to the reaction mixture of a small quantity of reaction mixture kept from a previous batch. When organolithium reagents were made from the metal and alkyl halides, they had an even worse reputation than Grignard reagents

Some relevant examples may be found in the group entries:

ALKYL NITRATES: Lewis acids

DIALKYLZINCS

GRIGNARD REAGENTS

OXIME CARBAMATES

and in the individual entries:

- † Acrylaldehyde
  - Aluminium tetrahydroborate, : Alkenes, Oxygen
  - Benzeneseleninic acid, : Hydrazine derivatives
  - Benzyltriethylammonium permanganate
  - Bis(4-hydroxyphenyl) sulfone
  - tert*-Butyllithium, : 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine
  - Calcium acetylide, : Methanol
- \* 2-Chloro-*N*-(2-hydroxyethyl)aniline
  - 2-Cyano-4-nitrobenzenediazonium hydrogen sulfate
  - 2,6-Dibromobenzoquinone-4-chloroimide
  - Dichlorine oxide
  - 2,6-Dichlorobenzoquinone-4-chloroimide
  - Diethyl acetylenedicarboxylate
  - Dimethyl 2-chloro-4-nitrophenyl thionophosphate
  - Dimethyl 3-chloro-4-nitrophenyl thionophosphate
  - Dimethyl 4-nitrophenyl thionophosphate
  - N,N*-Dimethyl-4-nitrosoaniline, : Acetic anhydride, Acetic acid
- † Dimethyl sulfoxide
  - 4,6-Dinitro-1,3-benzenediol
  - 2,4-Dinitrotoluene
  - Fluorine, : Water
  - Hydrogen chloride, : Chlorine, Dinitroanilines
  - Hydrogen peroxide
  - Hydrogen peroxide, : Nitrogenous bases
  - Lead(IV) oxide, : Carbon black, Chlorinated paraffin
  - Manganese(IV) oxide
  - Magnesium, : Methanol
  - Mercury(I) azide
- † Methanol, : Carbon tetrachloride, Metals
  - †Methyl acrylate
  - Nitric acid, : 1,3-Diacetoxybenzene
  - Nitric acid, : Formic acid
  - Phosphorus trichloride
  - Potassium dioxide
  - Potassium ethoxide
  - Sodium chlorite, : Phosphorus
  - Sodium dichromate, : Acetic anhydride
  - Sodium tetrahydroborate, : Dimethyl formamide
  - Succinodinitrile
- † Tetracarbonylnickel, : Oxygen, Butane
  - 2,4,6-Trichloro-1,3,5-triazine, : Dimethylformamide
  - 2,4,6-Tris(bromoamino)-1,3,5-triazine
  - Zinc, : Water

## INORGANIC ACIDS

H<sup>+</sup>

Many of the inorganic (mineral) acids have been involved in various incidents, either as catalysts or reactants, the most common, so far as frequency is concerned, being nitric acid in oxidation incidents. Individual acids are:

- Amidosulfuric acid, 4499
  - \* Bismuthic acid, 0228
  - Boric acid, 0144
  - Bromic acid, 0248
  - Chlorosulfuric acid, 3997
  - Chromic acid, 4229
  - Diamidophosphorous acid, 4547
  - Dioxonium hexamanganato(VII)manganate, 4553
  - Fluorophosphoric acid, 4297
  - Fluoroselenic acid, 4295
  - Hydriodic acid, 4423
  - Hydrogen azide, 4441
  - Hydrogen bromide, 0247
  - Hydrogen chloride, 3993
  - Hydrogen fluoride, 4294
  - Hydrogen hexafluorophosphate, 4360
  - Iodic acid, 4424
  - Nitric acid, 4436
  - Nitrosylsulfuric acid, 4438
  - Nitrous acid, 4435
  - Orthoperiodic acid, 4542
  - Orthophosphoric acid, 4505
  - Pentafluoroorthoselenic acid, 4354
  - Perchloric acid, 3998
  - Periodic acid, 4425
  - Permanganic acid, 4434
  - Peroxomonophosphoric acid, 4506
  - Peroxomonosulfuric acid, 4481
  - Phosphinic acid, 4503
  - Phosphonic acid, 4504
  - \* Sodium hydrogen sulfate, 4446
  - Sulfuric acid, 4479
  - Tetrafluoroboric acid, 0130
  - Tetraphosphoric acid, 4567
- See* ORGANIC ACIDS

## INORGANIC AZIDES

E(N<sub>3</sub>)<sub>x</sub>

1. Mellor, 1967, Vol. 8, Suppl. 2, 42
2. Evans, B. L. *et al.*, *Chem. Rev.*, 1959, **59**, 515
3. Deb, S. K. *et al.*, *Proc. 8th Combust. Symp.*, 1960, 289

Relationships existing between structure, stability and thermal, photochemical and explosive decomposition (sometimes spontaneous) of the inorganic azides has been extensively investigated and reviewed [1,2]. The ignition characteristics of explosive inorganic azides, with or without added impurities under initiation by heat or light have been discussed [3].

Relevant groups of inorganic azides are:

HALOGEN AZIDES, METAL AZIDE HALIDES,  
METAL AZIDES, NON-METAL AZIDES

## INORGANIC BASES

$\text{OH}^-$

Several of the inorganic bases have been involved in various laboratory or industrial scale incidents, individual entries being:

- † Ammonia, 4497
- Ammonium hydroxide, 4544
- Barium hydroxide, 0208
- Caesium amide, 4260
- Calcium carbonate, 0317
- Calcium hydroxide, 3928
- Calcium oxide, 3937
- Lead carbonate–lead hydroxide, 0726
- Lithium carbonate, 0533
- Magnesium carbonate hydroxide, 0534
- Magnesium oxide, 4695
- Potassium carbonate, 0531
- Potassium hydroxide, 4428
- Sodium carbonate, 0552
- Sodium hydroxide, 4445
- Sodium oxide, 4802

## INORGANIC PEROXIDES

$\text{O}_2^-$

1. Castrantas, 1970
2. Castrantas, 1965

The guide to safe handling and storage of peroxides also contains a comprehensive bibliography of detailed information [1]. The earlier publication contains tabulated data on fire and explosion hazards of inorganic peroxides [2].

See METAL PEROXIDES

PEROXOACIDS

PEROXOACID SALTS

Hydrogen peroxide, 4477

## INSULATION

1. Britton, L. G., *Plant/Oper. Progr.*, 1991, **10**(3) 27
2. McDermott, P. E., *Chem. Brit.*, 1976, **12**, 69

3. Markham, H., *Chem. Brit.*, 1976, **12**, 205
4. Carrettes, G. V., *Chem. Brit.*, 1976, **12**, 204
5. Hilado, C. J., *J. Fire Flamm.*, 1974, **5**, 326–333
6. Bowes, P. C., *Fires in Oil-Soaked Lagging*, CP35/74, Garston, Building. Res. Establ., 1974
7. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 32
8. McIntosh, A. C. *et al.*, *J. Chem. Soc., Faraday Trans.*, 1996, **92**(16), 2965

The porous and absorbent materials commonly used to lag industrial reactors may present active surfaces for the reaction of leaked contents with themselves or air. Resultant hotspots or fires can have devastating consequences, especially when endothermic materials are within. A study of exotherm and autoignition (from start temperatures as low as 65°C) of several polyamines, glycols, olamines and other compounds is detailed, together with an empirical method for predicting hazards from flash points and autoignition temperatures [1]. In these circumstances the temperature of ignition is often well below the conventionally determined AIT. Experiments showed an ignition temperature some 100–200°C below the AIT, depending on the nature of the oils and of the lagging material into which they were soaked [2]. The experimental technique was criticised on the grounds that excess air is supplied to the sample, whereas in practice access of air is often severely limited. An alternative procedure to simulate practice more closely is described, and the results for leakage of heat-transfer oils are given, ignition generally occurring at 160–200°C. The need for care to avoid fire when removing oil-contaminated lagging is stressed [3].

Attention was drawn to the existing test for the self-heating properties of textile oils, and the promoting (co-oxidant) effect of iron or copper in reducing the AIT of the oils [4]. The presence of combustibles incorporated into lagging materials during manufacture can give rise to significant self-heating effects in uncontaminated lagging [5]. The theoretical background and current experimental progress were reviewed [6]. Two incidents involving ignition of PCB heat transfer oil on calcium silicate lagging were reported. Foamed glass lagging appears to be advantageous for high-risk areas [7]. A computer model of lagging fire ignition has been developed [8].

*See* Ethylene oxide

*See also* PACKAGING INCIDENTS

## INTERHALOGENS

Kirk-Othmer, 1966, Vol. 9, 585–598

The fluorine-containing members of this group are oxidants almost as powerful as fluorine itself. Individually indexed compounds are:

Bromine fluoride, 0238

Bromine pentafluoride, 0243

Bromine trifluoride, 0241

Chlorine fluoride, 3971

Chlorine pentafluoride, 3989

Chlorine trifluoride, 3981

Iodine bromide, 0254  
Iodine chloride, 4013  
Iodine heptafluoride, 4378  
Iodine pentafluoride, 4355  
Iodine trichloride, 4139

## IODINE COMPOUNDS

Several iodine compounds are explosively unstable, individually indexed compounds being:

- 3-Acetoxy-4-iodo-3,7,7-trimethylbicyclo[4.1.0]heptane, 3544
- Ammonium iodate, 4513
- Ammonium periodate, 4514
- Azidoiodoiodonium hexafluoroantimonate, 4361
- [*I,I*-Bis(trifluoroacetoxy)iodo]benzene, 3239
- Boron triiodide, 0150
- 4-*tert*-Butyliodidylbenzene, 3319
- Caesium tetraperchloratiodate, 4161
- Calcium 2-iodylbenzoate, 3625
- Dicyanoiodonium triflate, 1048
- Diiodamine, 4426
- 1,2-Diiodobenzene, 2172
- 3,5-Dimethyl-4-[*I,I*-bis(trifluoroacetoxy)iodo]isoxazole, 3115
- \* 2-Ethoxy-1-iodo-3-butene, 2449
- Hexamethylenetetramine tetraiodide, 2471
- (Hydroxy)(oxo)(phenyl)- $\lambda^3$ -iodanium perchlorate, 2299
- Iodinated poly(sulfur nitride), 4622
- Iodic acid, 4424
- Iodine azide, 4621
- Iodine bromide, 0254
- Iodine chloride, 4013
- Iodine dioxide trifluoride, 4334
- Iodine heptafluoride, 4378
- \* Iodine isocyanate, 0524
- Iodine(V) oxide, 4627
- Iodine(VII) oxide, 4628
- Iodine pentafluoride, 4355
- Iodine(III) perchlorate, 4140
- Iodine triacetate, 2394
- Iodobenzene, 2249
- 4-Iodo-3,5-dimethylisoxazole, 1868
- Iododisilane, 4543
- 2(2-Iodoethyl)-1,3-dioxolane, 1928
- 1-Iodohepta-2,4-diene, 2393
- 3-Iodo-4-methoxy-4,7,7-trimethylbicyclo[4.1.0]heptane, 3412
- † 2-Iodopropane, 1252

† 3-Iodopropene, 1174  
 2-Iodosovinyl chloride, 0691  
 Iodosylbenzene, 2252  
 Iodosylbenzene tetrafluoroborate, 2295  
 4-Iodosyltoluene, 2753  
 4-Iodotoluene, 2750  
 † Iodotrimethylsilane, 1306  
 4-Iodylanisole, 2755  
 Iodylbenzene, 2253  
 2-Iodylbenzoic acid, 2681  
 4-Iodyltoluene, 2754  
 2-Iodylvinyl chloride, 0692  
 Nitrogen triiodide, 4633  
 Nitrogen triiodide–ammonia, 4635  
 Nitrogen triiodide–silver amide, 4634  
 $\mu$ -OxO-*I,I*-bis(trifluoroacetato-*O*)-*I,I*-diphenyliodine (III), 3698  
 Oxybisphenyliodonium bistetrafluoroborate, 3475  
 Orthoperiodic acid, 4542  
 Pentafluoriodosylbenzene, 2058  
 Periodic acid, 4425  
 9-Phenyl-9-iodafluorene, 3747  
 Phenyliodine(III) chromate, 2247  
 Phenyliodine(III) nitrate, 2251  
 Phenyl, phenylethynyliodonium perchlorate, 3635  
*I*-Phenyl-*I*-(*p*-toluenesulfonyloxy)-(2-azido-2-phenyl)vinyliodine(III)  
 Phosphorus triiodide, 4636  
 Poly(dimercuryimmonium iodide hydrate), 4455  
 Potassium iodate, 4619  
 Potassium periodate, 4620  
 Sodium iodate, 4624  
 Tetrafluoriodosyl hypofluorite, 4356  
 Tetraiodoarsonium tetrachloroaluminate, 0057  
 Tetraiododiphosphane, 4637  
 Tetraiodoethylene, 0986  
 1,1,1-Triacetoxy-1,2-benziodoxol-3-one, 3610  
 Trifluoroacetylminoiodobenzene, 2903  
 Trifluoromethyliodine(III) isocyanate, 1045  
 Triiodocyclopropenium iodide, 1339

***vic*-IODO-ALKOXY or -ACETOXY COMPOUNDS**

–C(I)–C(OR)– or –C(I)–C(OAc)–

Dimmel, D. R., *Chem. Eng. News*, 1977, **55**(27), 38

Treatment of 3,7,7-trimethylbicyclo[4.1.0]heptane ( $\Delta^3$ -carene) with iodine and copper acetate in methanol gave 3-iodo-4-methoxy-4,7,7-trimethylbicyclo[4.1.0]heptane. A 50 g sample exploded violently after standing at ambient temperature in a closed container for 10 days. This and the corresponding iodoacetoxy



compound showed large exotherms at 90°C on DTA examination,  $\Delta H$  for the latter substance being calculated as 4.19 MJ/mol (13.1 kJ/g). Similar products derived from methylcyclohexene also exhibited substantial exotherms from 60°C upwards. It is recommended that *vicinal* iodo-alkoxy or -acetoxy derivatives of terpenes should be handled very cautiously.

See IODINE COMPOUNDS

## ION EXCHANGE RESINS

### Ammonia solution

Colman, C., *Chem. Engrg.* (New York), 1980, **87**, 274

Passage of a conc. solution of ammonia through a column of the acid form of a cation exchange resin led to a sudden neutralisation exotherm which damaged the bed, owing to its poor heat dissipation characteristics.

### Dichloromethane

See Dichloromethane: Azide form of quaternary etc.

### Dichromates

1. Earle, H., *Chem. & Ind.*, 1979, 391
2. Ardern, T. V., *Chem. & Ind.*, 1972, 532

The possibility is discussed of cleaning organically fouled ion exchange resins by treatment with weakly acid dichromate solutions [1]. The dangers of using separate dichromate treatment (which produces very high loading on the resin), and then mineral acid treatment, which liberates very high concentrations of chromic acid and leads to violent or explosive oxidation of the organic material (or of the resin), are stressed [2].

See Nitric acid: Ion exchange resins

### Sugar solution

Colman, C., *Chem. Engrg.* (New York), 1980, **87**, 224

When passage of a sugar solution at 90°C through a weak-base anion exchange resin was interrupted, an explosion occurred. This was attributed to an exothermic Maillard reaction (interaction of an amino acid with a glycosidic OH group) under the poor heat transfer conditions in a particulate bed without fluid flow.

### Water

1. Anon., *Chem. Eng. News*, 1953, **31**, 5120
2. Anon., *Chem. Eng. News*, 1948, **26**, 1480
3. *MCA Case History No. 2155*

A three-year-old sample of ion exchange resin was soaked in dilute hydrochloric acid, and then charged into a 2.5 cm diameter glass column. After soaking in distilled water for 15 min, the tube burst violently, presumably owing to swelling of the resin. Process resins as far as possible before charging into a column [1]. The earlier incident involved a column, charged with dry resin, which burst when

wetted [2]. The case history involved dry resin which expanded and split a glass column when wetted with an aqueous salt solution.

### **IRRADIATION DECOMPOSITION INCIDENTS**

Several instances are recorded where the energy of activation needed to initiate decomposition of various (usually unstable) materials has been provided by radiation of various types. Such incidents may be found under the group entries:

CHLOROPHYLL  
DIOXYGENYL POLYFLUOROSALTS  
IGNITION SOURCES  
INORGANIC AZIDES

and in the individual entries:

Azidoacetic acid, 0774  
Benzoyl nitrate, 2689  
Bis(cyclopentadienyldinitrosylchromium), 3275  
\* Bis(methylcyclopentadienyl)peroxoniobium chloride, 3522  
Borazine, 0176  
Caesium pentafluorotelluramide, 4257  
Caesium tetraperchloratiodate, 4161  
\* Calcium hypochlorite, 3924  
† Carbon disulfide, 0560  
Carbonic diazide, 0550  
Chlorine dioxide, 4042  
Dicyclopentadienylperoxyniobium chloride, 3271  
Difluorodiazirine, 0342  
1,8-Diphenyloctatetrayne, 3788  
Glyceryl trinitrate, 1196  
Hexaoxygen difluoride, 4327  
Iodine(III) perchlorate, 4140  
1-Iodo-1,3-butadiyne, 1381  
Isopropyl hypochlorite, 1247  
Mercury(I) cyanamide, 0523  
Nitrogen (Liquid), 4735  
Nitrogen trichloride, 4143  
Plutonium(IV) nitrate, 4768  
Potassium perchlorate, 4018  
Potassium triazidocobaltate(1-), 4212  
Radon, : Water, 4893  
\* Silver acetylide-silver nitrate, 0569  
Silver azide, 0023  
Trifluoromethyl hypofluorite, : Hydrocarbons, 0353

## ISOCYANIDES

RN=C:

### Acids

Sidgwick, 1950, 673

Acid catalysed hydrolysis of isocyanides ('carbylamines') to primary amines and formic acid is very rapid, sometimes explosively so.

See DIISOCYANIDE LIGANDS

## ISOPROPYLIDENE COMPOUNDS

Me<sub>2</sub>C=C

### Ozone

See Ozone: Isopropylidene compounds

## ISOXAZOLES

Cardillo, P., *Chim. e Ind.* (Milan), 1988, **70**(6), 90–91

After an incident involving the violent decomposition of hot 3-methyl-5-aminoisoxazole, the thermal stability of 7 other isoxazole derivatives was studied by DSC, TGA and ARC. Only 4-amino-3-isoxazolidinone decomposed exothermally in an open crucible, but all did so in sealed capsules, evolving much gas. The results below give isoxazole derivative, ARC onset temperature of decomposition (°C)/adiabatic exotherm (°C)/max. pressure (bar); and DSC heat of decomposition (kJ/g), respectively for all 9 compounds.

Isoxazole, 136/611/23, 1.36; 5-methyl-, 171/535/10, 1.08; 3,5-dimethyl-, 210/687/17, 3-amino-, 115/791/19, 2.67; 3-carbonamido-5-methyl-, 155/792/11, 1.22; 3-amino-5-methyl-, 140/77/above 170 (vent), 1.97; 5-amino-3-methyl-, 90/650/above 170 (vent), 1.43; 4-amino-3-isoxazolidinone, 76/647/11, 1.67; 3-phenyl-5-isoxazolone, 105°/659°/9 bar, 0.985 kJ/g.

Individual entries are :

3-Aminoisoxazole, 1136

5-Aminoisoxazole-3-carbonamide, 1476

4-Amino-3-isoxazolidinone, 1137

3-Amino-5-methylisoxazole, 1501

5-Amino-3-methylisoxazole, 1502

3,5-Dimethylisoxazole, 1888

† Isoxazole, 1110

5-Methylisoxazole, 1468

3-Phenyl-5-isoxazolone, 3122

See other GAS EVOLUTION INCIDENTS, N–O COMPOUNDS

## JOJOBA WAX

(Esters of C<sub>20–22</sub> monoene acids and alcohols)

### Ozone

Zabicky, J. *et al.*, *J. Am. Oil Chem. Soc.*, 1986, **63**, 1547–1550

The solid diozonide prepared from jojoba wax decomposed violently at 110–120°C  
*See other* OZONIDES

### KETONE PEROXIDES

1. Davies, 1961, 72
2. Kirk-Othmer, 1967, Vol. 14, 777

The variety of peroxides (monomeric, dimeric, trimeric or polymeric) which can be produced from interaction of a given ketone and hydrogen peroxide is very wide (see type groups below for structures). The proportions of the products in the reaction mixture depend on the reaction conditions used as well as the structure of the ketone. Many of the products appear to coexist in equilibrium, and several types of structure are explosive and sensitive in varying degrees to heat and shock. Extreme caution is therefore required in handling ketone peroxides in high concentrations, particularly those derived from ketones of low MW. Acetone is thus entirely unsuitable as a reaction or cleaning solvent whenever hydrogen peroxide is used [1,2]. Relevant groups are:

CYCLIC PEROXIDES  
1-OXYPEROXY COMPOUNDS  
POLYPEROXIDES

Individually indexed compounds are:

Bis(2-hydroperoxy-2-butyl) peroxide, 3078  
3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane, 3052  
3,6-Di(spirocyclohexane)-1,2,4,5-tetraoxane, 3546  
3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane, 3195  
3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, 2517  
3,6,9-Triethyl-3,6,9-trimethyl-1,2,4,5,7,8-hexoxonane, 3562  
Tri(spirocyclopentane)1,1,4,4,7,7-hexoxonane, 3693

### KETOXIMINOSILANES

**RSi(ON=CMeEt)<sub>3</sub>**

Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3

During preparation of tris(ketoximino)silanes, two violent explosions attributed to acid-catalysed exothermic rearrangement/decomposition reactions occurred. Although these silane derivatives can be distilled under reduced pressure, the presence of acidic impurities (e.g. 2-butanone oxime hydrochloride, produced during silane preparation) drastically reduces thermal stability. Iron(III) chloride at 500 ppm caused degradation to occur at 150°, and at 2% concentration violent decomposition set in at 50°C.

*See* 2-Butanone oxime hydrochloride

*See other* OXIMES

## KINETICS AND INSTABILITY

Grewer, T., *DECHEMA Monograph*, 1980, 88(1818–1835), 21–30

One of the principal causes of batch chemical processes becoming unstable is the combination of a high reaction exotherm and a low reaction rate (or rates if there is more than one component reaction in the overall process). A secondary cause of reaction delay leading to instability is too little mass transfer. To permit safe operation of such reaction systems, the reaction energy (which may be expressed as a dimensionless reaction number) and the reaction rate(s) must be known. The possibility of there being a lower safe limit as well as an upper safe limit to reaction temperature is discussed.

## KJELDAHL METHOD

1. Beet, A. E., *J. R. Inst. Chem.*, 1955, **79**, 163, 269
2. McDonald, M. S., *Lab. Pract.*, 1979, **28**, 927
3. Pick, R. W., Internet, 1996

Possible hazards introduced by variations in experimental techniques in Kjeldahl nitrogen determination were discussed [1]. Modern variations involving use of improved catalysts and hydrogen peroxide to increase reaction rates, and of automated methods, have considerably improved safety aspects [2]. An anecdote is given of the classic technique when sodium hydroxide was to be added to the sulphuric acid digestion and was allowed to trickle down the wall of the flask. It layered over the sulphuric acid. Gentle mixing then provoked rapid reaction and a steam explosion [3].

## KRYPTON COMPOUNDS

Very few are known, all may be seen as derived from  $\text{FKr}^+$ . All are thermodynamically unstable and energetic fluorinating agents. Listed are:

Fluorohydrocyanokrypton hexafluoroarsenate, 0367

Fluorokrypton hexafluoroarsenate, 0096

Krypton difluoride, 4313

*See also* XENON COMPOUNDS

## LAGGING

*See* INSULATION

## LANTHANIDE IODIDE SILICIDES

## MISi

Mattausch, H. *et al.*, *Angew. Chem. (Int.)*, 1998, **37**(4), 499

The MISi compounds of Lanthanum, Cerium and Praseodymium, and two slightly less iodinated lanthanum derivatives were prepared by fusing stoichiometric mixtures of the triiodides, the metal and silicon. They ignite violently on contact with water.

## LANTHANIDE METAL NITROBENZOATES



See Lanthanum 2-nitrobenzoate

Scandium 3-nitrobenzoate, 3816

Yttrium 4-nitrobenzoate, 3817

See other HEAVY METAL DERIVATIVES, NITROARYL COMPOUNDS

## LANTHANIDE METALS

Oxidants

Bailar, 1973, Vol. 4, 70

While there are considerable variations in reactivity, several of the series of lanthanide metals ignite in halogens above 200°, in air or oxygen above 150–180°C, or lower in presence of moisture.

See Europium

See other METALS

## LANTHANIDE–TRANSITION METAL ALLOY HYDRIDES



Imamoto, T. *et al.*, *J. Org. Chem.*, 1987, **52**, 5695

Several lanthanide–transition metal alloys (LaNi<sub>5</sub>, PrCo<sub>5</sub>, SmCo<sub>5</sub>) readily absorb large volumes of hydrogen under mild conditions, and some of these alloy hydrides function as active hydrogenation catalysts: e.g., the title structures, which are pyrophoric in air. Analogous hydrides may be expected to behave similarly.

See HYDROGENATION CATALYSTS, PYROPHORIC MATERIALS

## LASSAIGNE TEST

1. Lance, R. C. *et al.*, *Microchem. J.*, 1975, **20**, 103–110
2. Taylor, D. A. H., *Chem. Brit.*, 1978, **14**, 70
3. Mumford, C., *Chem. Brit.*, 1978, **14**, 170
4. Ingham, P. L., *Chem. Brit.*, 1978, **14**, 326
5. Sugden, T. M. *et al.*, *Chem. Brit.*, 1978, **14**, 326
6. Turfitt, G. E., *Chem. Brit.*, 1979, **15**, 614
7. McCulloch, A., *Chem. Brit.*, 1979, **15**, 614
8. Boulton, L. H., *Educ. Chem.*, 1973, **10**, 231
9. Guthrie, R. D. *et al.*, *Chem. Brit.*, 1979, **15**, 614
10. Mazor, L., *Acta Chim. Acad. Sci. Hung.*, 1979, **101**, 3–6

Correspondence on safety aspects of the Lassaigne sodium fusion test [1]–[3] included a description of the use of 3 mm lengths of 2 mm sodium wire (from an enlarged die) as a convenient source of small pieces of sodium [4]. Subsequently the safer characteristics of zinc–calcium hydroxide [5], or zinc–sodium carbonate [6] fusion methods were propounded, though these methods may not always work with volatile fluoro compounds [7]. Overall advantage is claimed, however, for an oxygen combustion technique [8], using a flask fitted with a pressure-relieving (Bunsen) valve [9]. A safe development for organic compounds containing the

hetero elements S, P, As, halogens and/or metals is to fuse the compound with potassium in vacuo at 300–500°C. After treating the cooled melt with ethanol and then water, normal microanalytical detection of ions can be used [10].

### LEAD SALTS OF NITRO COMPOUNDS

Fogel'zang, A. E. *et al.*, *Chem. Abs.*, 1978, **88**, 63813

The lead salts of nitromethane, mono-, di- or tri-nitrophenols burn at faster rates (up to 640-fold) than the parent compounds. Lead salts of trinitromethane, trinitrobutyric acid or dinitro-benzoic or -p-toluic acids burn at slightly faster rates (up to 10-fold) than the parent compounds.

*See other* HEAVY METAL DERIVATIVES

### LECTURE DEMONSTRATIONS

1. Bodner, C. M., *J. Chem. Educ.*, 1985, **62**(12), 1105–1107

2. Schibeci, R. A., *Educ. Chem.*, 1988, **25**(5), 150–153

A variety of chemical lecture demonstrations involving unstable or highly reactive materials which have led to accidents are reviewed, and practical suggestions made to avoid such incidents [1]. Safety aspects are discussed and some relevant books and articles reviewed [2].

### LIGHT ALLOYS

Anon., *Fire Prot. Assoc. J.*, 1959, (44), 28

Experiments to determine the probability of ignition of gas or vapour by incandive sparks arising from impact of aluminium-, magnesium- and zinc-containing alloys with rusty steel are described. The risk is greatest with magnesium alloys, where the higher the magnesium content, the lower the impact energy necessary for incandive sparking. Wide ranges of ignitable gas concentrations (flammability limits) also tend to promote ignition.

*See* Iron(III) oxide: Aluminium and subsequent entries

Magnesium Metal oxides, 4403

*See also* THERMITE REACTIONS

### LIME FUSION

*See* Calcium hydroxide: Polychlorinated phenols, etc.

### LINSEED OIL

*FPA H90*, 1980

1. Watts, B. G., private comm., 1965

2. Taradoire, F., *Rev. Prod. Chim.*, 1925, **28**, 114–115

Cloths used to apply linseed oil to laboratory benches were not burned as directed, but dropped into a waste bin. A fire developed during a few hours and destroyed

the laboratory. Tests showed that heating and ignition were rapid if a draught of warm air impinged on the oil-soaked cloth. Many other incidents involving ignition of autoxidisable materials dispersed on absorbent combustible fibrous materials have been recorded [1]. Practical tests on the spontaneous combustion of cotton waste soaked in linseed oil and other paint materials had been reported 40 years previously [2].

*See also* INSULATION

## LIQUEFIED GASES

### Water

1. Urano, Y. *et al.*, *Chem. Abs.*, 1976, **84**, 107979; 1977, 86, 108970
2. Porteous, W. M. *et al.*, *Chem. Eng. Progr.*, 1976, **72**(5), 83–89
3. Fowles, G. R., *Science*, 1979, **204**, 168–169
4. Hixson, R. S., *Diss. Abstr. Int.*, 1981, **B41**, 3070–3078
5. Flock, R. A. *et al.*, *Proc. Amer. Phys. Soc. Top. Conf.: Shock Waves in Condensed Matter*, 1984, 273–276

The explosive phenomena produced by contact of liquefied gases with water were studied. Chlorodifluoromethane produced explosions when the liquid–water temperature differential exceeded 92°C, and propene did so at differentials of 96–109°C. Liquid propane did, but ethylene did not, produce explosions under the conditions studied [1]. The previous literature on superheated vapour explosions has been critically reviewed, and new experimental work shows the phenomenon to be more widespread than had been thought previously. The explosions may be quite violent, and mixtures of liquefied gases may produce overpressures above 7 bar [2]. Alternative explanations involve detonation driven by phase changes [3,4] and do not involve chemical reactions. Explosive phase transitions from superheated liquid to vapour have also been induced in chlorodifluoromethane by 1.0 J pulsed ruby laser irradiation. Metastable superheated states (of 25°C) achieved lasted some 50 ms, the expected detonation pressure being 4–5 bar [5]. *See* LIQUEFIED NATURAL GAS, SUPERHEATED LIQUIDS, VAPOUR EXPLOSIONS

## LIQUEFIED NATURAL GAS

*FPA H30*, 1974

### Organic liquids, or Water

1. Katz, D. L. *et al.*, *Hydrocarbon Proc.*, 1971, **50**, 240
2. Anon., *Chem. Eng. News*, 1972, **50**(8), 57
3. Yang, K., *Nature*, 1973, **243**, 221–222
4. *NFPA 59A*, Quincy (Ma), Natl. Fire Prot. Assocn., 1985

The quite loud ‘explosions’ (either immediate or delayed) which occur when LNG (containing usually high proportions of heavier materials) is spilled onto water are non-combustive and harmless [1]. Superheating and shock-wave phenomena are involved [2]. There is a similar effect when LNG of normal composition (90% methane) is spilled on to some C<sub>5</sub>C<sub>8</sub>hydrocarbons or methanol, acetone or



2-butanone [3]. A recent US National Fire Code covers site selection, design, construction and fire prevention aspects of LNG installations [4].

See SUPERHEATED LIQUIDS

## LIQUEFIED PETROLEUM GASES

1. Various authors, *J. Haz. Mat.*, 1988, **20**, 3–62
2. Anon., *Loss Prev. Bull.*, 1987, (77)
3. *NFPA 58, 59, 59A*, Quincy (Ma), Natl. Fire Prot. Assocn., 1989, 1989, 1985, resp.
4. *Institute of Petroleum Model Code of Safe Practice*, Vol. 1, New York, Wiley, 1987
5. *The Storage of LPG at Fixed Installations*, Health and Safety Executive (UK), 1987
6. *The Keeping of LPG in Cylinders and Similar Containers*, Guidance Note CS4, Health and Safety Executive (UK), 1986
7. *Safe Handling of LPG* (2 videos), Inst. Chem. Eng. Rugby (UK).

Complete issues are devoted to various aspects of the fire and explosion hazards associated with bulk storage and transportation of liquefied petroleum gases, including fire exposure tests, simulation and prediction of various effects with computer programs, and preventive measures [1] and actual incidents [2]. Users should consult statutory requirements and codes of practice[3,4,5,6]. A video training package is available [7]

See also CRYOGENIC LIQUIDS, LIQUEFIED GASES, LIQUEFIED NATURAL GAS

## LIQUID AIR

Liquid air, formerly used widely as a laboratory or industrial cryogenic liquid, has been involved in many violent incidents. Many of these have involved the increased content of residual liquid oxygen produced by fractional evaporation of liquid air during storage. However, liquid air (with ~30 vol% oxygen content) is still a powerful oxidant in its own right. Liquid nitrogen, now widely available, is recommended as a safer coolant than liquid air, though care is still necessary to prevent condensation of atmospheric oxygen during its use.

### Carbon disulfide

Biltz, W., *Chem. Ztg.*, 1925, **49**, 1001

A mixture prepared as a cooling bath exploded violently and apparently spontaneously.

### Charcoal

Taylor, J., *J. Sci. Instrum.*, 1928, **5**, 24

Accidental contact via a cracked glass trap caused a violent explosion. Nitrogen is a safer coolant.

## Ether

Danckwort, P. W., *Angew. Chem.*, 1927, **40**, 1317

Addition of liquid air to ether in a dish caused a violent explosion after a short delay. Previous demonstrations had been uneventful, though it was known that such mixtures were impact- and friction-sensitive.

## Hydrocarbons

McCartey, L. V. *et al.*, *Chem. Eng. News*, 1949, **27**, 2612

All hydrocarbons (and most reducing agents) form explosive mixtures with liquid air.

*See* Nitrogen (Liquid)

Oxygen (Liquid), 4832

## LITHIUM PERALKYLURANATES

Li[UR<sub>n</sub>]

Sigurdson, E. R. *et al.*, *J. Chem. Soc., Dalton Trans.*, 1977, 818

In a series of solvated lithium peralkyluranate(IV) and (V) complexes, all were pyrophoric and the former type may explode unpredictably at ambient temperature.

*See related* ALKYL METALS

*See other* HEAVY METAL DERIVATIVES, PYROPHORIC MATERIALS

## LUBRICANTS

Several incidents involving reaction of various oxidants with lubricants used in or on moving parts of chemical plant have occurred, and this possibility should be guarded against when oxidants are to be used in equipment with lubricated parts. Some incidents may be found under the entries:

Bromine trifluoride: Silicone grease, 0241

Chlorine: Silicones, 4047

Dinitrogen tetroxide: Laboratory grease, 4747

Nitric acid: Silicone oil, 4436

Oxygen (Gas): Oil films, 4831

Sodium bromate: Grease, 0257

## LYCOPodium POWDER

Kubala, T. A. *et al.*, *Chem. Abs.*, 1982, **96**, 145450

In a study of discharge ignition of air suspensions of the powder, it was found that the wall layers deposited from air dispersions were as easily ignited as the dispersions.

*See* DUST EXPLOSION INCIDENTS (references 25, 29)

## MAGNETIC STIRRERS

(Editor's opinion)

The magnetic stirrer hotplates now commonly used, whereby a follower on the bottom of the reaction vessel is impelled by an electric motor beneath, are not very

effective. They do not disperse explosive solids, liquids, or mixtures very well, usually leaving an annulus at the bottom. They do, however, grind this against the wall, especially when restarted after removal of the flask. Several explosions in this book seem likely to have been initiated thus. An overhead stirrer, which does not permit grinding between surfaces, is to be preferred, and generally mixes better too. Contrary to some recommendations, the magnetic stirrer is not a way to avoid ignition by sparking electric motors; it includes one and most flammable vapours are denser than air, settling downwards and not up. Probably the safest laboratory agitator is an overhead air-turbine motor, especially if run on nitrogen.

### MAXIMUM REACTION HEAT

Yoshida, T., *Handbook of Hazardous Reactions with Chemicals*, Tokyo, Tokyo Fire Dept., 1980

The calculated figures for maximum reaction heat which are given throughout this text for various reactive pairs of chemicals are quoted from the extensive tables given in the above book. The figures indicate the heat release that could occur in 1 g of a binary mixture at the composition calculated to give the maximum, with the heat release in kJ and the composition in wt% of the compound against which the MRH figure is given. Most values are given in the form MRH 2.45/66, indicating that the maximum reaction heat of 2.45 kJ/g is developed for a mixture containing 66% of the component A against which the figure is quoted. In some instances the values are in the form 2.45/99+ or 2.45/tr. In the former case this implies that the component A is decomposed catalytically by traces of the other component B, and in the latter case that traces of the component A catalyse decomposition of the other component B.

The book also gives a rating of probability of ignition for each reactive pair, based on whether the energy release is above 2.9 kJ/g (Grade A, high probability), between 1.25 and 2.9 (B, medium probability), between 0.42 and 1.25 (C, low probability) or below 0.42 kJ (D, nil). Nearly 400 pages of tables of binary mixtures are given in the book, but only the figures for binary mixtures already in this Handbook for other reasons have been inserted, to permit a rough correlation to be made between the calculated figures for energy release and the physical effects in the incidents described.

### MERCURY COMPOUNDS

A number of mercury compounds show explosive instability or reactivity in various degrees, including the group:

*See also* POLY(DIMERCURYIMMONIUM) COMPOUNDS

and the individually indexed compounds:

- \* Acetoxymercurio(perchloratodimercurio)ethenone, 1413
- \* Acetoxymercurio(perchloratomercurio)ethenone, 1412
- Allylmercury(II) iodide, 1173
- N,N*-Bis(bromomercurio)hydrazine, 0268
- N,N'*-Bis(chloromercurio)hydrazine, 4064

- \*  $\mu$ -1,2-Bis(cyanomercurio)ethanediylidenedimercury(II), 1798
- \* Bis(dimethylarsinyldiazomethyl)mercury, 2467
- Bis(ethoxycarbonyldiazomethyl)mercury, 2978
- 1,2-Bis(hydroxomercurio)-1,1,2,2-bis(oxydimercurio)ethane, 0708
- Bis-*N*(imidosulfurdifluoridato)mercury, 4342
- \* Bis(trimethylsilyl)mercury, 2593
- Chloratomercurio(formyl)methylenemercury(II), 0654
- Chloromercuriodiphenylgold, 3473
- \* Di[bis(trifluoromethyl)phosphido]mercury, 1375
- Diisopentylmercury, 3368
- \* Dimercury dicyanide oxide, 0983
- Dimethylmercury, 0907
- Diphenylmercury, 3480
- Dipropylmercury, 2537
- 2-Hydroxyethylmercury(II) nitrate, 0857
- Mercury(II) acetylide, 0975
- Mercury(II) amide chloride, 3999
- Mercury(I) azide, 4612
- Mercury(II) azide, 4604
- Mercury 5,5'-azotetrazolide, 0980
- Mercury bis(chloroacetylide), 1356
- Mercury(I) bromate, 0271
- Mercury(II) bromate, 0270
- Mercury(II) bromide, 0269
- Mercury(I) chlorite, 4080
- Mercury(II) chlorite, 4077
- Mercury(I) cyanamide, 0523
- \* Mercury(II) cyanate, 0977
- Mercury(II) cyanide, 0976
- Mercury(II) *aci*-dinitromethanide, 0707
- Mercury(I) fluoride, 4312
- Mercury(II) formohydroxamate, 0804
- Mercury(II) fulminate, 0978
- Mercury(I) hypophosphate, 4617
- Mercury(II) iodide, 4602
- Mercury(I) nitrate, 4609
- Mercury(II) nitrate, 4603
- Mercury nitride, 4615
- Mercury(II) 5-nitrotetrazolide, 0981
- Mercury(II) oxalate, 0982
- 'Mercury(I) oxide', 4613
- Mercury(II) oxide, 4605
- Mercury(II) *N*-perchlorylbenzylamide, 3651
- Mercury peroxide, 4606
- Mercury(II) peroxybenzoate, 3637
- Mercury(II) picrate, 3433

- Mercury(II) sulfide, 4607
- \* Mercury(II) thiocyanate, 0979
- Mercury(I) thionitrosylate, 4610
- 2-Methyl-1-nitratodimercurio-2-nitratomercuriopropene, 1592
- 2-Naphthalenediazonium trichloromercurate, 3248
- Poly(diazomethylenemercury), 0522
- Poly(dimercuryimmonium hydroxide), 4422
- Potassium tetracyanomercurate(II), 1797
- Sodium 2-hydroxymercurio-4-*aci*-nitro-2,5-cyclohexadienonide, 2171
- Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2111
- Tetra(3-aminopropanethiolato)trimercury perchlorate, 3582
- Tetrakis(hydroxymercurio)methane, 0471
- Trimercury tetraphosphide, 4616
- \* Tris(iodomercurio)phosphine, 4614

### METAL ABIETATES

Anon., *Fire Prot. Assoc. J.*, 1958, 255

Aluminium, calcium, cobalt, lead, manganese, sodium and zinc abietates ('resinates'), when finely divided are subject to spontaneous heating and ignition. Store in sealed metal containers away from fire hazards.

Individually indexed compounds are:

Aluminium abietate, 3917

Calcium abietate, 3900

Lead abietate, 3902

Manganese abietate, 3901

Sodium abietate, 3805

Zinc abietate, 3903

See *other* SELF-HEATING AND IGNITION INCIDENTS

### METAL ACETYLIDES

**C≡CM**

1. Brameld, V. F. *et al.*, *J. Soc. Chem. Ind.*, 1947, **66**, 346

2. Houben-Weyl, 1970, Vol. 13.1, 739

3. Rutledge, 1968, 85–86

4. Miller, 1965, Vol. 1, 486

5. Dolgopolskii, I. M. *et al.*, *Chem. Abs.*, 1947, **41**, 6721

6. Roger, E. C. *et al.*, *Inorg. Chim. Acta*, 1984, **90**(3), L47–L49

7. Köhn, J., *Chem. Abs.*, 1986, **104**, 212405

Previous literature on formation of various types of copper acetylides is discussed and the mechanism of their formation is examined, with experimental detail. Whenever a copper or copper-rich alloy is likely to come into contact with atmospheres containing [1] ammonia, water vapour and acetylene, or [2] lime-sludge, water vapour and acetylene, or a combination of these two, there is the probability of acetylide formation and danger of explosion. The action is aided by the presence

of air, or air with carbon dioxide, and hindered by the presence of nitrogen. Explosive acetylides may be formed on copper or brasses containing more than 50% copper when these are exposed to acetylene atmospheres. The acetylides produced by action of acetylene on ammoniacal or alkaline solutions of copper(II) salts are more explosive than those from the corresponding copper(I) salts [1]. The hydrated forms are less explosive than the anhydrous material [2].

Catalytic forms of copper, mercury and silver acetylides, supported on alumina, carbon or silica and used for polymerisation of alkanes, are relatively stable [3]. In contact with acetylene, silver and mercury salts will also give explosive acetylides, the mercury derivatives being complex [4]. Many of the metal acetylides react violently with oxidants. Impact sensitivities of the dry copper derivatives of acetylene, buten-3-yne and 1,3-hexadien-5-yne were determined as 2.4, 2.4 and 4.0 kg m, respectively. The copper derivative of a polyacetylene mixture generated by low-temperature polymerisation of acetylene detonated under 1.2 kg m impact. Sensitivities were much lower for the moist compounds [5]. Explosive copper and silver derivatives give non-explosive complexes with trimethyl-, tributyl- or triphenyl-phosphine [6]. Formation of silver acetylide on silver-containing solders needs higher acetylene and ammonia concentrations than for formation of copper acetylide. Acetylides are always formed on brass and copper or on silver-containing solders in an atmosphere of acetylene derived from calcium carbide (and which contains traces of phosphine). Silver acetylide is a more efficient explosion initiator than copper acetylide [7].

Individually indexed compounds in this often dangerously explosive class are:

- \* Acetylenebis(triethyllead), 3672
- \* Acetylenebis(triethyltin), 3674
- Barium acetylide, 0575
- \* Bis(dimethylthallium)acetylide, 2519
- 3-Buten-1-ynyldiethylaluminium, 3017
- 3-Buten-1-ynyldiisobutylaluminium, 3549
- 3-Buten-1-nyltriethyllead, 3357
- \* 1-Butoxyethyl 3-trimethylplumbylpropionate, 3552
- Caesium acetylide, 0614
- Calcium acetylide, 0585
- Copper(II) acetylide, 0615
- Copper(I) benzene-1,4-bis(ethynide), 3236
- Copper 1,3,5-octatrien-7-ynide, 2933
- Dicopper(I) acetylide, 0619
- Dicopper(I) 1,5-hexadiynide, 2165
- Dimethyl(phenylethynyl)thallium, 3298
- Dimethyl-1-propynylthallium, 1938
- Gold(I) acetylide, 0573
- Lithium acetylide, 0992
- Lithium bromoacetylide, 0580
- Lithium chloroacetylide, 0599
- Lithium 1-heptynide, 2834

- \* Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide, 1820
  - Lithium trifluoropropynide, 1046
  - Manganese(II) bis(acetylide), 1396
  - Mercury(II) acetylide, 0975
  - Mercury bis(chloroacetylide), 1356
  - 3-Methyl-3-buten-1-ynyltriethyllead, 3413
  - Monocaesium acetylide, 0661
  - Monolithium acetylide, 0673
  - \* Monolithium acetylide–ammonia, 0674
  - Monopotassium acetylide, 0671
  - Monorubidium acetylide, 0685
  - Monosilver acetylide, 0650
  - Monosodium acetylide, 0684
  - 1,3-Pentadiyn-1-ylcopper, 1819
  - 1,3-Pentadiyn-1-ylsilver, 1815
  - Potassium acetylide, 0987
  - 1-Propynylcopper(I), 1098
  - Rubidium acetylide, 1025
  - Silver acetylide, 0568
  - \* Silver acetylide–silver nitrate, 0569
  - Silver buten-3-ynide, 1408
  - \* Silver chloroacetylide, 0566
  - Silver cyclopropylacetylide, 1838
  - Silver 1,3,5-hexatrienide, 2052
  - Silver 3-hydroxypropynide, 1088
  - Sodium acetylide, 1022
  - Sodium bromoacetylide, 0581
  - Sodium chloroacetylide, 0601
  - Sodium ethoxyacetylide, 1478
  - Sodium methoxyacetylide, 1123
  - Sodium phenylacetylide, 2911
  - Strontium acetylide, 1026
  - Tetraethynylgermanium, 2895
  - Tetraethynyltin, 2901
  - Thallium(I) iodacetylide, 0984
  - \* Tributyl(phenylethynyl)lead, 3811
  - Triethynylaluminium, 2095
  - Triethynylantimony, 2125
  - \* Triethynylarsine, 2096
- See other* ACETYLENIC COMPOUNDS

## METAL ALKOXIDES

## M(OR)<sub>n</sub>

1. *Alkali and Alkali-Earth Metal Alkoxides*, Brochure, Troisdorf-Oberlaar, Dynamit Nobel AG, 1974

2. Hopper, S. P. *et al.*, *Synth. React. Inorg. Metal-Org Chem.*, 1977, **7**, 162; *J. Organomet. Chem.*, 1977, **134**, 178

An appendix to the brochure is devoted to safe handling of the alkoxides indicated by a suffixed asterisk in the list below, and not all of which are represented as indexed entries with page numbers. These materials are readily hydrolysed and the exotherm may ignite the solids in presence of moist air, the potassium derivatives being the most reactive. This tendency is increased by acidic conditions, and combustion of solids spreads rapidly. Potassium *tert*-butoxide is especially reactive towards a range of liquids and solvent vapours [1]. Heating of sodium methoxide, ethoxide or potassium *tert*-butoxide (at 100°C) must always be under nitrogen to prevent ignition, which occurs in presence of air, especially if moist [2].

*See* Potassium *tert*-butoxide: Acids, or Reactive solvents

Dicyclopentadienylchromium: Alcohols, 3273

Individually indexed compounds are:

- Aluminium isopropoxide, 3216
- \* Bis(2,4-pentanedionato)chromium, 3326
- Molybdenum hexamethoxide, 2596
- Potassium *tert*-butoxide, 1650
- Potassium ethoxide, 0861
- Potassium methoxide, 0450
- \* Potassium methylselenide, 0451
- Rhenium hexamethoxide, 2603
- Sodium ethoxide, 0878
- Sodium isopropoxide, 1270
- Sodium methoxide, 0464
- \* Sodium 2,2,2-trifluoroethoxide, 0705
- \* Tetrakis(butylthio)uranium, 3731
- \* Tetrakis(ethylthio)uranium, 3096
- Titanium butoxide, 3730
- Titanium(III) methoxide, 1317
- Titanium tetraisopropoxide, 3579
- Tungsten hexamethoxide, 2604
- Zinc ethoxide, 1704

## METAL AMIDOSULFATES

## H<sub>2</sub>NSO<sub>2</sub>OM

Metal nitrates or nitrites

Heubel, J. *et al.*, *Compt. rend. [3]*, 1963, **257**, 684

Heating mixtures of barium, potassium or sodium amidosulfates or amidosulfuric acid, with sodium or potassium nitrates or nitrites, leads to reactions which may be explosive. TGA plots are given.

Heating mixtures of barium, potassium or sodium amidosulfates or amidosulfuric acid, with sodium or potassium nitrates or nitrites, leads to reactions which may be explosive. TGA plots are given.



Barium amidosulfate, 0209  
Potassium amidosulfate, 4457  
Sodium amidosulfate, 4467  
*See other N-S COMPOUNDS*

### METAL AZIDE HALIDES

**MXN<sub>3</sub>**

Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 243  
Metal halides and halogen azides react to give a range of metal azide halides, many of which are explosive. Individually indexed compounds are:  
Azidopentafluorotungsten, 4358  
Chromyl azide chloride, 3968  
Diamminedichloroaminotrichloroplatinum(IV), 4179  
Molybdenum azide tribromide, 0288  
Molybdenum diazide tetrachloride, 4164  
Silver azide chloride, 0009  
Tin azide trichloride, 4146  
Titanium azide trichloride, 4147  
Titanium diazide dibromide, 0273  
Tungsten azide pentabromide, 0297  
Tungsten azide pentachloride, 4182  
Uranium azide pentachloride, 4181  
Vanadium azide tetrachloride, 4166  
Vanadyl azide dichloride, 4090  
*See AMMINEMETAL AZIDES*

### METAL AZIDES

**MN<sub>3</sub>**

1. Mellor, 1940, Vol. 8, Suppl. 2, 16–54
2. *Energetic Materials*, Fair, H. D. and Walker, R. F. (Eds.), Vols. 1 and 2, New York, Plenum, 1977

This large and well documented group of explosive compounds contains some which are widely used industrially [1]. The text gives a thorough treatment of all aspects of the physics and chemistry (Vol. 1) and of the applications (Vol. 2) of this important group of energetic compounds [2].

#### Acids

The majority of the metal azides are sensitive explosives and exposure to heat, friction or impact is usually undesirable. Contact of most azides, particularly readily soluble ones, with acids will produce hydrogen azide, itself an explosive and highly toxic low-boiling liquid. In presence of heavy metals, it may give other equally hazardous heavy metal azides. These may also be formed from contact of soluble azides with heavy metals.

*See Hydrogen azide*

### Halogenated solvents

Bretherick, L., *Chem. & Ind.*, 1986, 729; *Chem. Eng. News*, 1986, **64**(51), 2

Attention is drawn to the possibility of slow formation of explosive organic azides from long contact of halogenated solvents with metal azides.

*See* Dichloromethane: Azide form etc.

Relevant group entries are:

AMMINOMETAL AZIDES

AZIDE COMPLEXES OF COBALT(III)

and individually indexed compounds are:

- Aluminium azide, 0082
- \* Azidogermane, 4416
- Barium azide, 0214
- \* Bis(2-aminoethyl)aminocobalt(III) azide, 1775
- \* Bis(cyclopentadienyl)tungsten diazide oxide, 3285
- \* Bis(cyclopentadienyl)vanadium diazide, 3286
- Cadmium azide, 3957
- Caesium azide, 4262
- Calcium azide, 3936
- Cerium azide, 3966
- \* Chromyl azide, 4239
- Cobalt(II) azide, 4216
- Copper(I) azide, 4287
- Copper(II) azide, 4280
- \* Copper(II) azide hydroxide, 4270
- \* Diazo-bis(1,2-diaminoethane)ruthenium(II) hexafluorophosphate, 1789
- \* Dicarbonyl- $\pi$ -cycloheptatrienyltungsten azide, 3123
- \* Dicarbonylmolybdenum diazide, 0995
- \* Dicarbonyltungsten diazide, 1013
- \* Dodecamethyltetraplatinum(IV) azide, 3590
- \* Hydrogen hexaazidothallate(III), 4502
- \* Lead(IV) acetate azide, 2402
- Lead (II) azide, 4782
- Lead(IV) azide, 4790
- Lithium azide, 4685
- \* Lithium hexaazidocuprate(4-), 4278
- \* Lithium tetraazidoaluminate, 0081
- Magnesium azide, 4694
- \* Manganese(III) azide, 4702
- \* Manganese diazide hydroxide, 4433
- Mercury(I) azide, 4612
- Mercury(II) azide, 4604
- \* Methylcadmium azide, 0431
- Nickel azide, 4777
- Palladium(II) azide, 4783
- \* Pentaammineazidoruthenium(III) chloride, 4073

- \* Phenylthallium diazide, 2286
- \* Poly(dimercuryimmonium azide), 4611  
Potassium azide, 4652
- \* Potassium azidopentacyanocobaltate(3-), 1809
- \* Potassium hexaazidoplatinate(IV), 4665
- \* Potassium triazidocobaltate(1-), 4212  
Silver azide, 0023  
Sodium azide, 4758  
Sodium triazidoaurate(?), 0113  
Strontium azide, 4785
- \* Tetraamminecopper(II) azide, 4277
- \* *trans*-Tetraamminediazidocobalt(III) *trans*-  
diamminetetraazidocobaltate(1-), 4220
- \* Tetramethylammonium azidocyanatoiodate(I), 2006
- \* Tetramethylammonium azidocyanioiodate(I), 2005
- \* Tetramethylammonium azidoselenocyanatoiodate(I), 2005  
Tetramethyldigold diazide, 1739  
Thallium(I) azide, 4765
- \* Thallium(I) tetraazidothallate, 4792  
Zinc azide, 4786

#### METAL AZOTETRAZOLIDES

Reddy, G. O. *et al.*, *Thermochim. Acta*, 1983, **66**, 231–244

Of the four salts with  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$  and  $2\text{Na}^+$ , the thermal sensitivity and impact-, friction- and static spark-sensitivities decreased in that order, as expected.

These and other entries are:

Barium 5,5'-azotetrazolide, 0577

Disodium 5,5'-azotetrazolide, 1018

- \* Disodium 5,5'-azoxytetrazolide, 1019

Lead 5,5'-azotetrazolide, 1020

Mercury 5,5'-azotetrazolide, 0980

*See other* TETRAZOLES

#### METAL CHLORATES



*NSC 371*, 1977

Acids

1. Mellor, 1941, Vol. 2, 315

2. Stossel, E. *et al.*, US Pat. 2 338 268, 1944

In addition to being oxidants in contact with strong acids, metal chlorates liberate explosive chlorine dioxide gas. With conc. sulfuric acid, a violent explosion may occur unless effective cooling is used [1]. Heating a moist mixture of a metal chlorate and a dibasic organic acid (tartaric or citric acid) liberates chlorine dioxide diluted with carbon dioxide [2].

#### Ammonium salts

Mixtures are incompatible.

See Ammonium chlorate

#### Phosphorus, or Sugar, or Sulfur

1. Black, H. K., *School Sci. Rev.*, 1963, **44**(53), 462
2. *59th Ann. Rep. HM Insp. Explos. (Cmd. 4934)*, 5, London, HMSO, 1934
3. Berger, A., *Arbeits-Schutz.*, 1934, **2**, 20
4. Taradoire, F., *Chem. Abs.*, 1938, **32**, 1455<sub>6</sub>

The extremely hazardous nature of mixtures of metal chlorates with phosphorus, sugar or sulfur, sometimes with addition of permanganates and metal powders, frequently prepared as amateur fireworks, is stressed. Apart from being powerfully explosive, such mixtures are dangerously sensitive to friction or shock, and spontaneous ignition sometimes occurs [1]. Chlorates containing 1–2% of bromates or sulfur as impurities are liable to spontaneous explosion [3]. The danger of mixtures of chlorates with sulfur or phosphorus is such that their preparation without a Home Office licence was prohibited in the UK by Orders in Council over 50 years ago [2]. Mixtures of sulfur with lead, silver, potassium or barium chlorates ignited at 63–67, 74, 160–162 and 108–111°C, respectively [4].

#### Sulfur, Initiators

1. Taradoire, F., *Bull. Soc. Chim. Fr.*, 1942, **9**, 610–620
2. Ellern, 1968, 304
3. Chapman, D. *et al.*, *J. Pyrotech.*, 1997, (6), 30

The effect of initiators (diluted sulfuric acid, chlorine dioxide, sulfur dioxide or disulfur dichloride) on ignition of mixtures of barium, lead or potassium chlorates with sulfur was examined [1]. Presence of copper ion or metal (e.g. from a sieve) may also lead to explosion of such mixtures [2]. A review of hazards of sulphur/chlorate mixtures in the firework industry has been published [3].

Individually indexed compounds are:

Aluminium chlorate, 0065

Barium chlorate, 0205

Cadmium chlorate, 3952

Chloric acid, 3996

Lead(II) chlorate, 4105

Magnesium chlorate, 4083

Manganese(II) chlorate, 4087

Potassium chlorate, 4017

Silver chlorate, 0011

Sodium chlorate, 4039

Zinc chlorate, 4106

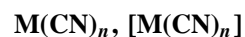
See other METAL HALOGENATES

**METAL CYANATES**

1. Singmaster, J. A., *Chem. Eng. News*, 1985, **63**(7), 2
2. Pilznienski, J. F., *Chem. Eng. News*, 1985, **63**(16), 2
3. Weast, 1979, D-67–D-79

Disregarding the differences in structure, it was argued that because the empirical formulae of fulminate and cyanate ions are identical, metal cyanates are likely to be as unstable as metal fulminates [1]. The results of practical tests, in which samples of various metal cyanates were heated in a flame, coupled with long industrial experience of the use of molten salt process baths containing over 40% of cyanates, show that the assumption on explosive instability of metal cyanates is not warranted [2]. The observation that silver or copper(II) cyanates burned smoothly on exposure to flame [2] suggests that the explosion recorded for silver cyanate (*ibid.*) may have involved close confinement or other unusual conditions during heating. Although mercury(II) cyanate (*ibid.*) vapourised gradually and completely without flaming on heating [2], two incidents of explosion during grinding or crushing operations have been recorded. The unusual tendency for many derivatives of silver and mercury to decompose forcefully (with separation of the metal, rather than the oxide as with other metals), suggests that other metal cyanates are likely to be rather more stable. This view is supported by available thermodynamic data [3], which show that while several cyanides are endothermic compounds, the few cyanates for which figures are quoted are all exothermic compounds and unlikely to be intrinsically unstable. A few reports of mishap could involve hydrolysis of the cyanate, liberating ammonia, followed by formation of "fulminating" noble metals. See Mercury(II) cyanate, Potassium cyanate, Silver cyanate

See also FULMINATING METALS

**METAL CYANIDES(AND CYANO COMPLEXES)**

1. von Schwartz, 1918, 399, 327; Pieters, 1957, 30
2. *Res. Rept. No. 2*. New York, Nat. Board Fire Underwriters, 1950

Several members of this (often endothermic) group of compounds which contain heavy metals tend to explosive instability, and most are capable of violent oxidation under appropriate circumstances. Fusion of mixtures of metal cyanides with metal chlorates, perchlorates, nitrates or nitrites causes a violent explosion [1]. Addition of one solid component (even as a residue in small amount) to another molten component is also highly dangerous [2]. Individually indexed compounds are:

- \* Ammonium hexacyanoferrate(II), 2577
- \* Barium thiocyanate, 0576
- \*  $\mu$ -1,2-Bis(cyanomercurio)ethanediylienedimercury(II), 1798
- Cadmium cyanide, 0588
- \* Chromyl isocyanate, 0613
- \* Chromyl isothiocyanate, 0612
- Copper(I) cyanide, 0620
- Copper(II) cyanide, 0616
- Copper(II) thiocyanate, 0618
- \* Dimercyry dicyanide oxide, 0983

Gold(I) cyanide, 0308  
 Iron(III) hexacyanoferrate(4-), 3739  
 Lead(II) cyanide, 0999  
 \* Lead(II) thiocyanate, 1000  
 \* Lithium thiocyanate, 0532  
 \* Mercury(II) cyanate, 0977  
   Mercury(II) cyanide, 0976  
 \* Mercury(II) thiocyanate, 0979  
 Nickel(II) cyanide, 0997  
 \* Potassium azidopentacyanocobaltate(3-), 1809  
   Potassium cyanide, 0526  
   Potassium hexacyanoferrate(II), 4279  
   Potassium hexacyanoferrate(III), 4242  
   Potassium octacyanodicyanocobaltate(8-), 2880  
 \* Potassium tetracyanomercurate(II), 1797  
   Potassium tetracyanotitanate(IV), 1800  
 \* Potassium thiocyanate, 0529  
 \* Silver cyanate, 0300  
   Silver cyanide, 0299  
   Sodium cyanide, 0536  
 \* Sodium pentacyanonitrosylferrate(2-), 1813  
 \* Sodium tetracyanatopalladate(II), 1802  
 \* Sodium thiocyanate, 0538  
   Zinc cyanide, 1004  
*See also* MOLTEN SALT BATHS, METAL THIOCYANATES

## METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

Although the C-F bond is a stronger than average single covalent bond, the extreme electronegativity of fluorine makes the formation of ionic fluorides far more favourable thermodynamically. The stability of organofluorine compounds is therefore largely kinetic. Although metallated organofluorine derivatives can often be isolated they are far from thermodynamically stable and may show it. Alkoxides derived from fluorinated alcohols and phenols have also exploded. Such compounds should be treated with caution if isolated and are best handled in solution. Salts of fluorinated acids are certainly more stable and have not yet been reported as giving trouble. The metals involved are usually lithium and aluminium, but cadmium, sodium, magnesium and zirconium also feature and the thermodynamic situation changes little, whatever the metal.

*See* Pentafluoroethylithium

Sodium

*See* FLUORINATED ORGANOLITHIUM COMPOUNDS

**N-METAL DERIVATIVES****N-M**

Many metal derivatives of nitrogenous systems containing one or more bonds linking nitrogen to a metal (usually, but not exclusively, a heavy metal) show explosive instability. Individually indexed compounds are:

- \* Amminebarium bis(nitrophenylide), 3518
- Amminepentahydroxyplatinum, 4571
- Ammonium nitridoosmate, 4523
- Antimony(III) nitride, 4729
- Barium nitride, 0219
- Barium nitridoosmate, 0213
- Barium perchlorylamide, 0203
- Barium *N*-perchlorylbzylamide, 3649
- Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt, 3868
- N,N*-Bis(bromomercurio)hydrazine, 0268
- N,N'*-Bis(chloromercurio)hydrazine, 4064
- Bis(dihydroxygold)imide, 0114
- Bis(dimethylamino)dimethylstannane, 2597
- Bismuth amide oxide, 0229
- Bismuth nitride, 0230
- cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615
- Cadmium amide, 3954
- Cadmium nitride, 3960
- Caesium amide, 4260
- Caesium nitride, 4266
- Caesium pentafluorotelluramide, 4257
- Calcium cyanamide, 0316
- Calcium nitride, 3946
- Cerium nitride, 3965
- Chromium nitride, 4237
- Cobalt(III) amide, 4201
- Cobalt(III) nitride, 4214
- Copper bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3861
- Copper(II) 1,3-di(5-tetrazolyl)triazene, 1429
- Copper(I) nitride, 4289
- Diamminedihydroxyosmium, 4572
- \* Dibutylthallium isocyanate, 3193
- Dilithium 1,1-bis(trimethylsilyl)hydrazide, 2595
- \* Dipyridinesodium, 3280
- Disilver cyanamide, 0305
- Disodium *N,N'*-dimethoxysulfonyldiamide, 0911
- Germanium imide, 4414
- Gold(I) nitride-ammonia, 0117
- Gold(III) nitride trihydrate, 0118
- \* Hexaamminecalcium, 3933
- Hexafluoroisopropylideneaminolithium, 1052
- \* Hydrogen hexaazidothallate(III), 4502

Lead bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3862  
 Lead(II) imide, 4439  
 Lead nitride, 4753  
 Lithium amide, 4462  
 Lithium bis(trimethylsilyl)amide, 2594  
 Lithium diethylamide, 1686  
 Lithium nitride, 4688  
 Lithium triethylsilylamide, 2578  
 Magnesium nitride, 4698  
 Mercury(II) amide chloride, 3999  
 Mercury(I) cyanamide, 0523  
 Mercury nitride, 4615  
 Mercury(II) *N*-perchlorylbenzylamide, 3651  
 Monopotassium perchlorylamide, 3994  
 Nitrogen triiodide–silver amide, 4634  
 Nitrosylruthenium trichloride, 4144  
 Pentaaminedinitrogenruthenium(II) salts, 4596  
 Pentakis(dimethylamino)tantalum, 3384  
 Pentasilver diamidophosphate, 0046  
 Pentasilver orthodiamidophosphate, 0044  
 Plutonium nitride, 4726  
 Poly(dimercuryimmonium hydroxide), 4422  
 \* Poly(disilicon nitride), 4757  
 Potassium amide, 4456  
 Potassium diethylamide, 1685  
 \* Potassium dinitrogentris(trimethylphosphine)cobaltate(1–), 3228  
 Potassium methylamide, 0472  
 Potassium nitride, 4671  
 Potassium nitridoosmate, 4651  
 Potassium perchlorylamide, 4019  
 Potassium sulfurdiiimide, 4664  
 Potassium thiazate, 4648  
 Potassium triamidothallate ammoniate, 4551  
 Potassium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide, 4672  
 Rhenium nitride tetrafluoride, 4344  
 Rubidium nitride, 4727  
 \* Seleninyl bis(dimethylamide), 1758  
 Silver amide, 0015  
 Silver 5-aminotetrazolide, 0392  
 Silver hexanitrodiphenylamide, 3429  
 Silver imide, 0030  
 Silver nitride, 0038  
 Silver *N*-nitrosulfuric diamidate, 0016  
 Silver *N*-perchlorylbenzylamide, 2734  
 Silver tetrazolide, 0366  
 Silver 2,4,6-tris(dioxoselena)perhydrotriazine-1,3,5-triide, 0039



3-Sodio-5-(5'-nitro-2'-furfurylideneamino)imidazolidin-2,4-dione, 2908  
 Sodium amide, 4465  
 Sodium 5-azidotetrazolide, 0551  
 Sodium *N*-chlorobenzenesulfonamide, 2229  
 Sodium diethylamide, 1688  
 Sodium hydrazide, 4500  
 Sodium nitride, 4723  
 Sodium tetrasulfur pentanitride, 4775  
 \* Sodium triamine, 4581  
 Tetrakis(dimethylamino)titanium, 3104  
 \* Tetramethylammonium amide, 1782  
 \* Tetraselenium tetranitride, 4771  
 Tetrasilver diimidodioxosulfate, 0043  
 Tetrasilver diimidotriphosphate, 0042  
 Tetrasilver orthodiamidophosphate, 0041  
 \* Tetratellurium tetranitride, 4773  
 Thallium(I) nitride, 4731  
 Thallium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide, 4761  
*N,N*,4-Trilithioaniline, 2180  
 Tris(dimethylamino)antimony, 2598  
 Trisilver tetranitride, 0040  
 Tris(thionitrosyl)thallium, 4764  
 Trithorium tetranitride, 4774  
 Uranium(III) nitride, 4732  
 Zinc bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3863  
 Zinc dihydrazide, 4563  
 Zirconium nitride, 4733  
 See METAL AZIDE HALIDES, METAL AZIDES, METAL HYDRAZIDES, NITRIDES, PER-  
 CHLORYLAMIDE SALTS

## METAL DUSTS

1. Jacobson, M. *et al.*, *Rept. Invest. 6516(9)*, Washington, US Bur. Mines, 1961
2. Brown, H. R., *Chem. Eng. News*, 1956, **34**, 87
3. Nedin, V. V. *et al.*, *Chem. Abs.*, 1972, **77**, 167636–167641
4. Martin, R., *Powder. Metall.*, 1976, **19**, 70–73
5. Alekseev, A. G. *et al.*, *Chem. Abs.*, 1977, **86**, 175311
6. Hulanichi, S. *et al.*, *Chem. Abs.*, 1977, **87**, 87208
7. Popov, E. I. *et al.*, *Chem. Abs.*, 1981, **94**, 194483
8. Cashdollar, K. L., *Proc. Safety Progress*, 1994, **13**(3), 139.
9. Schulz, W. D., *Korrosion* (Dresden), 1986, **17620**(1), 42–44
10. Burachonok, I. N., *Chem. Abs.*, 1987, **107**, 12139
11. Boiko, V. M. *et al.*, *Arch. Combust.*, 1988, **8**(2), 101

Of the 313 samples examined, the dust explosion hazards of finely divided aluminium, aluminium–magnesium alloys, magnesium, thorium, titanium and uranium, and the hydrides of thorium and uranium, are rated highest [1]. The

need to exercise caution when handling dusts of some recently introduced reactive metals was discussed briefly. Some form explosive mixtures, not only with air or oxygen, but also with nitrogen and carbon dioxide, reacting to give the nitride or carbonate. Intimate mixtures with generally non-oxidising oxosalts may also be explosive. Beryllium, cerium, germanium, hafnium, lithium, niobium, potassium, sodium, thorium, titanium, uranium and zirconium are discussed [2]. The pyrophoric capabilities of titanium and titanium–aluminium alloys were studied, the effect of particle size on flammability and explosion parameters of aluminium and magnesium powders dispersed in air was determined, and explosion hazards of aluminium, magnesium and aluminium-based alloy powders and use of inert gas media as preventives were assessed. In a study to determine explosivity of ferrochromium, ferromanganese, ferrosilicon, ferrotitanium, manganese and calcium–silicon powders, the latter proved to be the most active [3]. Metal dust and powder explosion risks were reviewed [4], including those during spraying operations in powder production [5]. Self-ignition characteristics and explosibility parameters were determined for dusts of aluminium, lead, magnesium, zinc and aluminium–magnesium alloys [6]. More accurate results (higher values) in determination of lower concentration limit for metal dusts are obtained in a conical explosion chamber [7]. Dust explosion studies (temperature, pressure, influence of particle size) on Mg, Al, Ti, Cr, Fe, Nb, Sn, Hf, Ta, W and the non-metals B, C, Si & S are reported. Under the conditions of test, Cu, Mo, Ni and Pb were not flammable [8]. Possible reasons for an explosion in a plant using acetylene–oxygen flame spraying of aluminium, tin–lead, or zinc were analysed [9]. The relationship between particle size of tool steel powders from machining operations and ignition temperatures in air suspensions or as a bed are expressed by two equations [10]. A study of ignition of metal powders in reflected shock waves is reported [11]. Relevant group entries are:

FERROALLOY POWDERS, FINELY DIVIDED METALS, THERMITE REACTIONS

## METAL FIRES

Mellottee, H., *Rév. Gen. Therm.*, (Fr), 1977, **16**, 523–538

Methods of extinguishing different types of metal fires are reviewed, with 86 references.

## METAL FULMINATES



1. Urbanski, 1967, Vol. 3, 157

2. Hackspill, L. *et al.*, *Chem. Abs.*, 1938, **32**, 4377a

The metal fulminates are all powerfully explosive. Of several salts examined, those of cadmium, copper and silver were more powerful detonators than mercury fulminate, while thallium fulminate was much more sensitive to heating and impact. Formally related salts are also explosive [1]. Sodium, potassium, rubidium and caesium fulminates are all easily detonated by feeble friction or heat. They all form double salts with mercury(II) fulminate which also explode readily, that of the rubidium salt at 45°C [2].

Individually indexed compounds are:

- Cadmium fulminate, 0589
- Copper(II) fulminate, 0617
- \* Dimethylthallium fulminate, 1211
- Mercury(II) fulminate, 0978
- Silver fulminate, 0301
- Sodium fulminate, 0537
- Thallium fulminate, 0539
- \* Tripropyllead fulminate, 3363

## METAL HALIDES

**MX<sub>n</sub>**

Members of this group have often featured as secondary reagents in hazardous combinations of chemicals. Individually indexed compounds are:

- Aluminium bromide, 0060
- Aluminium chloride, 0062
- Aluminium iodide, 0079
- Americium trichloride, 0090
- \* Ammonium bromide, 0251
- \* Ammonium chloride, 4001
- \* Ammonium fluoride, 4299
- \* Ammonium iodide, 4512
- \* Antimony(III) chloride oxide, 4041
- Antimony pentachloride, 4184
- Antimony trichloride, 4157
- \* Antimony trichloride oxide, 4150
- Beryllium chloride, 0221
- Beryllium fluoride, 0223
- \* Bis(1-chloroethylthallium chloride) oxide, 1591
- Bismuth pentafluoride, 0227
- \* *cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615
- Caesium fluoride, 4255
- Calcium bromide, 0262
- Calcium chloride, 3923
- \* Chloriminovanadium trichloride, 4165
- \* Chlorogermane, 3992
- Chromium(II) chloride, 4052
- Chromium(III) chloride, 4127
- Chromium pentafluoride, 4226
- \* Chromyl chloride, 4054
- Cobalt(II) bromide, 0263
- Cobalt(II) chloride, 4048
- Cobalt(III) chloride, 4122
- Cobalt trifluoride, 4200
- Copper(I) bromide, 0265
- Copper(I) chloride, 4056

- \* Dibromogermane, 0267
- Germanium tetrachloride, 4162
- Gold(III) chloride, 0111
- Indium bromide, 0289
- Iridium hexafluoride, 4362
- Iron(II) bromide, 0266
- Iron(III) bromide, 0286
- Iron(II) chloride, 4061
- Iron(III) chloride, 4133
- Iron(II) iodide, 4395
- Lead chloride, 4112
- Lead(II) fluoride, 4329
- Lead tetrachloride, 4172
- Magnesium chloride, 4081
- Manganese(II) chloride, 4085
- \* Manganese dichloride dioxide, 4086
- \* Manganese fluoride trioxide, 4301
- Manganese tetrafluoride, 4343
- \* Manganese trichloride oxide, 4141
- Manganese trifluoride, 4335
- Mercury(II) bromide, 0269
- Mercury(I) fluoride, 4312
- Mercury(II) iodide, 4602
- Molybdenum hexafluoride, 4365
- Molybdenum pentachloride, 4180
- Neptunium hexafluoride, 4366
- Osmium hexafluoride, 4370
- Palladium tetrafluoride, 4347
- Palladium trifluoride, 4341
- \* Pentaamminechlororuthenium chloride, 4137
- \* Phenylvanadium(V) dichloride oxide, 2246
- Platinum hexafluoride, 4371
- Platinum tetrafluoride, 4348
- Plutonium hexafluoride, 4372
- Potassium chloride, 4015
- \* Potassium heptafluorotantalate(V), 4379
- \* Potassium hexafluoromanganate(IV), 4363
- Potassium iodide, 4618
- \* Rhenium chloride trioxide, 4045
- Rhenium hexafluoride, 4373
- \* Rhenium nitride tetrafluoride, 4344
- \* Rhenium tetrachloride oxide, 4167
- Rhodium(III) chloride, 4155
- Rhodium tetrafluoride, 4349
- Ruthenium(III) chloride, 4156
- Silver chloride, 0008

Silver difluoride, 0014  
 Silver fluoride, 0013  
 Sodium chloride, 4036  
 Sodium iodide, 4623  
 Tantalum pentachloride, 4185  
 Tellurium tetrabromide, 0296  
 Thallium, 4922  
 Tin(II) chloride, 4116  
 Tin(IV) chloride, 4174  
 Tin(II) fluoride, 4331  
 Titanium(II) chloride, 4117  
 Titanium dibromide, 0284  
 Titanium diiodide, 4630  
 Titanium tetrachloride, 4176  
 Titanium tetraiodide, 4638  
 Titanium trichloride, 4158  
 \* Triethoxydialuminium tribromide, 2555  
 \* Triethylaluminium trichloride, 2556  
 Trirhenium nonachloride, 4196  
 Tungsten dichloride, 4119  
 Tungsten diiodide, 4631  
 Tungsten hexachloride, 4193  
 \* Tungsten tetrabromide oxide, 0294  
 Uranium hexachloride, 4192  
 Uranium hexafluoride, 4375  
 Vanadium dichloride, 4118  
 \* Vanadium tribromide oxide, 0292  
 Vanadium trichloride, 4159  
 \* Vanadium trichloride oxide, 4151  
 Zinc chloride, 4120  
 Zinc iodide, 4632  
 Zirconium(II) chloride, 4121  
 Zirconium dibromide, 0285  
 Zirconium tetrachloride, 4178  
 Zirconium tetraiodide, 4639  
 Zirconium trichloride, 4160  
*See also* METAL Pnictides

#### **METAL-HALOCARBON INCIDENTS**

1. Lenze, F. *et al.*, *Z. Ges. Schiess- u. Sprengstoffw.*, 1932, **27**, 255, 293, 337, 373; *Chem. Ztg.*, 1932, **56**, 921–923
2. Artz, G. D. *et al.*, *Sensitivity of Metal—Halogenated Solvent Combinations*, Rept. AD665057, Richmond (Va.), USNTIS, 1968
3. Cutler, D. P., *J. Haz. Mat.*, 1987, **17**(1), 99–108
4. U.S. Dept of Energy, 1994, HDBK-1081-94, (*Spontaneous Heating and Pyrophoricity*), 51

Various combinations of alkali- and alkaline earth-metals with halocarbon solvents were found to be highly heat- or impact-sensitive explosives [1]. Many combinations of more recently introduced metals with halocarbons have since been found hazardous, and the results of impact-testing of combinations of 9 powdered metals with 7 solvents are tabulated. Barium shavings showed the highest sensitivity [2]. Hazardous reactions of light metals (aluminium, magnesium, lithium, sodium, potassium) with halogenated hydrocarbons and polymers are reviewed, with 81 references [3]. Although largely a rehash of an earlier paper, a report describes several incidents in which carbon tetrachloride has contributed to ignition or explosion of zirconium, barium, sodium, uranium and plutonium [4].

Some examples of relevant incidents are:

- Barium, Halocarbons, 0200
- Beryllium, Halocarbons, 0220
- † Bromomethane, Metals, 0429
- Chloroform, Metals, 0372
- Plutonium, Carbon tetrachloride, 4888
- Samarium, 1,1,2-Trichlorotrifluoroethane, 4911
- Tin, Carbon tetrachloride, Water, 4912
- Titanium, Halocarbons, 4919
- Uranium, Carbon tetrachloride, 4923
- Zirconium, Carbon tetrachloride, 4928

*See also* HALOCARBONS: METALS

## METAL HALOGENATES



Metals and oxidisable derivatives, or  
Non-metals, or Oxidisable materials

1. Mellor, 1946, Vol. 2, 310; 1956, Vol. 2, Suppl. 1, 583–584; 1941, Vol. 3, 651
2. von Schwartz, 1918, 323

Intimate mixtures of chlorates, bromates or iodates of barium, cadmium, calcium, magnesium, potassium, sodium or zinc, with finely divided aluminium, arsenic, copper; carbon, phosphorus, sulfur; hydrides of alkali- and alkaline earth-metals; sulfides of antimony, arsenic, copper or tin; metal cyanides, thiocyanates; or impure manganese dioxide may react violently or explosively, either spontaneously (especially in presence of moisture) or on initiation by heat, friction, impact, sparks or addition of sulfuric acid [1]. Mixtures of sodium or potassium chlorate with sulfur or phosphorus are rated as being exceptionally dangerous on frictional initiation.

*See* METAL CHLORATES

Individually indexed compounds are:

- Barium bromate, 0202
- Barium iodate, Barium iodate, 0211
- Bromic acid, 0248
- Lead bromate, 0278

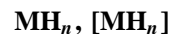
Mercury(I) bromate, 0271  
Potassium iodate, 4619  
Silver iodate, 0020  
Sodium iodate, 4624  
Zinc bromate, 0279  
*See other* METAL OXOHALOGENATES

### METAL HYDRAZIDES



*Hydrazine and its Derivatives*, Schmidt, F. W., New York, Wiley, 1984, 371  
This class of compounds has been little studied as they tend to explode during preparation and isolation. There are entries for:  
Calcium hydrazide, 3932  
Lithium hydrazide, 4496  
Sodium hydrazide, 4500  
*See also* N-METAL DERIVATIVES

### METAL HYDRIDES



1. Banus, M. D., *Chem. Eng. News*, 1954, **32**, 2424–2427
2. Mackay, 1966, 66
3. *Metal Hydrides*, Müller, W. M. *et al.*, New York, Academic Press, 1968
4. Hariguchi, S. *et al.*, *Chem. Abs.*, 1981, **94**, 159191
5. Vogman, L. P., *Chem. Abs.*, 1984, **101**, 116147
6. Klusever, P. A. A. *et al.*, *Angew. Chem. (Intern. Ed.)*, 1986, **25**, 465

Precautions necessary for safe handling of three main groups of hydrides of commercial significance were discussed. The first group (sodium hydride, lithium or sodium tetrahydroaluminates) ignite or explode in contact with liquid water or high humidity, while the second group (lithium, calcium, strontium or barium hydrides; sodium or potassium tetrahydroborates) do not. Burning sodium hydride is reactive enough to explode with the combined water in concrete. The 3rd group ('alloy' or non-stoichiometric hydrides of titanium, zirconium, thorium, uranium, vanadium, tantalum, and palladium) are produced commercially in very finely divided form. Though less pyrophoric than the corresponding powdered metals, once burning is established they are difficult to extinguish, and water-, carbon dioxide- or halocarbon-based extinguishers caused violent explosions. Powdered dolomite is usually effective in smothering such fires [1]. The trihydrides of the lanthanoid (rare earth) metals are pyrophoric in air and the dihydrides, though less reactive, must be handled under inert atmosphere [2]. A later reference states that finely divided metal hydrides of the second group (lithium, calcium, barium and strontium hydrides) will ignite in air or react violently, sometimes explosively, with water or air of high humidity [3]. In an examination of the lower concentration limits, explosion pressures and pressure-increase rates of a series of mixed metal hydride powders dispersed in air, hydrides of MgNi were the most hazardous [4]. The minimum oxygen concentrations for explosion of most volatile hydrides of group IIIA–VA elements is nearly zero, so complete

exclusion of air is essential for safe working. Presence of impurities in hydride mixtures increases the risk of ignition [5]. A new method of producing alkali-metal hydrides involves hydrogenation of butyllithium, butylsodium or butylpotassium in hexane–tetramethylethylenediamine. The hydrides so produced are superactive with a wide range of materials, and of course immediately pyrophoric in air [6].

Individually indexed compounds of this group of active reductants are:

- \* Aluminium hydride–diethyl ether, 0073
- \* Aluminium hydride–trimethylamine, 0072
- \* Azidogermane, 4416
  - Barium hydride, 0207
  - Beryllium hydride, 0224
- \* Bromogermane, 0246
  - Cadmium hydride, 3953
  - Caesium hydride, 4258
  - Calcium hydride, 3927
  - Cerium dihydride, 3962
  - Cerium trihydride, 3963
- \* Chlorogermane, 3992
  - Copper(I) hydride, 4286
- \* Dibromogermane, 0267
  - Digallane, 4410
- † Digermane, 4420
- † Germane, 4417
- † Hydrogen telluride, 4488
  - Lanthanum dihydride, 4461
  - Lanthanum hydride, 4495
- \* Lithium diphenylhydridotungstate(2–), 3503
  - Lithium hydride, 4432
  - Magnesium hydride, 4463
  - Magnesium–nickel hydride, 4464
  - Plutonium(III) hydride, 4509
  - Poly(germanium dihydride), 4415
  - Poly(germanium monohydride), 4413
  - Potassium hydride, 4427
  - Rubidium hydride, 4450
  - Sodium hydride, 4444
- † Stibine, 4510
  - Thorium dihydride, 4489
  - Thorium hydride, 4540
  - Titanium dihydride, 4490
  - Titanium–zirconium hydride, 4491
  - Trigermane, 4421
  - Uranium(III) hydride, 4511
  - Uranium(IV) hydride, 4541



Zinc hydride, 4492  
'Zirconium hydride', 4493

*See* COMPLEX HYDRIDES, PYROPHORIC MATERIALS

*See entry* LANTHANIDE-TRANSITION METAL ALLOY HYDRIDES

## METAL HYPOCHLORITES



A widely used group of industrial oxidants which has been involved in numerous incidents, some with nitrogenous materials leading to formation of nitrogen trichloride.

*See* BLEACHING POWDER

and the individually indexed compounds:

Calcium hypochlorite, 3924

Lead(II) hypochlorite, 4098

Magnesium hypochlorite, 4082

Sodium hypochlorite, 4037

*See* Chlorine: Nitrogen compounds

### Amines

Kirk-Othmer, 1963, Vol. 2, 104

Primary or secondary amines react with sodium or calcium hypochlorites to give *N*-chloroamines, some of which are explosive when isolated. Application of other chlorinating agents to amines or their precursors may also produce the same result under appropriate conditions.

*See related* HYPOHALITES *See other* METAL OXOHALOGENATES

## METALLURGICAL SAMPLE PREPARATION

Standard methods of preparing samples for metallurgical examination sometimes involve extremely hazardous combinations of oxidants, such as nitric or perchloric acid, and organic solvents. These are frequently destabilised by metal catalysis. Resultant incidents will be recorded under the entry for the oxidant in question.

## METAL NITRATES



### Aluminium

*See* Aluminium: Metal nitrates, etc.

### Citric acid

Shannon, I. R., *Chem. & Ind.*, 1970, 149

During vacuum evaporation of an aqueous mixture of unspecified mixed metal nitrates and citric acid, the amorphous solid exploded when nearly dry. This was attributed to oxidation of the organic residue by the nitrates present, possibly catalysed by one of the oxides expected to be produced.

### Esters, or Phosphorus, or Tin(II) chloride

Pieters, 1957, 30

Mixtures of metal nitrates with alkyl esters may explode, owing to formation of alkyl nitrates. Mixtures of a nitrate with phosphorus, tin(II) chloride or other reducing agents (i.e. redox combinations) may react explosively.

*See other* REDOX REACTIONS

#### Ethanol

Pitwell, L. R., *Chem. Eng. News*, 1978, **56**(37), 56

In the analysis of water, the use of ethanol to remove more than traces of nitrate or nitrite ion may lead to formation of fulminic acid, and if mercury(II) is used as a catalyst, explosive mercury fulminate may be formed.

*See* Mercury(II) nitrate: Ethanol

Silver nitrate: Ethanol, 0022

#### Metal phosphinates

1. Mellor, 1940, Vol. 8, 881

2. Costa, R. L., *Chem. Eng. News*, 1947, **25**, 3177

Mixtures of metal nitrates and phosphinates, previously proposed as explosives [1], explode on heating.

#### Organic matter

1. Bowen, H. J. M., *Anal. Chem.*, 1968, **40**, 969; private comm., 1968

2. Grewelling, T., *Anal. Chem.*, 1969, **41**, 540–541

3. Crutchfield, C. A. *et al.*, *J. Chem. Ed.*, 1991, **68**(7), 620

4. Editor's comments

When organic matter is destroyed for residue analysis by heating with equimolar potassium nitrate–sodium nitrate mixture to 390°C, a 20-fold excess of nitrate must be used. If over 10% of organic matter is present, pyrotechnic reactions occur which could be explosive [1]. Subsequent to an explosion while a citric acid–sodium nitrate mixture was being heated at below 500°C, experiments on the effect of heating various organic materials with metal nitrates showed the tendency for explosion to increase from magnesium through calcium to sodium nitrate. This is in the order of m.p. of the nitrates, and explosion may occur when the nitrates melt and make intimate contact with the organic matter. Pretreatment with nitric acid may reduce the explosion risk [2]. A slurry of nickel nitrate, starch, an amine and some presumably inert components proved to be a deflagrating explosive when cyclone dried, igniting above 135°C. Caution is advised when mixing nitrates with oxidisable materials [3].

Recent accidents suggest that the scientific world needs to be reminded that for the first 500 years of firearms and the first 300 of civil blasting the only explosive available was a mixture of one of the more stable and less oxidising metal nitrates with not very combustible carbonaceous material plus a catalyst. Gunpowder has been largely replaced by safer and more reliable explosives, but similar mixes remain unsafe because potentially explosive, especially if the mixing is at the molecular level in a complex. Substitutes for gunpowder are occasionally patented, they often consist of a carbohydrate and a metal nitrate. It cannot always be assumed that the safety of metal nitrates is the greater when they are hydrated [4].

*See* Citric acid, above  
*See also* Copper(II) nitrate

Potassium hexanitrocobaltate  
*See* Potassium hexanitrocobaltate(3-)

Vinyl sulfones  
*See* VINYL SULFOXIDES

Individually indexed compounds are:

- \* Ammonium hexanitrocerate, 3964
- \* Ammonium nitrate, 4522
- Barium nitrate, 0212
- Caesium nitrate, 4261
- Calcium nitrate, 3935
- \* Chromyl nitrate, 4238
- Cobalt(II) nitrate, 4215
- \* Copper(II) glycinate nitrate, 0905
- Copper(II) nitrate, 4279
- \* Dimethyltin dinitrate, 0914
- \* Heptasilver nitrate octaoxide, 0047
- \* 2-Hydroxyethylmercury(II) nitrate, 0857
- Iron(III) nitrate, 4397
- Lead(II) nitrate, 4749
- Lithium nitrate, 4684
- Magnesium nitrate, 4693
- Manganese(II) nitrate, 4701
- Mercury(I) nitrate, 4609
- Mercury(II) nitrate, 4603
- \* 2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1592
- Nickel(II) nitrate, 4743
- Plutonium(IV) nitrate, 4768
- Potassium nitrate, 4650
- Silver nitrate, 0022
- Sodium hexaoxodinitrate, 4740
- Sodium nitrate, 4721
- Sodium pentaoxodinitrate, 4739
- Sodium tetraoxodinitrate, 4738
- Sodium trioxodinitrate, 4737
- \* Tetrahydroxotritin(2+) nitrate, 4525
- Thallium(III) nitrate, 4762
- Tin(II) nitrate, 4750
- \* Triethylphosphinegold nitrate, 2558
- Uranyl nitrate, 4752
- \* Vanadium trinitrate oxide, 4763
- Zinc nitrate, 4751

*See* MOLTEN SALT BATHS *See other* METAL OXO-NONMETALLATES

**METAL NITRITES**

Metal Cyanides

*See* Sodium nitrite: Metal cyanides

Nitrogenous bases

Metal nitrites react with salts of nitrogenous bases to give the corresponding nitrite salts, many of which are unstable.

*See* NITRITE SALTS OF NITROGENOUS BASES

Potassium hexanitrocobaltate

*See* Potassium hexanitrocobaltate(3-)

Individually indexed compounds are:

Magnesium nitrite, 4692

\* Nitritonitrosylnickel, 4742

\* Potassium hexanitrocobaltate(3-), 4213

Potassium nitrite, 4649

Sodium nitrite, 4720

*See* MOLTEN SALT BATHS *See other* METAL OXONON-METALLATES, OXIDANTS

**METAL NITROPHENOXIDES**

Author's comments, 1988

Several metal salts of nitrophenols exhibit very limited thermal stability, especially heavy metal salts, and several instances of explosive decomposition at modest (or even ambient) temperatures have been recorded. Individual entries are:

\* Cobalt(II) picramate, 3460

\* Lead 2-amino-4,6-dinitrophenoxide, 3469

Lead 2,4,6-trinitroresorcinoxide, 2071

\* Lithium 4-nitrothiophenoxide, 2177

Manganese picrate hydroxide, 3742

Nickel 2,4-dinitrophenoxide hydroxide, 3745

Nickel 2-nitrophenoxide, 3464

4-Nitrophenol, : Potassium hydroxide, 2267

Potassium 4-nitrophenoxide, 2174

Silver 2-azido-4,6-dinitrophenoxide, 2075

\* Silver 4-nitrophenoxide, 2126

Sodium 2,4-dinitrophenoxide, 2115

Sodium 4-nitrophenoxide, 2183

\* Sodium 2-nitrothiophenoxide, 2182

Sodium picrate, 2086

Thallium(I) 2- or 4-nitrophenoxide, 0543

*See* PICRATES

**METAL NON-METALLIDES****M—E**

This class includes the products of combination of metals and non-metals except C (as acetylene), H, N, O, and S, which are separately treated in the groups:

METAL ACETYLIDES  
N-METAL DERIVATIVES  
METAL HYDRIDES  
METAL OXIDES  
METAL SULFIDES  
NITRIDES

Individually indexed compounds are:

- Aluminium carbide, 1031
- Aluminium phosphide, 0083
- Bismuth nitride, 0230
- Caesium graphite, 2882
- Calcium disilicide, 3944
- Calcium phosphide, 3947
- Calcium silicide, 3943
- Copper diphosphide, 4284
- Copper monophosphide, 4283
- Copper(II) phosphide, 4290
- Dialuminium octavanadium tridecasilicide, 0088
- Dicobalt boride, 0128
- Ditungsten carbide, 0564
- \* Ferrosilicon, 4390
- Hexalithium disilicide, 4689
- Iron carbide, 0365
- Lanthanum carbide, 0991
- Lead pentaphosphide, 4881
- Lithium heptapotassium di(tetrasilicide), 4676
- Lithium tripotassium tetrasilicide, 4675
- Magnesium boride, 0168
- Magnesium nitride, 4698
- Magnesium phosphide, 4699
- Magnesium silicide, 4697
- Manganese phosphide, 4711
- Manganese(II) telluride, 4708
- Platinum diarsenide, 0107
- Potassium graphite, 3107
- Potassium silicide, 4658
- Rubidium graphite, 3110
- Sodium phosphide, 4815
- Sodium silicide, 4801
- \* Tetraamminelithium dihydrogenphosphide, 4595
- Thorium dicarbide, 1027
- Titanium carbide, 0561

Trimercury tetraphosphide, 4616  
Tungsten carbide, 0563  
Uranium carbide, 0562  
Uranium dicarbide, 1028  
Zinc phosphide, 4876  
Zirconium dicarbide, 1029  
METAL PNICTIDES

## METAL OXALATES

(MOCO-)<sub>2</sub>

Mellor, 1941, Vol. 1, 706

The tendency for explosive decomposition of heavy metal oxalates is related to the value of the heat of decomposition. Individually entries are:

Copper(I) oxalate, 0622

Iron(III) oxalate, 2065

Mercury(II) oxalate, 0982

\* Potassium dinitrooxalatoplatinate(2-), 0988

Silver oxalate, 0572

*See other* HEAVY METAL DERIVATIVES

## METAL OXIDES

MO<sub>n</sub>

Malinin, G. V. *et al.*, *Russ. Chem. Rev.*, 1975, **44**, 392–397

Thermal decomposition of metal oxides was reviewed. Some oxides (cobalt(II, III) oxide, copper(II) oxide, lead(II, IV) oxide, uranium dioxide, triuranium octaoxide) liberate quite a high proportion of atomic oxygen, with a correspondingly higher potential for oxidation of fuels than molecular oxygen.

This large group covers a wide range of types of reactivity and there is a separate entry for the related group:

*See also* METAL PEROXIDES

Individually indexed compounds are:

Aluminium oxide, 0087

\* Antimony(III) chloride oxide, 4041

Antimony(III) oxide, 4851

\* Antimony trichloride oxide, 4150

Barium oxide, 0215

Beryllium oxide, 0225

\* Bis(1-chloroethylthallium chloride) oxide, 1591

Bismuth trioxide, 0233

\* Bis(trimethylsilyl) chromate, 2591

Cadmium oxide, 3958

Caesium oxide, 4264

Caesium trioxide, 4263

Calcium oxide, 3937

Chromium(II) oxide, 4241

Chromium(III) oxide, 4251

Chromium trioxide, 4242  
Cobalt(II) oxide, 4217  
Cobalt(III) oxide, 4221  
Copper(I) oxide, 4288  
Copper(II) oxide, 4281  
Dibismuth dichromium nonaoxide, 0232  
Dilead(II)lead(IV) oxide, 4861  
Disilver pentatin undecaoxide, 0036  
Gallium(I) oxide, 4411  
Indium(II) oxide, 4641  
Iridium(IV) oxide, 4644  
Iron(II) oxide, 4398  
Iron(III) oxide, 4403  
Iron(II,III) oxide, 4405  
Lanthanum oxide, 4679  
Lead(II) oxide, 4824  
Lead(IV) oxide, 4834  
Magnesium oxide, 4695  
\* Manganese chloride trioxide, 4022  
\* Manganese dichloride dioxide, 4086  
\* Manganese fluoride trioxide, 4301  
Manganese(II) oxide, 4704  
Manganese(IV) oxide, 4705  
Manganese(VII) oxide, 4709  
\* Manganese trichloride oxide, 4141  
'Mercury(I) oxide', 4613  
Mercury(II) oxide, 4605  
Molybdenum(IV) oxide, 4716  
Molybdenum(VI) oxide, 4717  
Nickel(II) oxide, 4821  
Nickel(III) oxide, 4823  
Nickel(IV) oxide, 4822  
Niobium(V) oxide, 4818  
Osmium(IV) oxide, 4833  
Osmium(VIII) oxide, 4858  
Palladium(II) oxide, 4825  
Palladium(III) oxide, 4848  
Palladium(IV) oxide, 4835  
\* Phenyl iodine(III) chromate, 2247  
Platinum(IV) oxide, 4836  
\* Potassium dioxide, 4656  
\* Potassium trioxide, 4657  
\* Rhenium chloride trioxide, 4045  
\* Rhenium tetrachloride oxide, 4167  
Ruthenium(VIII) oxide, 4862  
\* Selenium dioxide, 4838

- Silver(I) oxide, 0032
- Silver(II) oxide, 0025
- \* Sodium dioxide, 4799
- Sodium oxide, 4802
- \* Sodium trioxide, 4800
- Tantalum(V) oxide, 4865
- Thallium(III) oxide, 4854
- \* Thorium oxide sulfide, 4826
- Tin(II) oxide, 4829
- Tin(IV) oxide, 4840
- Titanium(IV) oxide, 4842
- Triuranium octaoxide, 4871
- Tungsten(IV) oxide, 4844
- Tungsten(VI) oxide, 4856
- \* Undecaamminetetraruthenium dodecaoxide, 4598
- Uranium(IV) oxide, 4843
- Vanadium(III) oxide, 4855
- Vanadium(V) oxide, 4866
- \* Vanadium trichloride oxide, 4151
- Zinc oxide, 4830
- \* Zirconium oxide sulfide, 4827

## METAL OXOHALOGENATES

## MXO<sub>n</sub>

Solymosi, F., *Acta Phys. Chem.*, 1976, **22**, 75–115

This class covers the four levels of oxidation represented in the series hypochlorite, chlorite, chlorate and perchlorate, and as expected, the oxidising power of the anion is roughly proportional to the oxygen content, though stability factors are also important. The class has been subdivided under the group headings below, each of which has its own listing of member compounds.

METAL HYPOCHLORITES, CHLORITE SALTS

METAL HALOGENATES, METAL PERCHLORATES

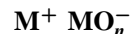
Some individually indexed compounds are:

- \* Ammonium iodate, 4513
- \* Ammonium periodate, 4514
- Cadmium chlorate, 3952
- Calcium chlorite, 3925
- \* Lead acetate–lead bromate, 1540
- Lead(II) chlorite, 4102
- Mercury(II) bromate, 0270
- Potassium bromate, 0255
- Potassium chlorate, 4017
- Potassium periodate, 4620
- Silver bromate, 0007
- Sodium bromate, 0257



Sodium chlorite, 4038  
Thallium bromate, 0260

### METAL OXOMETALLATES

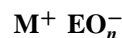


Salts with oxometallate anions function as oxidants, those with oxygen present as peroxy groups being naturally the more powerful, and separately grouped under *See also* PEROXOACID SALTS

Individually indexed oxometallate salts are:

- \* Bis(benzene)chromium dichromate, 3851
- Calcium chromate, 3926
- Copper chromate oxide, 4223
- Dibismuth dichromium nonaoxide, 0232
- Lead chromate, 4243
- Lithium chromate, 4236
- Magnesium permanganate, 4691
- Potassium dichromate, 4248
- Potassium permanganate, 4647
- Sodium dichromate, 4250
- Sodium molybdate, 4713
- Sodium permanganate, 4703
- Zinc permanganate, 4710

### METAL OXONON-METALLATES



This large and commonly used class of salts covers a wide range of oxidising potential. Among the more powerful oxidants are those grouped under

METAL OXOHALOGENATES  
PEROXOACID SALTS  
METAL NITRITES  
METAL NITRATES  
METAL SULFATES  
METAL AMIDOSULFATES

for which separate entries emphasise the individual features. Some less highly oxidised anions function as reductants which also have a separate entry. Individually indexed entries are:

- \* Ammonium iron(III) sulfate, 4393
- \* Ammonium sulfate, 4574
- Barium sulfate, 0217
- Calcium sulfate, 3939
- Chromium(II) sulfate, 4244
- Copper(II) phosphinate, 4272
- Copper(II) sulfate, 4282
- Iron(II) sulfate, 4399
- Lead sulfate, 4860

Lithium carbonate, 0533  
Lithium dithionite, 4687  
Magnesium carbonate hydroxide, 0534  
Magnesium nitrate, 4693  
Magnesium nitrite, 4692  
Magnesium sulfate, 4696  
Potassium carbonate, 0531  
Potassium nitrite, 4649  
Silver hyponitrite, 0031  
Sodium acetate, 0779  
Sodium carbonate, 0552  
Sodium disulfite, 4808  
Sodium dithionite, 4807  
Sodium hydrogen carbonate, 0390  
Sodium hydrogen sulfate, 4446  
Sodium metasilicate, 4805  
Sodium nitrite, 4720  
Sodium sulfate, 4806  
\* Sodium tetraborate, 0185  
Sodium thiosulfate, 4804

#### METAL PERCHLORATES



1. Burton, M., *Chem. Eng. News*, 1970, **48**(51), 55
2. Cook, R. E. *et al.*, *J. Chem. Res.*, 1982, (S) 267; (M) 2772–2783

Though metal perbromates and periodates are known (but not perfluorates), the perchlorates have most frequently been involved in hazardous incidents over a long period. These usually stable salts are powerful oxidants and contact with combustible materials or reductants must be under controlled conditions. A severe restriction on the use of metal perchlorates in laboratory work has been recommended [1]. Attention has been drawn, on the basis of experience with cobalt(II) perchlorate, to the possibility of stable hydrated metal perchlorates being converted by unintentional dehydration to unstable (endothermic) lower hydrates capable of explosive decomposition in absence of impurities. Great care to avoid dehydration (or desolvation) is urged [2].

*See* SOLVATED OXOSALT INCIDENTS

#### Calcium hydride

Mellor, 1941, Vol. 3, 651

Rubbing a mixture of calcium (or strontium) hydride with a metal perchlorate in a mortar causes a violent explosion.

*See other* REDOX REACTIONS

#### Organic ligands

Nair, M. R. G. *et al.*, *Talanta*, 1981, **28**, 395–396

A safe method for decomposing complexes of various organic ligands with metal perchlorates prior to analysis involves heating them with ammonium chloride, but

this method should be tested on the small scale when applied to complexes not previously decomposed in this way.

*See* AMMINOMETAL OXOSALTS

#### Sulfuric acid

Pieters, 1957, 30; Schumacher, 1960, 190

Metal perchlorates with highly concentrated or anhydrous acid form the explosively unstable anhydrous perchloric acid.

*See* Perchloric acid: Dehydrating agents

#### Trifluoromethanesulfonic acid

*See* Trifluoromethanesulfonic acid: Perchlorate salts

Individually indexed metal perchlorates are:

- † Acetonitrile, : Lanthanide perchlorate, 0758
- \* Acetoxymercurio(perchloratodimercurio)ethenone, 1413
- \* Acetoxymercurio(perchloratomercurio)ethenone, 1412
- Aluminium perchlorate, 0066
- \* Antimony(III) oxide perchlorate, 4046
- Barium perchlorate, 0206
- \* (Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614
- Beryllium perchlorate, 0222
- \* 1,1-Bis(dimethyl sulfoxide)telluracyclopentane diperchlorate, 1588
- Chromium(III) perchlorate . 6 dimethyl sulfoxide, 4130
- \* Chromyl perchlorate, 4055
- Cobalt(II) perchlorate hydrates, 4051
- Copper(I) perchlorate, 4058
- Copper(II) perchlorate, 4057
- \* Cyclopentadiene–silver perchlorate, 1859
- \* Diethylthallium perchlorate, 1682
- \* Dodecamethyltetraplatinum(IV) perchlorate, 3587
- Dysprosium perchlorate, 4131
- Erbium perchlorate, 4132
- \* Ethylphenylthallium(III) acetate perchlorate, 3302
- Gallium perchlorate, 4135
- Indium(I) perchlorate, 4014
- Iron(II) perchlorate, 4062
- Iron(III) perchlorate, 4134
- Lead perchlorate, 4108
- Lithium perchlorate, 4021
- Magnesium perchlorate, 4084
- Manganese(II) perchlorate, 4088
- Mercury(II) perchlorate, 4078
- Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide, 4079
- \* Methylmercury perchlorate, 0433
- Neodymium perchlorate . 2 acetonitrile, 4148

- Nickel perchlorate, 4094
- \* Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3778
  - Potassium perchlorate, 4018
  - Silver perchlorate, 0012
  - Sodium perchlorate, 4040
  - \* Tetrasulfurtetraimide–silver perchlorate, 0029
  - Tetrazirconium tetraoxide hydrogen nonaperchlorate, 4195
  - Tin(II) perchlorate, 4109
  - Titanium tetraaperchlorate, 4170
  - Uranyl perchlorate, 4111
  - Vanadyl perchlorate, 4152

*See other* METAL OXOHALOGENATES

### METAL PEROXIDES



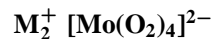
1. Castrantas, 1965, 1,4
2. Bailar, 1973, Vol. 2, 784

This group contains many powerful oxidants, the most common being sodium peroxide. Undoubtedly one of the most hazardous is potassium dioxide or superoxide, readily formed on exposure of the metal to air (but as the monovalent  $O_2^-$  ion it is not a true peroxide). Many transition metal peroxides are dangerously explosive. Individually indexed peroxides are:

- Barium peroxide, 0216
- Calcium peroxide, 3938
- Mercury peroxide, 4606
- \* Oxodiperoxomolybdenum–hexamethylphosphoramide, 4718
- \* Potassium dioxide, 4656
- Potassium peroxide, 4666
- \* Potassium trioxide, 4657
- Silver peroxide, 0033
- \* Sodium dioxide, 4799
- Sodium peroxide, 4803
- \* Sodium trioxide, 4800
- Strontium peroxide, 4841
- Zinc peroxide, 4845

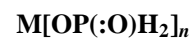
*See also* AMMINECHROMIUM PEROXOCOMPLEXES

### METAL PEROXOMOLYBDATES



*See other* PEROXOMOLYBDATES AND TUNGSTATES

### METAL PHOSPHINATES



This is a group of powerful reductants, several of which are of rather limited stability. Individually indexed compounds are:

- Aluminium phosphinate, 0078
- Barium phosphinate, 0210

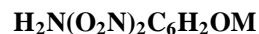
Calcium phosphinate, 3931  
Copper(II) phosphinate, 4272  
Dipotassium phosphinate, 4431  
Iron(III) phosphinate, 4394  
Lead(II) phosphinate, 4531  
Magnesium phosphinate, 4517  
Manganese(II) phosphinate, 4519  
Potassium phosphinate, 4431  
Silver phosphinate, 0017  
Sodium phosphinate, 4473  
*See other* REDUCANTS

### METAL PHOSPHORUS TRISULFIDES



Clement, R. *et al.*, *J. Chem. Soc., Dalton Trans.*, 1979, 1566  
When very finely divided metals (iron, manganese, nickel or zinc) are heated with elemental phosphorus and sulfur in evacuated ampoules to form the title compounds, explosions may occur, even at temperatures as low as 150–200°C.

### METAL PICRAMATES



Srivastava, R. S. *et al.*, *Chem. Abs.*, 1979, **91**, 76315  
Explosive properties of palladium(II) and uranyl picramates were determined.  
*See other* HEAVY METAL DERIVATIVES, POLYNITROARYL COMPOUNDS

### METAL Pnictides

#### Preparative hazard

1. Hector, A. L. *et al.*, *Z. Naturforsch. B: Chem. Sci.*, 1994, **49**(4), 477
2. Hector, A. *et al.*, *J. Mater. Sci. Lett.*, 1994, **13**(1), 1
3. Hector, A. *et al.*, *Polyhedron*, 1995, **14**(7), 913

(No, the editor didn't know what this name meant either.) It means salts of the trivalent anions of Group V, restricted in [1] to arsenides, antimonides and bismuthides and prepared by reaction of sodium pnictides with anhydrous halides of transition and lanthanide metals. This violently exothermic reaction may initiate as low as 25°C. Avoidance of hydrated halides is cautioned since these are likely to react uncontrollably on mixing. Another paper includes a similar reaction of phosphides, initiated by grinding [2]. Nitrides are reported made from the thermally initiated reaction of sodium azide with metal halides, a very large sealed ampoule is counselled to contain the nitrogen [3].

*See* Sodium azide

*See* METAL NON-METALLIDES

METAL HALIDES

METATHESIS REACTIONS

## METAL POLYHALOHALOGENATES

M<sup>+</sup> [XX'<sub>n</sub>]

Organic solvents, or Water

1. Whitney, E. D. *et al.*, *J. Amer. Chem. Soc.*, 1964, **86**, 2583
2. Sharpe, A. G. *et al.*, *J. Chem. Soc.*, 1948, 2135

Potassium, rubidium and caesium tetrafluorochlorates and hexafluorobromates react violently with water, and explosively with common organic solvents, like the parent halogen fluorides [1]. Silver and barium tetrafluorobromates ignite in contact with ether, acetone, dioxane and petrol [2]. Individual entries are:

Barium tetrafluorobromate, 0201  
Caesium hexafluorobromate, 0236  
Caesium tetrafluorochlorate(1-), 3969  
Potassium hexafluorobromate, 0244  
Potassium tetrafluorochlorate(1-), 3984  
Rubidium hexafluorobromate, 0245  
Rubidium tetrafluorochlorate(1-), 3988  
Silver tetrafluorobromate, 0006

## METAL PYRUVATE NITROPHENYLHYDRAZONES

MOCO.CC(Me)=NNHC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>

Ragno, M., *Gazz. Chim. Ital.*, 1945, **75**, 186–192

A wide range of the title salts of mono-, di- and tri-valent metals, with an *o*-, *m*- or *p*-nitro group present showed unstable or explosive behaviour on heating. The lead salt exploded violently at 240°C, while the aluminium, beryllium and silver salts are only feebly explosive.

*See other* NITROARYL COMPOUNDS

## METALS

M

Individually indexed metals are:

Aluminium, 0048  
Antimony, 4907  
Barium, 0200  
Beryllium, 0220  
Bismuth, 0226  
Cadmium, 3949  
Caesium, 4254  
Calcium, 3922  
Cerium, 3961  
Chromium, 4222  
Cobalt, 4199  
Copper, 4267  
Europium, 4292  
Gallium, 4406  
Germanium, 4412

Gold, 0110  
Hafnium, 4599  
Indium, 4640  
Iridium, 4643  
Lanthanum, 4677  
Lead, 4882  
Lithium, 4680  
Magnesium, 4690  
Manganese, 4700  
Mercury, 4600  
Molybdenum, 4712  
Neodymium, 4819  
Nickel, 4820  
Niobium, 4817  
Osmium, 4873  
Palladium, 4885  
Platinum, 4887  
Plutonium, 4888  
Potassium, 4645  
Praseodymium, 4886  
Rhenium, 4890  
Rhodium, 4892  
Rubidium, 4889  
Ruthenium, 4894  
Samarium, 4911  
\* Selenium, 4908  
\* Silicon, 4909  
Silver, 0001  
Sodium, 4796  
Strontium, 4913  
Tantalum, 4914  
Technetium, 4915  
\* Tellurium, 4916  
Thallium, 4922  
Thorium, 4917  
Tin, 4912  
Titanium, 4919  
Tungsten, 4925  
Uranium, 4923  
Vanadium, 4924  
Zinc, 4927  
Zirconium, 4928

#### Halocarbons

*See entry* METAL–HALOCARBON INCIDENTS

Other groups or topics related to this group are:

ALKALI-METAL ALLOYS, ALKALI METALS  
DEVARDA'S ALLOY, FERROALLOY POWDERS  
FINELY DIVIDED METALS, LANTHANIDE METALS  
LIGHT ALLOYS, METAL DUSTS  
METAL FIRES, MILD STEEL  
MOLTEN METAL EXPLOSIONS, PRECIOUS METAL DERIVATIVES  
PYROPHORIC METALS, REACTIVE METALS  
STEEL WOOL, THORIUM FURNACE RESIDUES

## METAL SALICYLATES

Nitric acid

*See* Nitric acid: Metal salicylates

## METAL SALTS

By far the largest class of compound in this Handbook, the metal (and ammonium) salts have been allocated into two sub-classes dependent on the presence or absence of oxygen in the anion.

The main groupings adopted for the non-oxygenated salts are:

METAL ACETYLIDES, METAL AZIDE HALIDES  
METAL AZIDES, METAL AZOTETRAZOLIDES  
METAL CYANIDES (AND CYANO COMPLEXES)  
*N*-METAL DERIVATIVES, METAL HALIDES  
METAL POLYHALOHALOGENATES, METAL THIOCYANATES

and for the oxosalts:

METAL ABIETATES, METAL FULMINATES,  
METAL NITROPHENOXIDES, METAL OXALATES  
METAL PYRUVATE NITROPHENYLHYDRAZONES  
METAL OXOHALOGENATES (anion an oxo derivative of a halogen)  
METAL OXOMETALLATES (anion an oxo derivative of a metal)  
METAL OXONON-METALLATES (anion an oxo derivative of a non-metal)  
PEROXOACID SALTS (anion a peroxo derivative of a metal or non-metal)

There is a separate entry for

OXOSALTS OF NITROGENOUS BASES

In some cases it has been convenient to sub-divide the oxosalt groups into smaller sub-groups, and such sub-division is indicated under the appropriate group heading.

## METAL SULFATES

$M(SO_4)_n$

Aluminium

*See* Aluminium: Metal oxides, etc.



## Magnesium

See Magnesium: Metal oxosalts

See other METAL OXONON-METALLATES

## METAL SULFIDES

$M_m S_n$

1. Byberg, K. G., *CANAMET Spec. Publ. SP87-3*, 1987, I 1.1–1.39
2. Nel, L. D., *ibid*, I 2.1–2.24
3. Hermann, F. W., *ibid*, I 3.1–3.7
4. Wheeland, K. G., *ibid*, I(B4) 5.1–5.48
5. Enright, R. J., *ibid*, II(viia) 27–44
6. Hall, A. E. (Ed.), *Sulphide Dust Explos. Proc. Spec. Sess. CIM Ann. Gen. Meeting*, Montreal, Canadian Inst. Min. Metall., 1989
7. Liu, Q. et al., *ibid.*, 125–49
8. Rosenblum, F. et al., *CIM Bull.*, 1995, **88**(989), 44; *Chem. Abs.*, 1995, **123**, 178477g

In a special publication devoted to sulfide ore dust explosions, a dust explosion in a copper–zinc sulfide mine is discussed and related to causes and preventive measures [1]. Control measures [2] and prevention of secondary explosions are also discussed [3], and surveyed, including the need for further work [4]. The results of experimental work on the use of limestone dust to suppress explosions in pyrites dusts are presented [5]. For another special publication on ore dust explosion with numerous incidents and further studies on mechanism and control see [6]. Explosibility declines in the order pyrrhotite, pyrite, chalcopyrite, sphalerite, covellite, chalcocite, galena. Pyrite at 1000 g/m<sup>3</sup> can give a peak pressure of 5.8 bar [7]. Self heating of broken sulfide ore, to possible ignition, has been studied. Pyrrhotite seems primarily responsible [8].

See DUST EXPLOSION INCIDENTS

Some metal sulfides are so readily oxidised as to be pyrophoric in air. Individually indexed compounds are:

- Aluminium copper(I) sulfide, 0084
- \* Ammonium sulfide, 4577
- Antimony trisulfide, 4906
- Barium sulfide, 0218
- Bismuth trisulfide, 0234
- \* Cadmium selenide, 3959
- \* Caesium selenide, 4265
- Calcium polysulfide, 3942
- Calcium sulfide, 3941
- Cerium trisulfide, 3967
- Chromium(II) sulfide, 4245
- Cobalt(II) sulfide, 4218
- Copper iron(II) sulfide, 4269
- Copper(II) sulfide, 4285
- Europium(II) sulfide, 4293

Germanium(II) sulfide, 4419  
 Gold(III) sulfide, 0116  
 Iron disulfide, 4401  
 Iron(II) sulfide, 4400  
 Iron(III) sulfide, 4404  
 Manganese(II) sulfide, 4706  
 Manganese(IV) sulfide, 4707  
 Mercury(II) sulfide, 4607  
 Molybdenum(IV) sulfide, 4719  
 Potassium sulfide, 4670  
 Rhenium(VII) sulfide, 4891  
 Ruthenium(IV) sulfide, 4895  
 Samarium sulfide, 4899  
 Silver sulfide, 0026  
 Sodium disulfide, 4812  
 Sodium polysulfide, 4813  
 Sodium sulfide, 4811  
 Strontium sulfide, 4901  
 Tantalum(IV) sulfide, 4903  
 \* Tetrakis(butylthio)uranium, 3731  
 \* Thorium oxide sulfide, 4826  
 Tin(II) sulfide, 4900  
 Tin(IV) sulfide, 4902  
 Titanium(IV) sulfide, 4904  
 Uranium(IV) sulfide, 4905  
 \* Zirconium oxide sulfide, 4827

## METAL THIOCYANATES



### Oxidants

1. von Schwartz, 1918, 299–300
2. *MCA Case History No. 853*

Metal thiocyanates are oxidised explosively by chlorates or nitrates when fused, or if intimately mixed, at 400°C or on spark or flame ignition [1]. Nitric acid violently oxidised an aqueous thiocyanate solution [2].

*See* Nitric acid: Metal thiocyanate

Sodium nitrite: Potassium thiocyanate

## METATHESIS REACTIONS

Parkin, *I.Chem. & Ind.*, 1997, (18), 725

These are usually reactions of anhydrous transition and B metal halides with dry alkali metal salts such as the sulphides, nitrides, phosphides, arsenides etc. to give exchange of anions. They tend to be very exothermic with higher valence halides and are frequently initiated by mild warming or grinding. Metathesis is

described as a controlled explosion. Mixtures considered in the specific reference above include lithium nitride with tantalum pentachloride, titanium tetrachloride and vanadium tetrachloride, also barium nitride with manganese II iodide, the last reaction photographically illustrated.

See METAL Pnictides

#### MICROWAVE OVEN HEATING

1. Gedye, R. *et al.*, *Tetrahedron Lett.*, 1986, **27**, 279–282
2. Watkins, K. W., *J. Chem. Educ.*, 1983, **60**, 1043
3. Bedson, A., *Chem. Brit.*, 1986, **23**, 894
4. Gadge, R. *et al.*, *Educ. Chem.*, 1988, **25**(2), 55–56
5. Gilman, L. *et al.*, *Anal. Chem.*, 1988, **60**, 1624–1625
6. Emsley, J., *New Scientist*, 1988, Nov. 12, 56–60
7. Anon., *Lab. News* (London), 31 Oct. 1988, (409), 2
8. Anon., *Safety Digest Univ. Safety Assoc.*, 1994, (50), 3
9. *Introduction to microwave sample preparation*, Kinston, H. M., Jassie, L. B. (eds.), ACS Professional Reference Ser., Washington, American Chemical Society, 1989
10. Anon., *Safety Digest Univ. Safety Assoc.*, 1992, **44**, 26

During an investigation of microwave oven heating on the oxidation of toluene by potassium permanganate in a sealed Teflon vessel, excessively high pressures developed and a violent explosion ensued [1]. The possibility of a second hazard, that of explosion of a flammable vapour in a microwave oven, had been foreseen previously [2]. The current state of development of microwave heating to speed up sample dissolution was reviewed [3]. Use of microwave ovens for rapid preparation of derivatives in sealed Teflon vessels for analytical purposes are discussed, and the need for caution to avoid explosions due to excessive solvent volumes is stressed [4]. The desirability of heating acid digestion mixtures, or indeed any liquid, by microwave heating in a sealed container without an adequate pressure relief device is questioned [5]. General aspects of microwave heating in chemical operations have been discussed [6]. A survey showed a large number of incidents, including 13 serious cases of scalding or oven doors being blown off, caused by misuse of microwave ovens and lack of precautions, largely among biologists [7]. A microwave oven was destroyed when agar jelly was (over)heated in a flask with (probably) a too tight stopper [8]. The new text book deals with preparation of mineral, metallic, biological and chemical samples, and safety aspects and precautions for the techniques [9]. Rupture of containers fitted with bursting discs, the bursting disc remaining undamaged, suggests that containers for microwave digestion of geological samples may not always be as strong as intended [10]. It should be noted that, with the foaming to be expected of a superheated liquid, vents would easily block even should a safety valve operate.

See also SAMPLE DISSOLUTION

## MILD STEEL

*MCA Case History No. 947*

A small mild steel cylinder suitable for high pressure at ambient temperature was two-thirds filled with liquid ammonia by connecting it to a large ammonia cylinder and cooling the smaller cylinder to  $-70^{\circ}\text{C}$  by immersion in a solid carbon dioxide–acetone bath. Some hours after filling, the cylinder burst, splitting cleanly along its length. This was caused by cryogenic embrittlement and weakening of the mild steel cylinder. Special alloys are required for operations at low temperatures and high pressures.

## MILK POWDER

1. Buma, T. J. *et al.*, *Chem. Abs.*, 1977, **87**, 83300
2. Anon, *Fire Prevention*, 1990, (228), 39
3. Anon., *Loss Prev. Bull.*, 1994, (119), 5.

Lumps of powdered milk formed near the hot-air inlet of spray driers may ignite spontaneously. The thermochemical mechanism has been investigated [1]. A case of probable spontaneous combustion in milk powder which had been accidentally wetted some weeks previously is described [2]. Following two explosions in a spray drier handling dairy products, investigation showed that milk powder, in air, showed exothermicity from  $195^{\circ}\text{C}$ . The drying air had been at  $210^{\circ}\text{C}$ , it was recommended that its temperature be reduced [3]. There are also carbon monoxide dangers in using alkaline cleaners on milk drying equipment without good ventilation

*See also* SUGARS

*See other* IGNITION SOURCES, AUTOIGNITION INCIDENTS

## MINIMUM IGNITION ENERGY (MIE)

1. Nuzhda, L. I. *et al.*, *Chem. Abs.*, 1984, **101**, 156838
2. Pratt, T. H., *Process Safety Progr.*, 1993, **12**(4), 203
3. Siwek, R. *et al.*, *Process Safety Progr.*, 1995, **14**(2), 107

The MIE of gas—air or vapour—air mixtures can be determined from the structural formula and the molar heat of combustion of the compounds studied, and equations for the calculation are presented. The method is stated to give more accurate results than conventional methods used to assess flammability of mixtures of gas or vapour with air [1]. It is claimed that in oxygen MIEs are about a hundred-fold lower than in air [2]. A study of the ignition behaviour of dusts, including correlation of electrical and mechanical minimum ignition spark energies and ignition temperature is made [3].

## MISTS

1. Eichorn, P., *Petroleum Refiner*, 1955, **34**(11), 194
2. Kletz, T. A., *Process Safety Progress*, 1995, **14**(4), 273

Mists are dust clouds in which the particles happen to be liquid. Should that liquid be combustible, even though it is nowhere near its flash-point, explosion is possible.

*See* DUST EXPLOSION INCIDENTS

## MIXING

1. Stuart, R. *et al.*, *Safety Digest Univ. Safety Assoc.*, 1993, **45**, 4

The safety, and the exact products, of reactions conducted at a significant scale can depend strongly upon the order and rate of mixing reagents and solvents. In general, the potential for full heat evolution or gas elimination should not be assembled until there is sufficient heat-sink, or vent, to control these. Reference [1] records a fatality which arose after alcohol was added to sodium, rather than sodium being added to excess alcohol, when disposing of surplus metal.

*See also* molybdenum nitride, AGITATION INCIDENTS

## MOLECULAR SIEVE INCIDENTS

### Air

Schoofs, G. R., *AIChE J.*, 1992, **38**(9), 1385

The larger size sieves preferentially absorb nitrogen from air and may therefore generate an oxygen enriched initial stream from large air-drying beds, when brought on line after regeneration. This increases fire risks if fuels be present. This phenomenon is not shown by 3A sieves, which are therefore to be preferred.

*See* OXYGEN ENRICHMENT

### Ethylene

Doyle, W. H., *Loss Prev.*, 1969, **3**, 15

A 5A molecular sieve, not previously soaked in dilute ethylene, was used to dry compressed ethylene gas in a flow system. An exothermic reaction attained red heat and caused explosive failure of the dryer. The smaller-pored 3A sieve is not catalytically active towards ethylene.

### Triaryl phosphates

Schmitt, C. R., *J. Fire Flamm.*, 1973, (4), 113–131

A molecular sieve bed was used to purify continuously the fire-resistant hydraulic fluid (a triaryl phosphate) in a large hydraulic press. Periodically the sieve bed was regenerated by treatment with steam, and then purified air at 205°C. After 9 years of uneventful operation, the bed ignited on admission of hot air. The fuel source was traced to the accumulation of organic residues (phenols or cresols?) on the sieve which were not removed by the steam/air treatment.

Other examples of molecular sieve incidents are:

Benzyl bromide, Molecular sieve, 2735

*tert*-Butyl hydroperoxide, Molecular sieves, 4477

Mercury(II) perchlorate · 6 (or 4)dimethyl sulfoxide, 4079

Nitromethane, Molecular sieve, 0456  
Oxygen difluoride, Adsorbents, 4317  
1,1,1-Trichloroethane, 0740

## MOLTEN METAL EXPLOSIONS

1. Frölich, G., *Chem. Ing. Tech.*, 1978, **50**, 861–866
2. *Molten Metals and Water Explosions*, HSE Rept., London, HMSO, 1979
3. Vaughan, G. J., *Rept. SRD R177*, Warrington, UKAEA, 1980
4. Tso, C. P., PhD Thesis, University of California, Berkely, 1979
5. Mitin, V. P. *et al.*, *Chem. Abs.*, 1981, **94**, 88514
6. Shoji, S. *et al.*, *Bull. Jap. Soc. Mech. Eng.*, 1983, **26**, 791–796

Factors which determine whether or not there will be a vapour explosion when a hot melt (glass or various metals) comes into contact with water have been studied experimentally. Vapour generation must be preceded by fragmentation of the melt to give enormous heat transfer coefficients [1]. This last report [2] in a series of 6 covers general aspects and precautions relevant to foundry practice, the earlier ones each dealing with specific metals and alloys. The molten metal–water explosion phenomenon has been reviewed with 130 references. [3]. A new thermal explosion model has been proposed and used to predict reaction zones in systems containing water and molten aluminium, lead and tin, among others [4]. The mechanisms of explosion when molten magnesium [5] or tin [6] contact water have been studied on the small scale. Other incidents of this type are:

SMELT

STEAM EXPLOSIONS

Aluminium, : Water (references 9,10), 0048

Copper, : Water, 4267

Tin, : Water (references 1–3), 4912

## MOLTEN SALT BATHS

1. *Guidelines for Safety in Heat Treatment, I: Use of Molten Salt Baths*, Birmingham, University of Aston, 1984
2. Baum, R., *Chem. Eng. News*, 1982, **60**(41), 29
3. Anon., *CISHC Chem. Safety Summ.*, 1980, **51**, 75
4. *Precautions in the Use of Nitrate Salt Baths*, Min. of Labour, SHW booklet, London, HMSO, 1964
5. Pieters, 1957, 30
6. *Potential Hazards in the Use of Salt Baths for Heat Treatment of Metals*, NBFU Res. Rept. No. 2., New York, 1946
7. Beck, W., *Aluminium*, 1935, **17**, 3–6
8. Clark, E. R. *et al.*, *Chem. Abs.*, 1987, **107**, 119389

The most recent summary of the considerable hazards which may arise from incorrect use of molten salt baths and the materials in them covers all aspects of material storage, bath use, maintenance and cleaning, disposal of used materials and fire-fighting [1]. An account of a disastrous laboratory explosion caused by melting

together 1.3 kg of the oxidant sodium nitrite and 0.4 kg of the reductant potassium thiocyanate is remarkable in that it was claimed that the violent redox reaction on melting could not have been foreseen [2]. As well as for heat treatment, molten salt baths are also used to oxidise impurities from metal components. When filter plates excessively contaminated with polymer were lowered into the bath, an unusually fierce fire (possibly involving liberated oxygen) ensued [3].

The booklet covers hazards attendant on the use of molten nitrate salt baths for heat treatment of metals, including storage and disposal of salts, starting up, electrical heating, and emptying of salt baths. Readily oxidisable materials must be rigorously excluded from the vicinity of nitrate baths [4]. Earlier it had been reported that aluminium and its alloys if contaminated with organic matter may explode in nitrate–nitrite fused salt heating baths [5]. Uses, composition, and precautions in the use of molten salt baths are discussed. Most common causes of accidents are: steam explosions, trapping of air, explosive reactions with reducing metals (magnesium) and organic matter or cyanides from other heat treatment processes [6]. Explosions involving use of aluminium in nitrate baths have also been attributed to corrosive failure of the iron container, rather than to direct interaction with aluminium [7]. Heat treatment of aluminium–lithium and aluminium–magnesium alloys in nitrite–nitrate salt baths was studied [8].

*See* Sodium nitrite: Potassium thiocyanate

## **MOLTEN SALTS**

Zhuchkov, P. A. *et al.*, *Chem. Abs.*, 1974, **80**, 28651

The causes of furnace blasts occurring in soda-regeneration plants when water is spilt into molten sodium carbonate, sodium chloride, sodium hydroxide, sodium sulfate or sodium sulfide are discussed, together with methods of prevention.

## **NATURAL FIBRES**

*See* DUST EXPLOSION INCIDENTS (reference 15)

*See* Calcium oxide: Water (reference 3)

Potassium chlorate: Fabric, 4017

Nitric acid: Cellulose, 4436

Hydrogen peroxide: Acetic acid, Jute, 4477

*See also* COTTON

## **NEUTRALISATION INCIDENTS**

Incidents of several different types have arisen from reactions involving neutralisation of an acid with a base where the exotherm (57.3 kJ/equivalent for strong acid–strong base reactions) has not occurred smoothly over an extended period, but has been sudden in effect for various reasons. Individually indexed neutralisation incidents are:

† Formaldehyde, : Magnesium carbonate hydroxide, 0416

Potassium hydroxide, : Acids, 4428

Sodium carbonate, 0552  
Sulfuric acid, : Diethylamine, 4479  
Sulfuric acid, : 4-Methylpyridine, 4479  
2,4,6-Trichloro-1,3,5-triazine, : 2-Ethoxyethanol, 1038  
*See related* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## NITRAMINE–METAL COMPLEXES

$O_2NN \rightarrow M$

Palopali, S. F. *et al.*, *Inorg. Chem.*, 1988, **27**, 2963–2971  
Complexes of the explosively unstable nitramine ligands *N*-nitromethylamine (HL), *N,N'*-dinitrodiaminoethane ( $H_2L'$ ), and 5-nitraminotetrazole ( $H_2L''$ ) with ammine derivatives of divalent copper, nickel or palladium explode on heating or under a hammer blow. Compounds prepared were :

$Cu(NH_3)_2L_2$ ,  $Cu(en)L_2$ ,  $Cu(NH_3)_2L'$ ,  $Ni(H_2O)_4L'$ ,  $Ni(NH_3)_3L'$ ,  $Pd(NH_3)_2L'$ ,  $[Cu(en)_2] \{ [Cu(en)_2L'_2]_2\mu L' \}$ .

Ligand bonding to metal was via O and/or N.

The individual ligands are:  
*N,N'*-Dinitro-1,2-diaminoethane, 0916  
5-*N*-Nitroaminotetrazole, 0415  
*N*-Nitromethylamine, 0478  
*See other* *N*-NITRO COMPOUNDS

## NITRATING AGENTS

1. Dubar, J. *et al.*, *Compt. rend. Ser. C*, 1968, **266**, 1114
2. Buckley, E. *et al.*, *Chem. & Ind.*, 1978, 124–125
3. Feuer, H. *et al.*, *J. Org. Chem.*, 1978, **43**, 4677

The potentially explosive character of various nitration mixtures (2-cyanopropyl nitrate in acetonitrile; solutions of dinitrogen tetraoxide in esters, ethers or hydrocarbons; dinitrogen pentaoxide in dichloromethane; nitronium tetrafluoroborate in sulfolane) are mentioned [1]. Use of mixtures of fuming nitric acid–sulfuric acid in acetic anhydride to highly nitrate naphthalene derivatives is accompanied by formation of tetranitromethane, and care is required [2]. When propyl nitrate is used as a nitrating agent, effective cooling at  $-60^\circ C$  is necessary to deal with the highly exothermic reaction [3].

## NITRATION INCIDENTS

1. Biasutti, 1974, 8, 123–125
2. Albright, Hanson, 1976
3. Obnovlenskii, P. A. *et al.*, *Chem. Abs.*, 1975, **83**, 168135
4. Raczynski, S., *Chem. Abs.*, 1963, **59**, 15114e
5. Rüst, 1948, 317–319
6. Biasutti, 1981
7. Albright, M. F., in Kirk-Othmer, 1981, Vol. 15, 841–853



8. Evans, F. W. *et al.*, *Loss Prev. Safety Prom. Proc. Ind.*, 191–197, Frankfort, DECHEMA, 1978
9. Zeller, J. R., Paper 28, *ACS CHAS Div. Symp. Chem. Haz. Proc. Rev.*, 1984; Ch. 11 in *Chem. Proc. Haz. Rev.*, ACS Sympo. Ser. No. 274, 107–114, Washington, ACS, 1985
10. Sokhenko, V. I. *et al.*, *Chem. Abs.*, 1987, **107**, 9818
11. Sommer, E. *et al.*, *Proc. 7th Sympos. Chem. Probl. Stabil. Explos.*, 1986, 175–180
12. Wiss, J. *et al.*, *J. Loss Prevention*, 1955, **8**(4), 205
13. Wörsdörfer, U. *et al.*, *Prax. Sicherheitstech.* 1997, **4**, 355; *Chem. Abs.*, 1998, **128**, 77116m
14. Urben, P. G., *J. Chem. Educ.*, 1992, **69**, 334
15. Editor's comments, 1993

Accident statistics reveal nitration as the most widespread and powerfully destructive industrial unit process operation. This is because nitric acid can, under certain conditions, effect complete and highly exothermic conversion of organic molecules to gases, the reactions often being capable of acceleration to deflagration or detonation. Case histories are described and safety aspects of continuous nitration processes are discussed in detail [1]. Of the 25 chapters of the book [2], each a paper presented at the symposium on 'Advances in Industrial and Laboratory Nitrations' at Philadelphia in 1975, 3 deal with safety aspects of nitration: Ch. 8, Hanson, C. *et al.*, *Side Reactions during Aromatic Nitration*; Ch. 22, Biasutti, G. S., *Safe Manufacture and Handling of Liquid Nitric Esters*; Ch. 23, Brunberg, B., *Safe Manufacture and Handling of Liquid Nitric Esters: the Injector Nitration Process*

Reaction parameters important for control of continuous nitration systems were identified, as were secondary parameters useful for diagnostic/protective purposes. The algorithms developed were successfully applied to a pilot plant for continuous nitration of 2-pyridone in acetic anhydride [3]. Technological difficulties associated with methods of reducing explosion hazards in aromatic nitration were discussed [4], and many case histories of violent incidents during nitration operations have been collected [5,6]. In a comprehensive review, general safety precautions and information relevant to nitration are reported [7]. Safety considerations relevant to the development and design of a new industrial nitration plant are detailed [8]. An account is given of the relatively inexpensive methods used to develop safe processing and reaction conditions for the conversion of 5-chloro-1,3-dimethyl-1*H*-pyrazole to the 4-nitro derivative [9]. A detailed study of safety optimisation of aromatic nitration, with the particular example of chlorobenzene is reported in [12].

Use of sensors to measure gas phase NO<sub>2</sub> concentration, electrical conductivity of the reaction mass, and gas phase temperatures at several critical points in semi-continuous nitration reactors permits safe operation of nitration processes [10]. The use of non-aqueous titration analysis in the control of nitration processes in explosives manufacture is discussed [11].

Nitration is also a frequent cause of laboratory accident. A mixed acid nitration of arylcarboxylic esters, the substrate dissolved in sulphuric acid and nitric added

to this mix, was found to be increasingly thermally unstable with increasing nitric acid excess. Process safety could not be guaranteed with above 10% excess [13]. Some suggestions on safer, cleaner nitration procedures are given in [14]. There would be fewer laboratory nitration mishaps if reaction equations were written in full and balanced so that the usual reaction was seen as an acid catalysed dehydration of nitric acid, the supposed substrate being only a scavenger of the product of dehydration (and often also a base in the nitration environment). The competing radical oxidation reaction which is the direct cause of accident is not greatly acid catalysed, but autocatalytic and catalysed by free  $\cdot\text{NO}_2$ . Consideration of mechanism can usually produce safer procedures than scholastic labours in the academic literature, whereby methods are often inherited unchanged from the last century. It should be noted that most of the studies above come from the heavy chemical industry, who are economically constrained to use rather wet conditions (and nitration is a dehydration!) and commonly work with two phase mixtures. Their conclusions do not necessarily, or even usually, represent optimal laboratory procedure, especially for homogeneous nitrations [15].

Individually detailed nitration incidents are found under:

2-Chloro-1,3-dinitro-5-trifluoromethylbenzene, 2637

Dimethyl 4-acetamidophthalate: Nitric acid, 3520

4,6-Dinitro-1,3-benzenediol, 2198

Dinitrogen tetraoxide, Laboratory grease, 4747

2-Methyl-4-nitroimidazole, 1475

3-Methyl-4-nitropyridine *N*-oxide, 2317

Nitric acid, 4436

3-Nitroaniline: Nitric acid, Sulfuric acid, 2314

Nitronium perchlorate, 1,2-Epoxydes, 4028

2,2'-Oxybis(ethyl nitrate), 3260

Sodium nitrate, Phenol, Trifluoroacetic acid, 4721

*See also* NITRATING AGENTS

*See other* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## NITRIDES

There are three anions that may loosely claim to be nitrides. Pentazolides (salts of cyclic  $\text{N}_5^-$ ) will all be explosive. Some azides (salts of  $\text{N}_3^-$ ) fall just short of being explosive but all are violently unstable. The true nitrides, nominal derivatives of  $\text{N}^{3-}$ , are more various. In addition to some ionic structures, there are polymeric covalent examples, and some monomeric covalent ones, while most of those of transition metals are best considered as alloys. Several are endothermic and explosive, almost all are thermodynamically very unstable in air with respect to the oxide. Many are therefore pyrophoric if finely divided and also may react violently with water and, more particularly, acids, especially oxidising acids. A few are of considerable kinetic stability in these circumstances. There is no very clear classification of probable safety by position in the periodic table but polymeric and alloy structures are in general the more stable. Individual nitrides having entries:

- \* Ammonium nitridoosmate, 4523
- Antimony(III) nitride, 4729
- Barium nitride, 0219
- \* Barium nitridoosmate, 0213
- Bismuth nitride, 0230
- Cadmium nitride, 3960
- Caesium nitride, 4266
- Calcium nitride, 3946
- \* Carbonyl(pentasulfur pentanitrido)molybdenum, 0535
- Cerium nitride, 3965
- \* Chloro-1,2,4-triselenadiazolium chloride, 4089
- Chromium nitride, 4237
- Cobalt(III) nitride, 4214
- Copper(I) nitride, 4289
- Diseleniumdisulfur tetranitride, 4769
- Disulfur dinitride, 4754
- Gold(I) nitride–ammonia, 0117
- Gold(III) nitride trihydrate, 0118
- \* Iodinated poly(sulfur nitride), 4622
- Lead nitride, 4753
- Lithium nitride, 4688
- Magnesium nitride, 4698
- Mercury nitride, 4615
- Molybdenum nitride (mixture of 3), 4714
- Pentasulfur hexanitride, 4784
- Plutonium nitride, 4726
- \* Poly(disilicon nitride), 4757
- \* Poly(selenium nitride), 4730
- Poly(sulfur nitride), 4728
- Potassium nitride, 4671
- \* Potassium nitridoosmate, 4651
- Rhenium nitride tetrafluoride, 4344
- Rubidium nitride, 4727
- Silver nitride, 0038
- \* Silver trisulfurpentanitride, 0024
- Sodium nitride, 4723
- \* Sodium tetrasulfur pentanitride, 4775
- \* Sodium tetrasulfur pentanitride, 4775
- Sodium trisulfurtrinitride, 4760
- Tetraselenium dinitride, 4756
- \* Tetraselenium tetranitride, 4771
- \* Tetratellurium tetranitride, 4773
- \* Tetratellurium tetranitride, 4773
- Tetrasulfur dinitride, 4755
- Tetrasulfur tetranitride, 4770
- Thallium(I) nitride, 4731

Trifluorosulfur nitride, 4338  
Trisilver tetranitride, 0040  
Tritellurium tetranitride, 4772  
Trithorium tetranitride, 4774  
Uranium(III) nitride, 4732  
Zirconium nitride, 4733

*See* Pentazole

*See* AZIDES, METAL Pnictides

### NITRITE SALTS OF NITROGENOUS BASES

$\text{N}^+ \text{NO}_2^-$

1. Mellor, 1940, Vol. 8, 289, 470–472
  2. Ray, P. C. *et al.*, *J. Chem. Soc.*, 1911, **99**, 1470; 1912, **101**, 141, 216
- Ammonium and substituted-ammonium nitrite salts exhibit a range of instability, and reaction mixtures which may be expected to yield these products should be handled with care. Ammonium nitrite will decompose explosively either as the solid, or in conc. aqueous solution when heated to 60–70°C. Presence of traces of acid lowers the decomposition temperature markedly. Hydroxylammonium nitrite appears to be so unstable that it decomposes immediately in solution. Hydrazinium(1+) nitrite is a solid which explodes violently on percussion, or less vigorously if heated rapidly, and hydrogen azide may be a product of decomposition [1]. Mono- and di-alkylammonium nitrites decompose at temperatures below 60–70°C, but usually without violence [2]. Individual entries are:

Ammonium nitrite, 4521

Hydrazinium nitrite, 4548

Methylammonium nitrite, 0505

*See other* OXOSALTS OF NITROGENOUS BASES

### NITROACYL HALIDES

$o\text{-O}_2\text{NArCO.Cl}$ , etc.

Aromatic acyl halides containing a nitro group adjacent to the halide function show a tendency towards violent thermal decomposition. The few individually indexed compounds are:

- \* 2,4-Dinitrobenzenesulfonyl chloride, 2099
- 2,4-Dinitrobenzenesulfonyl chloride, 2100
- 2,4-Dinitrophenylacetyl chloride, 2902
- 4-Hydroxy-3-nitrobenzenesulfonyl chloride, 2146
- 3-Methoxy-2-nitrobenzoyl chloride, 2915
- 4-Methoxy-3-nitrobenzoyl chloride, 2916
- 3-Methyl-2-nitrobenzoyl chloride, 2913
- 2-Nitrobenzoyl chloride, 2653
- 2-Nitrophenylacetyl chloride, 2914
- 4-Nitrothiophene-2-sulfonyl chloride, 1388

*See other* ACYL HALIDES

## NITROALKANES

## RNO<sub>2</sub>

1. *Nitroparaffins*, TDS1, New York, Commercial Solvents Corp., 1968
2. Hass, H. B. *et al.*, *Chem. Rev.*, 1943, **32**, 388
3. Noble, P. *et al.*, *Chem. Rev.*, 1964, **64**, 20
4. Murray, S. B. *et al.*, *Can. Pat. Appl.* 2123170, 1995

Nitromethane is a detonable explosive, nitroethane can be detonated if both hot and under strong confinement, other nitroalkanes are mild oxidants under ordinary conditions, but precautions should be taken when they are subjected to high temperatures and pressures, since violent reactions may occur [1]. Explosives are described consisting of nitromethane stabilised for transport by admixture with nitroethane or nitropropane, then resensitised by addition of an amine [4]. The polynitroalkanes, being more in oxygen balance than the mono-derivatives, tend to explode more easily [2], and caution is urged, particularly during distillation [3].  
*See also* POLYNITROALKYL COMPOUNDS

### Alkali metals, or Inorganic bases

Watts, C. E., *Chem. Eng. News*, 1952, **30**, 2344

Contact of nitroalkanes with inorganic bases must be effected under conditions which will avoid isolation in the dry state of the explosive metal salts of the isomeric *aci*-nitroparaffins.

### Hopcalite

*See* HOPCALITE

### Metal oxides

1. Hermoni, A. *et al.*, *Chem. & Ind.*, 1960, 1265
2. Hermoni, A. *et al.*, *Proc. 8th Combust. Symp.*, 1960, 1084–1088

Contact with metal oxides increases the sensitivity of nitromethane, nitroethane and 1-nitropropane to heat (and of nitromethane to detonation). Twenty-four oxides were examined in a simple quantitative test, and a mechanism was proposed. Cobalt, nickel, chromium, lead and silver oxides were the most effective in lowering ignition temperatures [1]. At 39 bar initial pressure, the catalytic decomposition by chromium or iron oxides becomes explosive at above 245°C [2].

### Sodium or Potassium bicarbonate

Kirk-Othmer, 1996, Vol. 17, 216

Dry powder fire extinguishers containing bicarbonate should not be used on nitromethane or nitroethane.

*See aci*-NITRO SALTS, *C*-NITRO COMPOUNDS

Individually indexed compounds are:

- \* Aluminium chloride–nitromethane, 0063
- \* Chloronitromethane, 0396
- \* Ethyl 2-nitroethyl ether, 1662
- \* Nitroacetone, 1184
- tert*-Nitrobutane, 1660
- Nitroethane, 0869

- Nitromethane, 0456
- \* Nitrooximinomethane, 0409
  - 1-Nitropropane, 1263
  - 2-Nitropropane, 1264
- \* Potassium 1-nitroethane-1-oximate, 0756
- \* Tribromonitromethane, 0314
- \* Trichloronitromethane, 0331
- \* Tris(hydroxymethyl)nitromethane, 1664

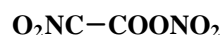
## NITROALKENES



Several nitroalkenes show high reactivity and/or low stability, individually indexed compounds being:

- \* 3,3-Dimethyl-1-nitro-1-butyne, 2395
  - 1,1-Dinitro-3-butene, 1508
  - 2,3-Dinitro-2-butene, 1509
  - 4-Fluoro-4,4-dinitrobutene, 1458
- \* 3-Methyl-4-nitro-1-buten-3-yl acetate, 2835
- \* 3-Methyl-4-nitro-2-buten-1-yl acetate, 2836
  - 4-Nitro-1-butene, 1572
  - 2-Nitropropene, 1183
  - Tetranitroethylene, 1010

## NITROALKYL PEROXONITRATES



*See* Dinitrogen tetraoxide: Cycloalkenes, etc.

## NITROANILINES



Chlorine (or other oxidant)

Hydrochloric acid

*See* Hydrogen chloride: Chlorine, Dinitroanilines

## NITROAROMATIC-ALKALI HAZARDS

1. Merz, V. *et al.*, *Ber.*, 1871, **4**, 981–982
2. Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389–390
3. (*MCA Data Sheets*); *Haz. Chem. Data*, 1975; *491M*, 1975
4. Bretherick, L., *Proc. 6th Int. Symp. Prev. Occ. Risks Chem. Ind.*, 539–546, Heidelberg, ISSA, 1979 (and additional bibliography)
5. Howes, R. J., private comm., 1979
6. Capellos, C. *et al.*, *Chem. Abs.*, 1982, **96**, 88003

It is widely stated in the usual reference texts that nitroaromatic compounds and more particularly polynitroaromatic compounds may present a severe explosion risk if subjected to shock, or if heated rapidly and uncontrollably, as in fire

situations. However, the same reference texts make no mention of the fact that there is also a risk of violent decomposition or explosion when nitroaromatic compounds are heated more moderately with caustic alkalis, even when water or organic solvents are also present. It was known more than 100 years ago that mononitroaromatics (nitro-benzene, -toluene, -naphthalene) would react violently on heating with caustic alkalis 'with generation of 1½ foot flames', and that dinitro compounds were almost completely carbonised [1]. By 1914 the potential hazards involved in heating di- or tri-nitroaryl compounds with alkalis or ammonia were sufficiently well recognised for a general warning on the possibilities of violent or explosive reactions in such systems to have been published [2]. Knowledge of these potential hazards apparently had faded to the point where they were not mentioned in standard sources of information [3].

Several industrial explosions have occurred during the past 40 years which appear to be attributable to this cause, but here has been little recognition of this or of the common features in many of the incidents. Too little investigational work in this area has been published to allow any valid conclusions to be drawn as to the detailed course of the observed reactions. However, it may be more than coincidence that in all the incidents reported, the structures of the nitroaromatic compounds involved were such that *o*- or *p*-*aci*-nitroquinonoid salt species could have been formed under the reaction conditions. Many of these salts are of very limited thermal stability. All of the available (circumstantial) evidence was collected and published [4]. Limited work by DTA showed that *o*-nitrophenol and sodium hydroxide gave a sharp exotherm at 46°, and *p*-nitrophenol at 95°, while *m*-nitrophenol gave no significant evidence of reaction below 200°C. *o*-Nitroaniline gave a sharp exotherm at 217°, and *p*-nitroaniline at 246°C [5]. Electronic excitation of TNT leads to formation of *aci*-quinonoid transient intermediates, and action of various bases leads to deflagration of molten TNT [6].

Individually indexed incidents of this type are:

2-Chloro-4-nitrotoluene, : Sodium hydroxide, 2711

2,4-Dinitrotoluene, 2726

2,4-Dinitrotoluene, : Sodium oxide, 2726

Lithium 4-nitrothiophenoxide, 2177

4-Methyl-2-nitrophenol, 2767

2-Nitroanisole, : Sodium hydroxide, Zinc, 2768

Nitrobenzene, : Alkali, 2262

Sodium 2,4-dinitrophenoxide, 2115

Sodium 4-nitrophenoxide, 2183

Sodium 2-nitrothiophenoxide, 2182

2,4,5-Trinitrotoluene, 2702

*See also aci-NITROQUINONOID COMPOUNDS, C-NITRO COMPOUNDS*

## NITROARYL COMPOUNDS

ArNO<sub>2</sub>

1. Chervin, S. *et al.*, *Proc. Workshop Microcalorim. Energ. Mater.*, 1997, R1; *Chem. Abs.*, 1998, **129**, 262429z

This group covers aromatic nuclei bearing one nitro group; most mono-nitro benzenes can be persuaded to detonate by a tetryl booster; few are an immediate danger in the absence of other sources of energy. Calorimetric studies [1] suggest that nitroaryl compounds decompose by an autocatalytic mechanism, and thus stability may depend upon thermal history. Individually indexed compounds are:

- 4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3266
- 2-(2-Aminoethylamino)-5-methoxynitrobenzene, 3172
- 2-Amino-5-nitrophenol, 2316
- \* Amminebarium bis(nitrophenylide), 3518
- 1,3-Bis(trifluoromethyl)-5-nitrobenzene, 2885
- 3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2645
- N*-Bromo-3-nitrophthalimide, 2884
- tert*-Butyl 4-nitroperoxybenzoate, 3400
- 4-Chloro-2,5-diethoxynitrobenzene, 3301
- 6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2102
- N*-Chloro-4-nitroaniline, 2231
- 2-Chloro-5-nitrobenzaldehyde, 2649
- 2-Chloro-6-nitrobenzaldehyde, 2650
- 4-Chloro-3-nitrobenzaldehyde, 2651
- 5-Chloro-2-nitrobenzaldehyde, 2652
- 2-Chloronitrobenzene, 2141
- 4-Chloronitrobenzene, 2142
- 2-Chloro-5-nitrobenzenesulfonic acid, 2144
- 2-Chloro-5-nitrobenzyl alcohol, 2715
- 4-Chloro-2-nitrobenzyl alcohol, 2716
- 4-Chloro-3-nitrobenzyl alcohol, 2717
- 5-Chloro-2-nitrobenzyl alcohol, 2718
- 6-Chloro-2-nitrobenzyl bromide, 2671
- 2-Chloro-4-nitrobenzyl chloride, 2678
- 4-Chloro-2-nitrobenzyl chloride, 2679
- 1-Chloro-4-(2-nitrophenyl)-2-butene, 3270
- 2-Chloro-4-nitrotoluene, 2711
- 4-Chloro-3-nitrotoluene, 2712
- 2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2668
- 4-Cyano-3-nitrotoluene, 2917
- 2,6-Di-*tert*-butyl-4-nitrophenol, 3666
- Dichloronitrobenzene, 2103
- Diethyl 4-nitrophenyl phosphate, 3329
- Diethyl 4-nitrophenyl thionophosphate, 3328
- 2,4-Difluoronitrobenzene, 2109
- Dimethyl 4-acetamino-5-nitrophthalate, 3515
- Disodium 4-nitrophenylphosphate, 2185
- 5-Fluoro-2-nitrophenol, 2167
- 3-Hydroxy-4-nitrobenzaldehyde, 2690
- 4-Hydroxy-3-nitrobenzaldehyde, 2691
- 5-Hydroxy-2-nitrobenzaldehyde, 2692



Lanthanum 2-nitrobenzoate, 3815  
2-Methoxy-5-nitroaniline, 2802  
3-Methoxy-2-nitrobenzaldehyde, 2937  
3-Methoxy-2-nitrobenzoyldiazomethane, 3124  
2-Methyl-5-nitroaniline, 2801  
\* *N*-Methyl-*p*-nitroanilinium 2(*N*-methyl-*N*-*p*-nitrophenylaminosulfonyl) ethylsulfate, 3713  
3'-Methyl-2-nitrobenzanilide, 3645  
2-Methyl-5-nitrobenzenesulfonic acid, 2772  
4-Methyl-3-nitrobenzenesulfonic acid, 2773  
2-Methyl-5-nitrobenzimidazole, 2940  
\* 2-Methyl-4-nitroimidazole, 1475  
3-Methyl-4-nitrophenol, 2766  
Nickel 2-nitrophenoxide, 3464  
4-Nitroacetanilide, 2950  
2-Nitroacetophenone, 2936  
2-Nitroaniline, 2313  
3-Nitroaniline, 2314  
4-Nitroaniline, 2315  
4-Nitroaniline-2-sulfonic acid, 2319  
4-Nitroanilinium perchlorate, 2350  
2-Nitroanisole, 2768  
2-Nitrobenzaldehyde, 2686  
3-Nitrobenzaldehyde, 2687  
4-Nitrobenzaldehyde, 2688  
Nitrobenzene, 2262  
3-Nitrobenzenesulfonic acid, 2268  
2-Nitrobenzoic acid, 2693  
3-Nitrobenzoic acid, 2694  
4-Nitrobenzoic acid, 2695  
2-Nitrobenzotrile, 2662  
3-Nitrobenzoyl nitrate, 2664  
2-Nitrobenzyl alcohol, 2769  
3-Nitrobenzyl alcohol, 2770  
4-Nitrobenzyl alcohol, 2771  
2-Nitrobenzyl bromide, 2710  
2-Nitrobenzyl chloride, 2713  
4-Nitrobenzyl chloride, 2714  
4-Nitrodiphenyl ether, 3472  
*miso*-Nitroindane, 3140  
4-Nitroisopropylbenzene, 3157  
Nitromesitylene, 3158  
1-Nitronaphthalene, 3249  
3-Nitroperchlorylbenzene, 2143  
2-Nitrophenol, 2265  
3-Nitrophenol, 2266

4-Nitrophenol, 2267  
 4-Nitrophenylacetic acid, 2938  
 3-Nitrophenylacetylene, 2905  
*N*-(2-Nitrophenyl)-1,2-diaminoethane, 3001  
 3-(2-Nitrophenyl)-2-hydroxyiminopropanoic acid, 3131  
 1-(2-Nitrophenyl)-5-phenyltetrazole, 3602  
 4-Nitrophenylphosphorodichloridate, 2158  
 4-Nitrophenylpropan-2-one, 3142  
 2-Nitrophenylpropionic acid, 3113  
 2-Nitrophenylsulfonyldiazomethane, 2700  
 3-Nitrophthalic acid, 2906  
 3-Nitropropiofenone, 3141  
 5-Nitrosalicylhydrazide, 2778  
 Nitroterephthalic acid, 2907  
 4-Nitrotoluene, 2764  
*miso*-Nitrotoluene, 2762  
 Potassium 4-nitrophenoxide, 2174  
 Scandium 3-nitrobenzoate, 3816  
 Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3505  
 Sodium 3-nitrobenzenesulfonate, 2184  
 5,10,15,20-Tetrakis(2-nitrophenyl)porphine, 3907  
 Thallium(I) 2- or 4-nitrophenoxide, 2186  
 Yttrium 4-nitrobenzoate trihydrate, 3817

*See also* LANTHANIDE METAL NITROBENZOATES, NITROALKANES, POLYNITROARYL COMPOUNDS

#### NITROARYLPHOSPHINIC ACIDS

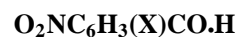


Rowbotham, P. M. *et al.*, UK Pat. 2 048 883, 1980

These may be explosive under some conditions.

*See other* NITROARYL COMPOUNDS

#### NITROBENZALDEHYDES



Cardillo, P. *et al.*, *Proc. 5th Int. Sympos. Loss Prev. Saf. Prom. Process Ind.*, Cannes, Paper P16, 1–14, SCI (Paris), 1986

A series of 11 nitrobenzaldehydes was examined by TGA, DSC and ARC techniques. Only 5-hydroxy-2-nitrobenzaldehyde decomposed exothermally in an unsealed container, but all did so in sealed capsules, under dynamic, isothermal or adiabatic conditions, with evolution of much gas. Initial decomposition temperatures in °C (compound, ARC value, and DSC value at 10°/min, respectively, followed by ARC energy of decomposition in kJ/g) were:- 2-nitro-, 176, 220, 1.44; 3-nitro-, 166, 218, 1.94; 4-nitro-, 226, 260, 1.27; 2-chloro-5-nitro-, 156, 226, 697; 2-chloro-6-nitro-, 146, 220, .832; 4-chloro-3-nitro-, 116, 165, 1.42; 5-chloro-2-nitro-, 240, 3-hydroxy-4-nitro-, 200, 4-hydroxy-3-nitro-, 200, 5-hydroxy-2-nitro-, 175, 3-methoxy-4-nitrobenzaldehyde, 245°C, -. 4-Nitrobenzaldehyde showed by

far the highest self-heating rate in ARC tests (approaching 100°/min at 240°C) and the final pressure exceeded 170 bar when the pressure relief operated. The results are compared with those from various nitrobenzyl derivatives.

Individually indexed compounds are:

- 2-Chloro-5-nitrobenzaldehyde, 2649
- 2-Chloro-6-nitrobenzaldehyde, 2650
- 4-Chloro-3-nitrobenzaldehyde, 2651
- 5-Chloro-2-nitrobenzaldehyde, 2652
- 3-Hydroxy-4-nitrobenzaldehyde, 2690
- 4-Hydroxy-3-nitrobenzaldehyde, 2691
- 5-Hydroxy-2-nitrobenzaldehyde, 2692
- 3-Methoxy-2-nitrobenzaldehyde, 2937
- 2-Nitrobenzaldehyde, 2686
- 3-Nitrobenzaldehyde, 2687
- 4-Nitrobenzaldehyde, 2688

See NITROBENZYL COMPOUNDS (next below)

## NITROBENZYL COMPOUNDS

## O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>X

1. Cardillo, P. *et al.*, *J. Chem. Eng. Data*, 1984, **29**, 348–351
2. Cardillo, P. *et al.*, *Proc. 5th Nat. Congr. Calorim. Therm. Anal.*, Trieste, 1983
3. Cardillo, P. *et al.*, *Proc. 15th Nat. Congr. Ital. Chem. Soc.*, 349–350, 1984; *Chim. e Ind. (Milan)*, 1986, **68**(6), 68–70
4. Cardillo, P. *et al.*, *Chim. e Ind. (Milan)*, 1985, **67**, 403–405

Thermal stabilities of the six *o*-, *m*- and *p*-nitrobenzyl bromides and chlorides were studied comparatively by TGA, DSC and ARC techniques. In open sample containers, only *o*-nitrobenzyl bromide decomposed exothermally, but in sealed capsules all the compounds decomposed exothermally after melting, with abundant gas evolution. The bromides were less stable than the chlorides, and *o*-isomers less stable than others. Very high self-heating rates (>10°C/min), pressure increase rates (20 bar/min) and final pressures (>170 bar, when relief valve opened) were observed for all samples in the ARC runs [1]. The effect of halogen substitution in the ring upon thermal stability of nitrobenzyl halides was studied by DTA, DSC and ARC techniques. The latter gave the following results for sealed bombs (onset of exotherm °C, maximum temperature °C and calculated energy of decomposition in kJ/g, respectively). 6-Chloro-2-nitrobenzyl bromide, 165, 306, 0.85; 4-chloro-2-nitrobenzyl chloride, 151, 230, 1.01. The bromide was the least stable, and above 190°C the self-heating rate (>10°/min) prevented adiabatic operation of the calorimeter, and the pressure very rapidly approached 130 bar [2]. ARC examination of some industrially important potentially thermally unstable nitrobenzyl alcohols gave the following results (onset of exothermic decomposition °C, final temperature °C and calculated energy of decomposition in kJ/g, respectively). 2-Nitrobenzyl alcohol, 201, 343, 1.78; 3-nitro, 221, 332, 1.32; 4-nitro, 236, 310, 0.93; 5-chloro-2-nitro, 191, 286, 1.15; 4-chloro-3-nitro, 211, 315, 1.15; 4-chloro-2-nitro, 201, 229, 1.19; 2-chloro-5-nitro, 211, 329, 1.38 [3]. ARC results for 2-chloro-4-nitrobenzyl chloride are 216, 261, 1.01 [4].

Individually indexed compounds are:  
 2-Chloro-5-nitrobenzyl alcohol, 2715  
 4-Chloro-2-nitrobenzyl alcohol, 2716  
 4-Chloro-3-nitrobenzyl alcohol, 2717  
 5-Chloro-2-nitrobenzyl alcohol, 2718  
 6-Chloro-2-nitrobenzyl bromide, 2671  
 2-Chloro-4-nitrobenzyl chloride, 2678  
 4-Chloro-2-nitrobenzyl chloride, 2679  
 2,6-Dinitrobenzyl bromide, 2672  
 2-Nitrobenzyl alcohol, 2769  
 3-Nitrobenzyl alcohol, 2770  
 4-Nitrobenzyl alcohol, 2771  
 2-Nitrobenzyl bromide, 2710  
 2-Nitrobenzyl chloride, 2713  
 4-Nitrobenzyl chloride, 2714  
*See other* BENZYL COMPOUNDS

## NITRO COMPOUNDS

C-NO<sub>2</sub>, N-NO<sub>2</sub>

The presence of one or more nitro groups (with 69.6% oxygen) linked to C or N in an organic compound may have a significant effect on the reactivity, oxygen balance and stability of the compound. (Compounds with a nitro group linked to O, nitrate esters, are of very much lower stability and are dealt with separately). The class has been subdivided into the separately treated groups:

METAL NITROPHENOXIDES, NITROACYL HALIDES  
 NITROALKANES, NITROALKENES  
 NITROALKYL PEROXONITRATES, NITROARYL COMPOUNDS  
 NITROARYLPHOSPHINIC ACIDS, NITROBENZYL COMPOUNDS  
 C-NITRO COMPOUNDS, N-NITRO COMPOUNDS  
*aci*-NITROQUINONOID COMPOUNDS, *aci*-NITRO SALTS  
 POLYNITROALKYL COMPOUNDS, POLYNITROARYL COMPOUNDS  
 POLYNITROAZOPYRIDINES

Other relevant entries are:

NITROAROMATIC-ALKALI HAZARDS

## C-NITRO COMPOUNDS

C-NO<sub>2</sub>

1. Engelke, R. *et al.*, *Int. J. Chem. Kinetics*, 1986, **18**, 1205
2. Constantinou, C. P., *Phil. Trans. R. Soc. London Ser. A*, 1992, **339**, 403

In general, C-nitro compounds are more stable than N-nitro compounds because of the higher bonding energies in the former type. Evidence is offered [1] that decomposition and explosion of many nitro-derivatives proceeds through the *aci*-form, and that sensitivity corresponds to the proportion of that present. In terms of this work, sensitisation by very small proportions of soluble organic bases is most important; this is not limited to nitroalkanes. TNT can apparently be brought to the sensitivity of lead azide by this means. For a physicist's view of this sensitisation,

see [2]. All but one of the separately treated groups named in the previous entry deal with *C*-nitro compounds, and some individually indexed compounds are:

- 2-Amino-4,6-dihydroxy-5-nitropyrimidine, 1436
- 2-Carbamoyl-2-nitroacetonitrile, 1116
- 5-Chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole, 1864
- Mercury(II) 5-nitrotetrazolide, 0981
- 1-Methylamino-1-methylthio-2-nitroethene, 1596
- Methylnitrothiophene, 1850
- Nitroacetaldehyde, 0763
- 2-Nitroethanol, 0871
- 2-Nitroethanonitrile, 0711
- Nitromethane, 0456
- 5-Nitrotetrazole, 0387
- 3-Nitro-1,2,4-triazolone, 0716
- Potassium 2,5-dinitrocyclopentanone, 1847
- Potassium 1-nitroethoxide, 0806
- \* Sodium diformylnitromethanide hydrate, 1076
- Sodium 5-nitrotetrazolide, 0547

## ***N*-NITRO COMPOUNDS**

## **N–NO<sub>2</sub>**

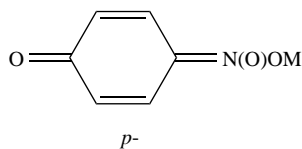
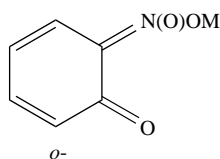
van Romburgh, P., *Chem. Weekblad*, 1934, **31**, 732–733

Many *N*-nitro compounds show explosive instability, arising from the low N–N bonding energy, and the explosive properties of *N*-alkyl-*N*-nitroarylamines have been discussed. Individually indexed compounds are:

- 1-Amino-3-nitroguanidine, 0495
- Ammonium 1,2-ethylenebis(nitramide), 0972
- Azo-*N*-nitroformamidine, 0825
- 3,3'-Azo-(1-nitro-1,2,4-triazole), 1401
- Bis(2-azidoethoxymethyl)nitramine, 2481
- 1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0803
- \* Bis(2-nitratoethyl)nitric amide, 1602
- N*-Butyl-*N*-2-azidoethylnitramine, 2528
- N,N'*-Diacetyl-*N,N'*-dinitro-1,2-diaminoethane, 2426
- 1,12-Diazido-3,10-dioxo-5,8-dinitrazadodecane, 3049
- 1,3-Diazido-2-nitroazapropane, 0824
- N,N'*-Dimethyl-*N,N'*-dinitrooxamide, 1513
- Dinitramine, 4442
- N,N'*-Dinitro-1,2-diaminoethane, 0916
- 1,3-Dinitro-2-imidazolidinone, 1142
- N,N'*-Dinitro-*N*-methyl-1,2-diaminoethane, 1276
- N*-Fluoro-*N*-nitrobutylamine, 1645
- 2-Hydroxy-4,6-bis(nitroamino)-1,3,5-triazine, 1122
- Lead methylenebis(nitramide), 4882
- Methylenebis(nitramine), 0483
- Methylenebis(3-nitramino-4-methylfurazan), 2805

1-Methyl-3-nitroguanidinium nitrate, 0947  
 1-Methyl-3-nitroguanidinium perchlorate, 0939  
 1-Methyl-3-nitro-1-nitrosoguanidine, 0876  
 Nitric amide, 4471  
 2-(*N*-Nitroamino)pyridine *N*-oxide, 1851  
 4-(*N*-Nitroamino)pyridine *N*-oxide, 1852  
 5-*N*-Nitroaminotetrazole, 0415  
 1-Nitro-3-(2,4-dinitrophenyl)urea, 2705  
 Nitroguanidine, 0482  
*N*-Nitromethanimine, 0408  
*N*-Nitromethylamine, 0478  
 Nitrourea, 0460  
 Silver *N*-nitrosulfuric diamidate, 0016  
*N*,2,3,5-Tetranitroaniline, 2121  
*N*,2,4,6-Tetranitroaniline, 2123  
*N*,2,4,6-Tetranitro-*N*-methylaniline, 2706  
 1,3,5,7-Tetranitroperhydro-1,3,5,7-tetrazocine, 1605  
*trans*-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecahydronaphthalene, 2427  
 1,3,5-Trinitrohexahydro-1,3,5-triazine, 1219  
 See also *N*-AZOLIUM NITROIMIDATES

#### ***aci*-NITROQUINONOID COMPOUNDS**



Generally, aromatic nitro compounds cannot form *aci*-nitro salts with bases unless there is an *o*- or *p*-substituent present (or is introduced by the action of the base) bearing a labile hydrogen atom. Then, isomerisation to produce *o*- or *p*-quinonoid *aci*-nitro species, then the salt, may be possible. Many salts of this type are unstable or explosive, and such species may have been involved in various incidents with nitro-aromatics and bases. Although more stable to acids than alkalis, nitroaromatic compounds, especially heterocyclic ones, are sometimes found to undergo vigorous decomposition on drying, which can be acid catalysed. Good washing is advisable before insertion in drying ovens. Individually indexed *aci*-nitro salts are:

- \* 1-Fluoro-2,4-dinitrobenzene, 2108
- Lithium 4-nitrothiophenoxide, 2177
- Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienonide, 2722
- Potassium 6-*aci*-nitro-2,4-dinitro-2,4-cyclohexadieniminide, 2113
- Potassium 6-*aci*-nitro-2,4-dinitro-1-phenylimino-2,4-cyclohexadienide, 3451
- Potassium 4-nitrophenoxide, 2174
- \* Silver 4-nitrophenoxide, 2126

Sodium 1,4-bis(*aci*-nitro)-2,5-cyclohexadienide, 2188  
 Sodium 3,5-bis(*aci*-nitro)cyclohexene-4,6-diiminide, 2203  
 Sodium 4,4-dimethoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide, 2951  
 Sodium 3-hydroxymercurio-2,6-dinitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2083  
 Sodium 2-hydroxymercurio-4-*aci*-nitro-2,5-cyclohexadienonide, 2171  
 Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2111  
 Sodium 6-*aci*-nitro-4-nitro-2,4-cyclohexadieniminide, 2200  
 Sodium 4-nitrophenoxide  
 Sodium 2-nitrothiophenoxide, 2182  
 2,4,6-Trinitrotoluene, : Potassium hydroxide, 2683  
*See* NITROAROMATIC-ALKALI HAZARDS

### ***aci*-NITRO SALTS**



Many *aci*-nitro salts derived from action of bases on nitroalkanes are explosive in the dry state. Individually indexed compounds are:

- Ammonium *aci*-nitromethanide, 0504
- Dipotassium *aci*-nitroacetate, 0672
- Mercury(II) *aci*-dinitromethanide, 0707
- Nitromethane, : Lithium tetrahydroaluminate, 0456
- \* Potassium phenyldinitromethanide, 2682
- \* Sodium diformylnitromethanide hydrate, 1076
- Sodium 1,3-dihydroxy-1,3-bis(*aci*-nitromethyl)-2,2,4,4-tetramethylcyclobutandiide, 3344
- Thallium *aci*-phenylnitromethanide, 2723

*See* NITROALKANES: alkali metals, or inorganic bases

*See also aci*-NITROQUINONOID COMPOUNDS, (next above)

### **NITROSATED NYLON**



Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 20

Nylon, nitrosated with dinitrogen trioxide according to Belg. Pat. 606 944 and stored cold, exploded on being allowed to warm to ambient temperature. The *N*-nitroso nylon would be similar in structure to *N*-nitroso-*N*-alkylamides, some of which are thermally unstable. Nylon components should therefore be excluded from contact with nitrosating agents.

*See other* NITROSO COMPOUNDS

### **NITROSO ARENES**



Koikov, L. N. *et al.*, *J. Org. Chem. USSR*, 1985, **21**, 1564–1574

The general reaction of nitroso arenes with  $\alpha$ -dimethylaminostyrenes in benzene or ether to produce  $\text{ArCO} \cdot \text{C}(\text{NMe}_2)=\text{NC}_6\text{H}_4\text{R}$  is vigorously exothermic, and with large quantities the reaction mixture may be ejected from the reaction vessel.

*See* NITROSO COMPOUNDS, (next below)

## NITROSO COMPOUNDS

## C-N:O, N-N:O

A number of compounds containing nitroso or coordinated nitrosyl groups exhibit instability under appropriate conditions. Individually indexed compounds are:

- Ammonium *N*-nitrosophenylaminoxide, 2399
- N*-(2-Chloroethyl)-*N*-nitrosocarbamoyl azide, 1131
- 1-Chloro-1-nitrosocyclohexane, 2419
- 2-Chloro-1-nitroso-2-phenylpropane, 3147
- $\mu$ -Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino) titanium, 3028
- N,N'*-Dimethyl-*N,N'*-dinitrosooxamide, 1512
- N,N'*-Dimethyl-*N,N'*-dinitrosoterephthalamide, 3284
- N,N*-Dimethyl-4-nitrosoaniline, 2980
- 1,2-Dimethylnitrosohydrazine, 0946
- 3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1954
- Dinitrosylnickel, 4741
- Ethyl *N*-methyl-*N*-nitrosocarbamate, 1597
- Lead(II) trinitrosobenzene-1,3,5-trioxide, 3594
- 1-Methyl-3-nitro-1-nitrosoguanidine, 0876
- N*-Methyl-*N*-nitrosoourea, 0875
- Nitritonitrosylnickel, 4742
- N*-Nitrosoacetanilide, 2949
- Nitrosobenzene, 2261
- N*-Nitrosodiphenylamine, 3486
- N*-Nitrosoethyl-2-hydroxyethylamine, 1691
- Nitrosoguanidine, 0481
- N*-Nitroso-6-hexanelactam, 2424
- 1-Nitroso-2-naphthol, 3250
- 2-Nitrosophenol, 2263
- 4-Nitrosophenol (1,4-Benzoquinone monoxime), 2264
- Nitrosyl chloride, 4023
- Nitrosyl cyanide, 0541
- Nitrosylruthenium trichloride, 4144
- Nitrosylsulfuric acid, 4438
- Nitrosyl tetrafluorochlorate, 3985
- Perfluoro-*tert*-nitrosobutane, 1370
- \* Potassium nitrosodisulfate, 4661
- Sodium 4-nitrosophenoxide, 2181
- 1,3,5-Trinitrosohexahydro-1,3,5-triazine, 1217
- Trinitrosophloroglucinol, 2117

See also NITROSO ARENES, NITROSATED NYLON, 3-NITROSOTRIAZENES

## 3-NITROSOTRIAZENES

## N=N-N(N:O)

Müller, E. *et al.*, *Chem. Ber.*, 1962, **95**, 1255

A very unstable series of compounds, many decomposing at well below 0°C. The products formed from *N*-sodio triazenes and nitrosyl chloride explode violently on



being disturbed with a wooden spatula, and are much more sensitive than those derived from silver triazenes. These exploded under a hammer-blow, or on friction from a metal spatula.

*See other* TRIAZENES

## ***N*–*O* COMPOUNDS**

## ***N*–*O***

There are a number of compounds containing *N*–*O* single bonds which are of limited or low stability. As well as the groups:

1,3,4-DIOXAZOLONES, FURAZAN *N*-OXIDES  
HYDROXYLAMINIUM SALTS, ISOXAZOLES, 2*H*-1,2,4-  
OXADIAZOLO[2,3-*a*]PYRIDINE-2-THIONES  
OXIMES, OXIME CARBAMATES

there are the individually indexed compounds:

3-Aminoisoxazole, 1136  
5-Aminoisoxazole-3-carbonamide, 1476  
4-Amino-3-isoxazolidinone, 1137  
3-Amino-5-methylisoxazole, 1501  
5-Amino-3-methylisoxazole, 1502  
2-Amino-4-methyloxazole, 1500  
5-Amino-3-methylthio-1,2,4-oxadiazole, 1192  
Ammonium *N*-nitrosophenylaminooxide, 2399  
2-Aza-1,3-dioxolanium perchlorate, 0898  
Azoformaldoxime, 0815  
Bis(1-benzo[*d*]triazolyl) carbonate, 3598  
Bis(1-benzo[*d*]triazolyl) oxalate, 3629  
Bis(trifluoromethyl) nitroxide, 0638  
2-*tert*-Butyl-3-phenyloxaziridine, 3406  
Calcium bis(*O*-hydroxylamide), 3930  
Calcium hydroxide *O*-hydroxylamide, 3929  
*N*-(Chlorocarbonyloxy)trimethylurea, 1924  
2-Chloro-5-methylphenylhydroxylamine, 2796  
2-Cyano-2-propyl nitrate, 1506  
 $\mu$ -Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino)  
titanium, 3028  
3,4-Dichlorophenylhydroxylamine, 2243  
Dicyanofurazan, 1803  
3,4-Dimethyl-4-(3,4-dimethyl-5-isoxazolylazo)isoxazolin-5-one, 3309  
3,5-Dimethylisoxazole, 1888  
Dimethylthallium *N*-methylacetohydroxamate, 2008  
*O*-(2,4-Dinitrophenyl)hydroxylamine, 2279  
Disodium *N,N'*-dimethoxysulfonyldiamide, 0911  
\* 3-Ethyl-4-hydroxy-1,2,5-oxadiazole, 1504  
2-Heptafluoropropyl-1,3,4-dioxazolone, 1812  
1-Hydroxybenzotriazole, 2272

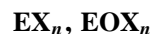
4-Hydroxy-3,5-dimethyl-1,2,4-triazole, 1575  
*N*-Hydroxydithiocarbamic acid, 0454  
*O*-(2-Hydroxyethyl)hydroxylamine, 0944  
 1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0817  
 1-Hydroxyimidazole-2-carboxaldoxime 3-oxide, 1477  
 1-Hydroxyimidazole *N*-oxide, 1134  
 Hydroxylamine, 4498  
*N*-Hydroxysuccinimide, 1469  
 Hydroxyurea  
 Hyponitrous acid, 4470  
 4-Iodo-3,5-dimethylisoxazole, 1868  
 † Isoxazole, 1110  
   Lead hyponitrite, 4745  
   Lithium sodium nitroxylate, 4683  
   Mercury(II) formohydroxamate, 0804  
 \* *N*-Methoxy-*N*-methylbenzylidenimmonium methylsulfate, 3334  
   Methyl 4-bromobenzenediazoate, 2737  
   5-Methylisoxazole, 1468  
 † Methyl nitrite, 0455  
 † 2-Methyl-2-oxazoline, 1569  
 \* *N*-(Methylphenylphosphinoyl)hydroxylamine, 2823  
   2-(4-Nitrophenoxyazo)benzoic acid, 3601  
 † Oxazole, 1111  
   2,2'-Oxybis(iminomethylfuran) mono-*N*-oxide, 3260  
   *N*-Phenylhydroxylamine, 2356  
   Phenylhydroxylaminium chloride, 2366  
   3-Phenyl-5-isoxazolone, 3122  
 \* Potassium cyclohexanehexone 1,3,5-trioximate, 2625  
   Potassium hydroxylamine-*O*-sulfonate, 4458  
 \* Potassium methanediazoate, 0449  
   Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, 4662  
   Potassium 1-phenylethanediazoate, 2964  
   Potassium *O*-propionhydroxamate, 1210  
   Silver benzo-1,2,3-triazole-1-oxide, 2127  
 \* Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1409  
 \* Sodium 4-chloroacetophenone oximate, 2927  
 \* Sodium 3-methylisoxazolin-4,5-dione-4-oximate, 1419  
   Sodium nitroxylate, 4722  
   Sodium 3-phenylisoxazolin-4,5-dione-4-oximate, 3114  
 \* Sodium tris(*O,O'*-1-oximatonaphthalene-1,2-dione)ferrate, 3871  
   Thallium(I) methanediazoate, 0458  
   *N*-Trifluoroacetoxy-2,4-dinitroaniline, 2892  
   *N*-Trimethylsilyl-*N*-trimethylsilyloxyacetoacetamide, 3375

**NON-METAL AZIDES**

This group contains compounds with azide groups linked to non-oxygenated non-metals, individually indexed compounds being:

- \* Aluminium tetraazidoborate, 0059
- Ammonium azide, 4526
- Azidodimethylborane, 0888
- Azidoiodoiodonium hexafluoroantimonate, 4361
- Azidosilane, 4501
- Bis(trifluoromethyl) phosphorus(III) azide, 0639
- \* Boron azide dichloride, 0126
- \* Boron azide diiodide, 0148
- Boron triazide, 0153
- Diazidodichlorosilane, 4092
- Diazidodimethylsilane, 0918
- \* Diphenyl azidophosphate, 3489
- Diphenylphosphorus(III) azide, 3488
- Disulfuryl diazide, 4780
- 1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine, 4795
- Hydrazinium azide, 4550
- Hydrogen azide, 4441
- \* Lithium tetraazidoborate, 0151
- 4-Nitrobenzenediazonium azide, 2209
- Nitrosyl azide, 4766
- \* Phosphorus azide difluoride, 4315
- \* Phosphorus azide difluoride–borane, 4316
- Phosphorus triazide, 4789
- \* Phosphorus triazide oxide, 4788
- Silicon tetraazide, 4791
- \* Sodium hexaazidophosphate, 4794
- Sulfinyl azide, 4778
- Sulfuryl azide chloride, 4031
- Sulfuryl diazide, 4779
- \* Tetramethylammonium diazidoiodate(I), 1750
- Triazidoarsine, 0103
- Triazidochlorosilane, 4035
- † Trimethylsilyl azide

*See related* ACYL AZIDES, HALOGEN AZIDES

**NON-METAL HALIDES AND THEIR OXIDES**

This highly reactive class includes the separately treated groups:

HALOBORANES, *N*-HALOGEN COMPOUNDS  
HALOPHOSPHINES, HALOSILANES  
PERFLUOROSILANES

as well as the individually indexed compounds:

- Arsenic pentafluoride, 0095
- Arsenic trichloride, 0094
- \* Arsine–boron tribromide, 0101
- Bis(*S,S*-difluoro-*N*-sulfimido)sulfur tetrafluoride, 4381
- \* Bis(trichlorophosphoranylidene)sulfamide, 4188
- \* Borane–phosphorus trifluoride, 0140
- \* Boron azide diiodide, 0148
- Boron bromide diiodide, 0120
- \* Boron diiodophosphide, 0149
- Boron tribromide, 0122
- Boron trichloride, 0127
- Boron trifluoride, 0129
- \* Boron trifluoride diethyl etherate, 1674
- Boron triiodide, 0150
- \* *N*-Carboethoxyiminophosphoryl chloride, 1170
- \* *N*-Carbomethoxyiminophosphoryl chloride, 0743
- Carbonyl dichloride, 0329
- Chlorotetrafluorophosphorane, 3987
- \* Chloro-1,2,4-triselenadiazolium chloride, 4089
- Diboron tetrachloride, 0161
- Diboron tetrafluoride, 0162
- \* Dibromoborylphosphine, 0121
- \* Dichloroborane, 0124
- \* Dichlorodisilylaminoborane, 0125
- \* Diethylaminosulfur trifluoride, 1684
- Diphosphoryl chloride, 4168
- Diselenium dichloride, 4115
- Disulfur dibromide, 0282
- Disulfur dichloride, 4114
- Disulfuryl dichloride, 4103
- \* Hexachlorocyclotriphosphazine, 4189
- Hydriodic acid, 4423
- Hydrogen bromide, 0247
- Hydrogen chloride, 3993
- Hydrogen fluoride, 4294
- Krypton difluoride, 4313
- \* 4-Nitrophenylphosphorodichloridate, 2158
- Nitrosyl fluoride, 4302
- Nitryl fluoride, 4303
- \* Pentafluoroorthoselenic acid, 4354
- \* Phenylphosphonyl dichloride, 2245
- \* Phosphorus azide difluoride, 4315
- \* Phosphorus azide difluoride–borane, 4316
- Phosphorus chloride difluoride, 3979
- \* Phosphorus diiodide triselenide, 4629

Phosphorus pentachloride, 4183  
 Phosphorus tribromide, 0293  
 Phosphorus trichloride, 4153  
 \* Phosphorus tricyanide, 1343  
 Phosphorus trifluoride, 4339  
 Phosphorus triiodide, 4636  
 Phosphoryl chloride, 4149  
 \* Phosphoryl dichloride isocyanate, 0327  
 \* Poly(dibromosilylene), 0283  
 \* Poly(difluorosilylene), 4330  
 \* Potassium hexafluorosilicate(2-), 4364  
 Seleninyl bromide, 0275  
 Seleninyl chloride, 4097  
 Selenium difluoride dioxide, 4321  
 Selenium tetrabromide, 0295  
 Selenium tetrafluoride, 4351  
 \* Silicon dibromide sulfide, 0281  
 Silicon tetrafluoride, 4352  
 Sulfinyl bromide, 0274  
 Sulfinyl chloride, 4096  
 Sulfinyl fluoride, 4318  
 Sulfonyl chloride, 4099  
 Sulfur dibromide, 0280  
 Sulfur dichloride, 4113  
 Sulfur hexafluoride, 4374  
 Sulfur tetrafluoride, 4350  
 Tellurium tetrachloride, 4175  
 \* Tetracarbon monofluoride, 1362  
 Tetrachlorodiphosphane, 4171  
 Tetrachlorosilane, 4173  
 Tetraiododiphosphane, 4637  
 Thiazyl fluoride, 4306  
 \* Thiophosphoryl chloride, 4154  
 \* Thiophosphoryl chloride difluoride, 3980  
 \* Thiophosphoryl fluoride, 4340  
 Thiotriethiazyl chloride, 4033  
 Triboron pentafluoride, 0175  
 \* *B*-1,3,5-Trichloroborazine, 0174  
 1,3,5-Trichloro-2,4,6-trifluoroborazine, 0173  
 Trifluoromethanesulfinyl fluoride, 0354  
 \* Trifluoroselenium hexafluoroarsenate, 0099  
 Trifluorosulfur nitride, 4338  
 Xenon difluoride, 4332  
 Xenon difluoride oxide, 4319  
 Xenon hexafluoride, 4377  
 Xenon tetrafluoride, 4353

**NON-METAL HYDRIDES****EH<sub>n</sub>**

Vogman, L. P., *Chem. Abs.*, 1984, **101**, 116147

The minimum oxygen concentration for explosion of most volatile hydrides of Group IIIA–VA elements is nearly zero, so complete exclusion of air or oxygen is essential for safe working. Presence of impurities in hydride mixtures further increases the danger of ignition.

There are separate group entries for:

BORANES, PHOSPHINES, SILANES

Most members of this readily oxidised class ignite in air, individually indexed compounds being:

- † Ammonia, 4497
- \* Ammonium hydroxide, 4544
- † Arsine, 0100
- \* Arsine–boron tribromide, 0101
- \* Borazine, 0176
- \* Cobalt tris(dihydrogenphosphide), 4203
- \* Dibromoborylphosphine, 0121
- \* Dichlorodisilylaminoborane, 0125
- \* 1,1-Diethoxy-1,3-disiladioxetane, 1762
- † Hydrazine, 4520
  - Hydrogen bromide, 0247
  - Hydrogen chloride, 3993
- † Hydrogen disulfide, 4484
  - Hydrogen fluoride, 4294
  - Hydrogen iodide
- † Hydrogen selenide, 4486
- † Hydrogen sulfide, 4483
- † Hydrogen telluride, 4488
  - Hydrogen trisulfide, 4485
- \* Phospham, 4440
- † Phosphine, 4508
  - ‘Solid Phosphorus hydride’, 4449
  - Silicon monohydride, 4451
- † Stibine, 4510
  - ‘Unsaturated’ Silicon hydride, 4452

*See related* ALKYLNON-METAL HYDRIDES

**NON-METAL OXIDES****E<sub>m</sub>O<sub>n</sub>**

The generally acidic materials in this group may function as oxidants, some rather powerful, under appropriate conditions. Individually indexed compounds are:

- Arsenic pentaoxide, 0106
- Arsenic trioxide, 0105
- Boron trioxide, 0170
- Carbon dioxide, 0557
- † Carbon monoxide, 0555

- † Carbonyl sulfide, 0556
- Deuterium oxide, 4291
- Diboron oxide, 0169
- Dinitrogen oxide, 4744
- Dinitrogen pentaoxide, 4748
- Dinitrogen tetraoxide, 4747
- Dinitrogen trioxide, 4746
- \* Diphenylselenone, 3494
- Disulfur heptaoxide, 4870
- Nitrogen dioxide, 4725
- Nitrogen oxide, 4724
- \* Poly(dihydroxydioxodisilane), 4480
- \* Potassium hexaoxoxenonate–xenon trioxide, 4674
- Selenium trioxide, 4852
- Silicon dioxide, 4839
- Silicon oxide, 4828
- Sulfur dioxide, 4837
- Sulfur trioxide, 4849
- \* Sulfur trioxide–dimethylformamide, 4850
- Tellurium trioxide, 4853
- \* Tetrahydroxydioxotrisilane, 4536
- Tetraphosphorus decaoxide, 4872
- Tetraphosphorus hexaoxide, 4867
- \* Tetraphosphorus hexaoxide–bis(borane), 4868
- \* Tetraphosphorus hexaoxide tetrasulfide, 4869
- \* Tetraphosphorus tetraoxide trisulfide, 4859
- Xenon(IV) hydroxide, 4533
- Xenon tetraoxide, 4863
- Xenon trioxide, 4857

*See* GRAPHITE OXIDE, HALOGEN OXIDES

#### NON-METAL PERCHLORATES

**E(ClO<sub>4</sub>)<sub>n</sub>**

1. Solymosi, F., *Chem. Abs.*, 1972, **77**, 42498
2. Sunderlin, K. G. R., *Chem. Eng. News*, 1974, **52**(31), 3

The thermal stability, structures and physical properties of various non-metal perchlorates (nitrosyl, nitronium, hydrazinium, ammonium, etc.) have been reviewed [1]. Many organic perchlorates were examined for sensitivity to impact. The salts of cations containing only C, H and S exploded quite consistently, while those with C, H, and N, or C, H, N, and S did not explode, except 1,2-bis(ethylammonio)ethane diperchlorate [2].

#### Trifluoromethanesulfonic acid

Several perchlorate derivatives of non-metallic elements (including some non-nitrogenous organic compounds) are noted for explosive instability.

*See* Trifluoromethanesulfonic acid: Perchlorate salts  
 ALKENE BIS(SULFONIUM PERCHLORATES)  
 ORGANOSILYL PERCHLORATES  
 PERCHLORATE-DOPED CONDUCTING POLYMERS  
 PERCHLORATE SALTS OF NITROGENOUS BASES  
 and the individually indexed entries:  
 $\eta$ -Benzenecyclopentadienyliron(II) perchlorate  
 1,3-Benzodithiolium perchlorate  
 \* 1,1-Bis(dimethyl sulfoxide)telluracyclopentane diperchlorate, 1588  
 \* Bis(triperchloratosilicon) oxide, 4190  
 Caesium tetraperchloratoiodate, 4161  
 1-Chloro-2,3-di(2-thienyl)cyclopropenium perchlorate, 3388  
 Chloronium perchlorate, 4065  
 4,4'-Diphenyl-2,2'-bi(1,3-dithiol)-2'-yl-2-ylum perchlorate, 3746  
 Diphenylcyclopropenylium perchlorate, 3680  
 1,3-Dithiolium perchlorate, 1094  
 Ferrocenium perchlorate, 3269  
 Fluoronium perchlorate, 3972  
 (Hydroxy)(oxo)(phenyl)- $\lambda^3$ -iodanium perchlorate, 2299  
 Iodine(III) perchlorate, 4140  
 Nitronium perchlorate, 4028  
 Nitrosyl perchlorate, 4027  
 Nitryl perchlorate, 4029  
 \* Peroxypropionyl perchlorate, 1167  
 Perylenium perchlorate, 3790  
 Phenyl, phenylethynyliodonium perchlorate, 3635  
 2-Tetrahydrofuranlydene(dimethylphenylphosphine-trimethylphosphine)-  
 2,4,6-trimethylphenylnickel perchlorate, 3854  
 2-Tetrahydropyranlydene-bis(dimethylphenylphosphine)-3,4,6-trimethyl-  
 phenylnickel perchlorate, 3877  
 2,3,4,6-Tetramethylpyrilium perchlorate, 3167  
 Tetraperchloratosilicon, 4169  
 Thianthrenium perchlorate, 3455  
 Thiotriazolium perchlorate, 4032  
 Triferrocenylcyclopropenium perchlorate, 3885  
 2,4,6-Trimethylpyrilium perchlorate, 2992  
 Trimethylsilyl perchlorate, 1302  
 2,4,6-Triphenylpyrilium perchlorate, 3839  
 Tris(ethylthio)cyclopropenium perchlorate, 3179  
 \* 1,4,7-Trithia[7]ferrocenophene-acetonitrilecopper(I) perchlorate, 3710  
 Tropylium perchlorate, 2742  
 Xenon(II) fluoride perchlorate, 3977  
*See other* PERCHLORATES



**NON-METALS****E**

Some members of this group of elements are readily oxidised with more or less violence dependent upon the oxidant and conditions of contact. Individually indexed elements (and some binary compounds) are:

- Argon, 0091
- Arsenic, 0092
- Boron, 0119
- \* Boron nitride, 0152
- \* Boron phosphide, 0156
- Carbon, 0298
- \* Carbon tetraboride, 0309
- † Hydrogen (Gas), 4453
- † Hydrogen (Liquid), 4454
- Nitrogen (Gas), 4734
- Nitrogen (Liquid), 4735
- Oxygen (Gas), 4831
- Oxygen (Liquid), 4832
- Ozone, 4846
- † Phosphorus, 4874
- \* Selenium, 4908
- \* Silicon, 4909
- † Sulfur, 4897
- \* Tellurium, 4916
- Xenon, 4926

**NON-METAL SULFIDES** **$E_m S_n$** 

In this group of readily oxidised materials, individually indexed compounds are:

- Arsenic trisulfide, 0108
- Bis(2,4-dinitrophenyl) disulfide, 3449
- Bis(2-nitrophenyl) disulfide, 3465
- Boron trisulfide, 0172
- † Carbon disulfide, 0560
- Carbon sulfide, 0559
- † Carbonyl sulfide, 0556
- \* Disilyl sulfide, 4568
- † Hydrogen disulfide, 4484
- † Hydrogen selenide, 4486
- † Hydrogen sulfide, 4483
- Hydrogen trisulfide, 4485
- \* Phosphorus diiodide triselenide, 4629
- Propadienedithione, 1350
- \* Silicon dibromide sulfide, 0281
- Silicon monosulfide, 4898
- Tetraarsenic tetrasulfide, 0109
- \* Tetramethyldiphosphane disulfide, 1766

- Tetraphosphorus decasulfide, 4878
- \* Tetraphosphorus decasulfide . pyridine complex
- \* Tetraphosphorus hexaoxide tetrasulfide, 4869
- \* Tetraphosphorus tetraoxide trisulfide, 4859
- \* Tetraphosphorus triselenide, 4880
- Tetraphosphorus trisulfide, 4877
- \* Tris(2-propylthio)phosphine

## N-S COMPOUNDS

## N-S

1. Bojes, J. *et al.*, *Inorg. Synth.*, 1989, **25**, 30

Many compounds containing either single or multiple bonds between N and S show a considerable degree of instability. Information is given on hazards of, and precautions in handling derivatives of cyclic N-S compounds [1]. Individually indexed compounds are:

- Amidosulfuric acid, 4499
- 5-Amino-1,2,3,4-thiazotriazole, 0413
- \* Ammonium amidoselenate, 4557
- Ammonium amidosulfate, 4556
- \* Ammonium thiosulfate, 4573
- \* Ammonium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide
- Benzo-1,2,3-thiadiazole, 2199
- Benzo-1,2,3-thiadiazole 1,1-dioxide, 2191
- Bis(*S,S*-difluoro-*N*-sulfimido)sulfur tetrafluoride, 4381
- Bis(dimethylamino) sulfoxide, 1757
- Bis-*N*(imidosulfurdifluoridato)mercury, 4342
- 3,4-Bis(1,2,3,4-thiazotriazol-5-ylthio)maleimide, 2073
- Bis(1,2,3,4-thiazotriazol-5-ylthio)methane, 1084
- \* Bis(trichlorophosphoranylidene)sulfamide, 4188
- \* Carbonyl(pentasulfur pentanitrido)molybdenum, 0535
- (Chlorocarbonyl)imidosulfur difluoride, 0318
- \* Chlorosulfonyl isocyanate, 0324
- 5-Chloro-1,2,3-thiadiazole, 0655
- \* Chloro-1,2,4-triselenadiazolium chloride, 4089
- Cyclopentaazathienium chloride, 4034
- 1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3392
- N,N*-Dichloropentafluorosulfanylamine, 4060
- S*-Diethylamino(methylimino)sulfur(IV) fluoride
- Diethylaminosulfinyl chloride, 1679
- Diethylaminosulfur trifluoride, 1684
- S,S*-Dimethylpentasulfur hexanitride, 3647
- \* 2,2-Diphenyl-1,3,4-thiadiazoline, 3647
- Disulfur dinitride, 4754
- \* Disulfur thiocyanate, 1003
- Ethyl 4-bromo-1,1,3-trioxoisothiazoleacetate, 2792
- Ethyl 6-ethoxycarbonyl-3,4-dihydro-1,1,3-trioxo-2-pyrazolo[3,4-d]isothiazole-2-acetate, 3403

*N*-Fluoroiminosulfur tetrafluoride, 4357  
 5-Hydrazino-1,2,3,4-thiaziazole, 0462  
 Iodinated poly(sulfur nitride), 4622  
 Mercury(I) thionitrosylate, 4610  
 4-Morpholinesulfenyl chloride, 1586  
 4,4'-Oxybis(benzenesulfonylhydrazide), 3525  
 Pentamethylcyclopentadienyl-bis(thiolatothiaziazyl)rhodium, 3534  
 Pentasulfur hexanitride, 4784  
*N*-Phenyl-1,2,3,4-thiaziazolamine, 2729  
 \* Poly(selenium nitride), 4730  
 Poly(sulfur nitride), 4728  
 \* Potassium azodisulfonate, 4663  
 Potassium 4-nitrobenzeneazosulfonate, 2175  
 Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, 4662  
 Potassium sulfurdiimidate, 4664  
 Potassium thiazate, 4648  
 5-(Prop-2-ynoxy)-1,2,3,4-thiaziazole, 1420  
 \* Seleninyl bis(dimethylamide), 1758  
 Silver trisulfurpentanitride, 0024  
 Sodium tetrasulfur pentanitride, 4775  
 Sodium trisulfurtrinitride, 4760  
 Sulfinylcyanamide, 0542  
 Sulfur oxide-(*N*-fluorosulfonyl)imide, 4305  
 \* Sulfur thiocyanate, 1002  
 \* Tetraselenium dinitride, 4756  
 \* Tetraselenium tetranitride, 4771  
 Tetrasulfur dinitride, 4755  
 \* Tetrasulfurtetraimide–silver perchlorate, 0029  
 Tetrasulfur tetranitride, 4770  
 \* Tetratellurium tetranitride, 4773  
 Thiazyl fluoride, 4306  
 Thiotriazyl chloride, 4033  
 Thiotriazyl nitrate, 4767  
 Thiotriazyl perchlorate, 4032  
 2-Thioxo-4-thiazolidinone, 1112  
 1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine, 4145  
 1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum, 4142  
*N*-(Trifluoromethylsulfinyl)trifluoromethylimidodisulfinyl azide, 0640  
 Trifluorosulfur nitride, 4338  
 Tris(thionitrosyl)thallium, 4764  
*See also N* -HALOGEN COMPOUNDS

## NUCLEAR WASTES

1. MacIlwhain., C. *Nature*, 1996, **383**(6599), 21
2. MacKenzie, D., *New Scientist*, 1993, (1869), 6; *ibid.*, 1993, (1870), 5

3. Scheele, R. D. *et al.*, *Chem. Abs.*, 1993, **119**, 262597a
4. Ashby, E. C. *et al.*, *J. Amer. Chem. Soc.*, 1993, **115**, 1171
5. Silva, M., *Nucl. Saf.*, 1992, **33**(2), 220
6. Anon., *Chem. Eng. News*, 1993, **71**(51), 14
7. Hyder, M. L., *Nucl. Technol.*, 1996, **116**(3), 327
8. Johnson, J., *Chem. Eng. News*, 1997, **75**(31), 10

There are chemical explosion hazards associated with stored reprocessing residues. The explosion near Chelyabinsk in the Urals in 1958 was, it has been suggested, powered by interaction of sodium nitrate and/or nitric acid with sodium acetate/acetic acid in nitrate wastes neutralised with sodium acetate, then stored and allowed to concentrate by radioactive heating [1]. A reprocessing incident at Tomsk in 1993 was apparently caused by adding nitric acid to an inadequately stirred tank of actinide salts, mostly uranium, with a butyl phosphate/paraffin extraction solvent. The substantial explosion was probably caused by nitric acid oxidation of the organics [2]. Explosive 'red oils', apparently organic nitrate by-products, are a hazard of such processing [6]. Experiment shows that, when heated above 160°C with nitric acid or metal nitrates, (tri)butyl phosphate generates gas mixtures which can autoignite. Pressures of tens of bars may be generated. It is suggested that this mechanism explains some reprocessing explosions [7]. A study of the risks with nitrate residues containing ferrocyanide as fuel has been published [3]. Explosions from extremely prolonged storage of nitric acid and hydroxylamine solutions, with and without hydrazine, which are used as reagents in reprocessing are also reported. Initial concentration by evaporation seems to be involved [8]. Gas evolution, by radiation induced dissociation of water and other components, can also permit build-up of pressure behind crusts forming on evaporation of solvent; should the hydrogen peroxide also formed from water later decompose, the gas produced could be an explosive mixture of hydrogen and oxygen. Alkaline reprocessing wastes containing ethylenediamine tetracetic acid (EDTA) evolve large volumes of hydrogen. It is postulated that this is by radiation cleavage of EDTA to formaldehyde, which is shown to produce hydrogen chemically when at low concentrations in aqueous alkali [4]. For a general consideration of largely chemical reaction hazards of concentrated wastes [5].

*See* Formaldehyde, Nitric acid

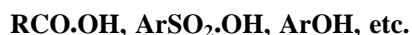
*See also* IRRADIATION DECOMPOSITION INCIDENTS

#### **OLEUM (FUMING SULFURIC ACID)**



*See* Sulfur trioxide: Sulfuric acid

#### **ORGANIC ACIDS**



This group has examples of many types of acids derived from aliphatic, aromatic and heterocyclic radicals, with carboxylic, phenolic or sulfonic or related functional substituents. Individually indexed acids are:

Acetic acid, 0833  
Acetylenedicarboxylic acid, 1405  
*O*-Acetylsalicylic acid, 3137  
1-Acetyl-4-(4'-sulfophenyl)-3-tetrazene, 2982  
Acrylic acid, 1148  
Adipic acid, 2441  
Azelaic acid, 3187  
Azidoacetic acid, 0774  
Azidodithioformic acid, 0386  
Benzeneseleninic acid, 2335  
Benzeneselenonic acid, 2338  
Benzoic acid, 2732  
Bis(3-carboxypropionyl) peroxide, 2990  
4-Bromomethylbenzoic acid, 2926  
Butyric acid, 1614  
\* 2-Carboxy-3,6-dimethylbenzenediazonium chloride, 3138  
\* *S*-Carboxymethylisothiuronium chloride, 1245  
2-Chloro-5-nitrobenzenesulfonic acid, 2144  
Citric acid, 2389  
Citronellic acid, 3352  
Cyanoacetic acid, 1113  
Diazirine-3,3-dicarboxylic acid, 1080  
Diazomalonic acid, 1081  
2,2-Dibromo-1,3-dimethylcyclopropanoic acid, 2364  
*N,N*-Dichloroglycine, 0739  
Difluoroacetic acid, 0702  
Dihydroxymaleic acid, 1447  
3,5-Dimethylbenzoic acid, 3152  
2,5-Dinitro-3-methylbenzoic acid, 2919  
\* Ferrocene-1,1'-dicarboxylic acid, 3479  
Formic acid, 4885  
Fumaric acid, 1446  
Glyoxylic acid, 0724  
2,4-Hexadienoic acid, 2385  
2,4-Hexadiyne-1,6-dioic acid, 2094  
4-Hydroxy-*trans*-cinnamic acid, 3136  
4-Hydroxy-3,5-dinitrobenzenearsonic acid, 2220  
*N*-Hydroxydithiocarbamic acid, 0454  
1-Hydroxyethylidene-1,1-diphosphonic acid, 0956  
2-Hydroxy-2-methylglutaric acid, 2445  
2-Iodylbenzoic acid  
Lactic acid, 1234  
Methacrylic acid, 1530  
Methanesulfonic acid, 0488  
2-Methyl-5-nitrobenzenesulfonic acid, 2772  
4-Methyl-3-nitrobenzenesulfonic acid, 2773

- 4-Nitroaniline-2-sulfonic acid, 2319
- 3-Nitrobenzenesulfonic acid, 2268
- 2-Nitrobenzoic acid, 2693
- 3-Nitrobenzoic acid, 2694
- 4-Nitrobenzoic acid, 2695
- 2-(4-Nitrophenoxyazo)benzoic acid, 3601
- \* 3-(2-Nitrophenyl) -2-hydroxyiminopropanoic acid, 3131
- 2-Nitrophenylpropionic acid, 3113
- 3-Nitrophthalic acid, 2906
- Nitroterephthalic acid, 2907
- 9,12,15-Octadecatrienoic acid, 3771
- cis*-9-Octadecenoic acid, 3774
- Octatetrayne-1,8-dicarboxylic acid, 3235
- Oxalic acid, 0725
- Pentanesulfonic acid, 2020
- Perfluorosuccinic acid, 1391
- 3-Peroxyamphoric acid, 3348
- Phthalic acid, 2923
- Picric acid, 2118
- \* Potassium hydrogen acetylenedicarboxylate, 1382
- \* Potassium hydrogen tartrate, 1462
- E*-Propene-1,2,3-tricarboxylic acid, 2342
- Propionic acid, 1086
- 2,5-Pyridinedicarboxylic acid, 2696
- Pyruvic acid, 1150
- Tartaric acid, 1545
- Terephthalic acid, 2924
- † Thiolacetic acid, 0832
- 4-Toluenesulfonic acid, 2808
- Trichloroacetic acid, 0658
- Trifluoroacetic acid, 0665
- Trifluoromethanesulfonic acid, 0375
- Trinitroresorcinol, 2119

## ORGANIC AZIDES

**RN<sub>3</sub>, ArN<sub>3</sub>**

1. Boyer, J. H. *et al.*, *J. Chem. Eng. Data*, 1964, **9**, 480; *Chem. Eng. News*, 1964, **42**(31), 6
2. Draper, R. W., *J. Chem. Soc., Perkin Trans. I*, 1983, 2787
3. Scheri, S. H. *et al.*, *J. Mol. Struct.*, 1986, **14** 7, 203–204
4. Petrie M. A. *et al.*, *J. Amer. Chem. Soc.*, 1997, **119**, 8802

The need for careful and small-scale handling of organic azides, which are usually heat- or shock-sensitive compounds of varying degrees of stability, sensitive to traces of strong acids and metallic salts which may catalyse explosive decomposition, has been discussed. The presence of more than one azido group, particularly if on the same atom (C or N), greatly reduces the stability [1]. Two reaction systems used to prepare steroidal azides are potentially dangerous, and should only be used

with extensive safety precautions. The first involves use of chromium trioxide, sodium azide and acetic acid, and is likely to produce chromyl azide and hydrazoic acid, both explosive. The second uses lead(IV) acetate and trimethylsilyl azide and could produce lead azide. Use of remote control handling equipment is recommended [2]. Unsaturated azides containing one or more double or triple bonds, and one or more azide groups, are particularly dangerous, and should be handled with the utmost care [3]. Not surprisingly, all salts of the triazido carbenium ion ( $N_3C^+$ ) were found to be sensitive explosives, the perchlorate was the most sensitive, the dinitramide the most powerful [4].

This class contains the separately treated groups:

*See also* ACYL AZIDES, 2-AZIDOCARBONYL COMPOUNDS

as well as the individually indexed compounds:

- Azidoacetonitrile, 0714
- Azidoacetyl chloride, 0693
- 4-Azidobenzaldehyde, 2697
- 7-Azidobicyclo[2.2.1]hepta-2,5-diene, 2777
- Azido-2-butyne, 1473
- 2-*trans*-1-Azido-1,2-dihydroacenaphthyl nitrate, 3466
- \* *N*-Azidodimethylamine, 0915
- 4-Azido-*N,N*-dimethylaniline, 3331
- 2-Azido-3,5-dinitrofurane, 1384
- 2-Azidoethanol, 0873
- 6-Azidohexyl 6-azidohexanoate, 3551
- 2-Azidomethylbenzenediazonium tetrafluoroborate, 2708
- 2-Azidoperfluoronaphthalene, 3234
- 2-Azido-2-phenylpropane, 3159
- 3-Azidopropene, 1188
- 3-Azidopropyne, 1114
- 5-Azidotetrazole, 0388
- 3-Azido-1,2,4-triazole, 0717
- Benzyl azide, 2779
- \* Bis(2-azidobenzoyl) peroxide, 3628
- 1,2-Bis(2-azidoethoxy)ethane, 2479
- Bis(2-azidoethoxymethyl)nitramine, 2481
- 3,3-Bis(azidomethyl)oxetane, 1902
- N*-Butyl-*N*-2-azidoethylnitramine, 2528
- 1,3-Diazidobenzene, 2207
- 1,4-Diazidobenzene, 2208
- 2,3-Diazido-1,3-butadiene, 1437
- 2,4-Diazido-6-dimethylamino-1,3,5-triazine, 1876
- 1,12-Diazido-3,10-dioxo-5,8-dinitrazadodecane, 3049
- 1,1-Diazidoethane, 0818
- 1,2-Diazidoethane, 0819
- Diazidomalononitrile, 1347
- Diazidomethane, 0414

- Diazidomethyleneazine, 1021
- Diazidomethylenecyanamide, 1017
- 1,3-Diazido-2-nitroazapropane, 0824
- 1,1-Diazidophenylethane, 2953
- 1,2-Diazido-1-phenylethane, 2954
- 2,2-Diazidopropane, 1216
- 1,3-Diazidopropene, 1143
- 2,3-Diazidopropionitrile, 1121
- 2,6-Diazidopyrazine, 1400
- 3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2403
- Ethyl azide, 0872
- Ethyl 2,3-diazidopropionate, 1903
- \* 1-Ferrocenyl-2-methylpropyl azide, 3661
- Glycidyl azide, 1191
- Fluorodinitromethyl azide, 0341
- Methyl azide, 0459
- Methyl 2-azidobenzoate, 2939
- Methyl 3,3-diazido-2-cyanoacrylate, 1824
- 1,1'-Oxybis-2-azidoethane, 1604
- Phenyl azide, 2271
- Phenyldiazidomethane, 2730
- 2,2'-[1,4-Phenylenebis(azidomethylidene)]bis(propanedinitrile), 3622
- I*-Phenyl-*I*-(*p*-toluenesulfonyloxy)-(2-azido-2-phenyl)vinyl iodine(III)
- Picryl azide, 2092
- Silver 2-azido-4,6-dinitrophenoxide, 2075
- \* Thiocarbonyl azide thiocyanate, 1011
- 1,1,1-Triazidodinitroethane, 0683
- Triazidomethane, 0389
- \* Triazidomethylum hexachloroantimonate, 0335
- 2,4,6-Triazido-1,3,5-triazine, 1348
- Trifluoromethyl azide, 0347
- Triphenylmethyl azide, 3783
- Tris(2-azidoethyl)amine, 2482
- 1,1,1-Tris(azidomethyl)ethane, 1937
- Vinyl azide, 0770

*See related* NON-METAL AZIDES

## ORGANIC BASES

The separately treated METAL ALKOXIDES may perhaps be regarded as organic bases, as well as the more conventional nitrogenous bases below:

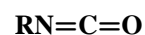
- Aminoguanidine, 0507
- 1-Amino-2-propanol, 1311
- Benzylamine, 2812
- Benzyl dimethylamine, 3168
- Bis(2-aminoethyl)amine, 1777



*N,N'*-Bis(2-aminoethyl)1,2-diaminoethane, 2599  
 † 1,2-Bis(dimethylamino)ethane, 2579  
   Bis(2-fluoro-2,2-dinitroethyl)amine, 1459  
 † Butylamine, 1723  
 † 2-Butylamine, 1724  
 † Butylethylamine, 2565  
 † Cyclohexylamine, 2521  
 † Cyclopentylamine, 1991  
 † Diallylamine, 2450  
   1,4-Diaminobenzene, 2371  
   1,2-Diaminoethane, 0953  
 † 1,2-Diaminopropane, 1325  
 † 1,3-Diaminopropane, 1326  
   1,11-Diamino-3,6,9-triazaundecane, 3101  
   1,4-Diazabicyclo[2.2.2]octane, 2473  
   Dibutylamine, 3083  
 † Di-2-butylamine, 3084  
   3-Dibutylaminopropylamine, 3416  
 † Diethylamine, 1726  
   3-Diethylaminopropylamine, 2877  
 † Diisobutylamine, 3085  
 † Diisopropylamine, 2566  
   3,3'-Dimethoxy-4,4'-diaminobiphenyl, 3660  
 † Dimethylamine, 0941  
   (Dimethylamino)acetylene, 1564  
 † 2-Dimethylaminoethylamine, 1755  
   *N,N*-Dimethylaniline, 2993  
 † 1,3-Dimethylbutylamine, 2567  
 † 1,2-Dimethylhydrazine, 0955  
 † 2,6-Dimethylpiperidine, 2868  
 † 1,1-Dimethylpropylamine, 2028  
 † 1,2-Dimethylpropylamine, 2029  
 † 2,2-Dimethylpropylamine, 2030  
 † *N,N*-Dimethylpropylamine, 2301  
 † Dipropylamine, 2568  
 † Ethylamine, 0942  
 † Ethyldimethylamine, 1727  
   5-Ethyl-2-methylpyridine, 2995  
 † 1-Ethylpiperidine, 2869  
 † 2-Ethylpiperidine, 2870  
   Hexamethylenetetramine, 2477  
   2-Hydroxyethylamine, 0943  
   *N*-2-Hydroxyethyl-1,2-diaminoethane, 1756  
   *N*-2-Hydroxyethyldimethylamine, 1729  
 † Isobutylamine, 1728  
 † Isopentylamine, 2032

- † Isopropylamine, 1308
- † Methylamine, 0493
- † *N*-Methylbutylamine, 2033
- † Methylhydrazine, 0503
- † 4-Methylmorpholine, 1995
- † 1-Methylpiperidine, 2522
- † 2-Methylpiperidine, 2523
- † 3-Methylpiperidine, 2524
- † 4-Methylpiperidine, 2525
- 2-Methylpyridine, 2355
- † *N*-Methylpyrrolidine, 1992
- Morpholine, 1657
- † Pentylamine, 2034
- † Perhydroazepine, 2526
- Phenylhydrazine, 2373
- N*-Phenylhydroxylamine, 2356
- Piperazine, 1689
- † Piperidine, 1993
- † Propylamine, 1309
- † Pyridine, 1848
- Quinoline, 3121
- † 1,2,3,6-Tetrahydropyridine, 1930
- 1,3,4,7-Tetramethylisoindole, 3528
- 1,2,4,5-Tetrazine, 0715
- Thiourea, 0480
- 3,6,9-Triaza-11-aminoundecanol, 3100
- 1,3,5-Triazine, 1115
- † Triethylamine, 2569
- † Trimethylamine, 1310
- 2,4,6-Tris(dimethylaminomethyl)phenol, 3694
- Tris(hydroxymethyl)methylamine, 1731
- Urea, 0475
- Vinylpyridine, 2759

## ORGANIC ISOCYANATES



1. Mumford, C. J. *et al.*, *Loss Prev. Bull.*, 1991, **102**, 7

These high energy species are extremely reactive, with themselves and with nucleophiles, and can generate runaway exotherms. With water, rapid evolution of carbon dioxide results. Some instances are reported [1]. A compound of this class was responsible for the worst chemical industry accident to date. Di-isocyanates are extensively employed, with polyols, to generate polyurethane polymers. The polymerisation temperature should be held below 180°C or decomposition may occur which, in the case of foams, may induce later autoignition.

Individually indexed compounds are:

- Butane-1,4-diisocyanate, 2376
  - † Butyl isocyanate, 1931
  - 4-Chlorophenyl isocyanate, 2648
  - 1,6-Diisocyanatohexane, 3008
  - Diisocyanatomethane, 1079
  - 2,4-Diisocyanatotoluene, 3117
  - † Methyl isocyanate, 0761
  - 1-Naphthyl isocyanate, 3390
  - 2-Phenylethyl isocyanate, 3139
  - Phenyl isocyanate, 2685
  - \* Trifluoromethyl iodine(III) isocyanate, 1045
- See Potassium cyanate

## ORGANIC PEROXIDES

C-00

1. Noller, D. C. *et al.*, *Anal. Chem.*, 1963, **35**, 887-893
2. Castrantas, 1970
3. Varjarvandi, J. *et al.*, *J. Chem. Educ.*, 1971, **48**, A451
4. *Code of Practice for Storing and Handling of Organic Peroxides*, P15.1, Luton, Interlox Chemicals, 1975  
*Storage and Handling of Organic Peroxides*, Guidance Note CS 21, HMSO, London.
5. Jackson, H. L., *J. Chem. Educ.*, 1970, **47**, A175
6. Castrantas, 1965
7. Davies, 1961
8. Swern, 1970, Vol. 1, 1-104
9. Houben-Weyl, 1952, Vol. 8.3, 1
10. Swern, 1972, Vol. 3, 341-364
11. Stevens, H. C., US Pat. 2 415 971, 1947
12. Cookson, P. G. *et al.*, *J. Chem. Soc., Chem. Comm.*, 1976, 1022-1023
13. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 32
14. Kotani, M. *et al.*, *Chem. Abs.*, 1980, **92**, 87594
15. Marisaki, S., *Chem. Abs.*, 1983, **98**, 34100
16. Matsunaga, T. *et al.*, *Chem. Abs.*, 1984, **101**, 113378
17. Halle, R., *Chem. Eng. News*, 1984, **62**(47), 4
18. Tamura, M. *et al.*, *J. Haz. Mat.*, 1987, **17**(1), 89-98
19. Mackenzie J., *Plant/Oper. Progr.*, 1991, **10**(3), 165
20. Anon., *Jahresber.*, 1987, 65

Of the general guides to the safe handling and use of peroxides, the third and second include details of hazard evaluation tests, and the first has a comprehensive bibliography [1,2,3]. Storage aspects are rather specific [2,4]. Procedures for the safe handling of peroxidisable compounds have also been described [5]. Tabulated data on fire and explosion hazards of classes of organic peroxides with an extensive bibliography were published [6]. Theoretical aspects have been considered [6,7,8], the practical hazards involved in synthesis of organic peroxides have been

detailed [9], and a further review on the evaluation and management of peroxide hazards appeared [10]. The use of iodine to stabilise liquid organic peroxides against explosive or incendiary decomposition has been claimed [11]. A new safe general method for rapid preparation of *n*-, *sec*- or *tert*-alkyl hydroperoxides has been described [12]. Leakage of an organic peroxide catalyst solution into pipe lagging exposed to direct solar radiation led to a fire [13].

Pyrolysis GLC has been used to develop a safe method for the qualitative determination of thermally unstable organic peroxides like benzyl peroxide. The mechanism of decomposition reactions and the temperature limits for safe handling of peroxides can also be determined by this technique [14]. In a study of adiabatic thermal decomposition, 2 g samples of di-*tert*-butyl and dibenzoyl peroxides, *tert*-butyl peroxybenzoate and peroxy-2-ethylhexanoate attained maximum self-heating rates and final pressures of 150–440°C/min and 4.5–9.5 kbar, respectively [15]. Group contributions to heat of formation ( $\Delta H_f^\circ$ ) were derived from suitable reference compounds and used to estimate  $\Delta H_f^\circ$  for peroxides by additivity methods. The agreement between calculated and observed values were good enough to estimate hazard properties for energetic materials such as peroxides [16]. A general measure of the degree of hazard associated with an organic peroxide may be gained from the content of 'active oxygen' (AO, or wt% of peroxidic oxygen) in the molecule. Thus 2,2-bis(hydroperoxy)propane (highly explosive) with 30.2% AO has an extremely high value compared to the 1–17% commonly encountered in commercial organic peroxides, e.g. MEK peroxide, which is supplied and handled safely as a solution diluted to a maximum AO content of 9% [17].

Work on the deflagration hazards of organic peroxides has been done using a revised Time–Pressure test, to determine the characteristics of ignition sensitivity and violence of deflagration. Some correlation is evident between these characteristics and the AO content within each structurally based peroxide type. Also, for the same AO content, the nature of the characteristics appears to decrease in the order diacyl peroxides, peroxyesters, dialkyl peroxides, alkylhydroperoxides [18].

Warning is given that sodium sulfite may not remove all peroxidic compounds if peroxyacids are present, with which it can form undetectable, but unstable, complex peroxides [19]. Peroxide test strips may not be sufficiently reliable as the sole means of testing for presence of peroxides in a wide range of peroxidisable liquids. It was recommended that an additional test (potassium iodide–acetic acid) should be used unless it is certain that the test strips will give a positive result with a particular peroxide-containing liquid [20].

Except for the peroxides individually listed below, all index entries have been assigned to the structurally based groups:

ALKYL HYDROPEROXIDES, *tert*-BUTYL PEROXOPHOSPHATE DERIVATIVES  
CYCLIC PEROXIDES, DIACYL PEROXIDES  
DIALKYL PEROXIDES, DIOXETANES  
KETONE PEROXIDES, 1-OXYPEROXY COMPOUNDS  
OZONIDES, PEROXYACIDS  
PEROXYCARBONATE ESTERS, PEROXYESTERS  
 $\alpha$ -PHENYLAZO HYDROPEROXIDES, POLYPEROXIDES

Individually indexed compounds are:

- \* Chloroperoxytrifluoromethane, 0319
- \* Perfluoro-*tert*-butyl peroxyhypofluorite, 1373
- \* Peroxypropionyl perchlorate, 1167
- \* 3,3,5-Triphenyl-4,4-dimethyl-5-hydroperoxy-4,5-dihydro(3H)pyrazole, 3841

See also COMMERCIAL ORGANIC PEROXIDES

## ORGANIC POWDER HANDLING

*Electrostatic hazards in powder handling*, Gior, M., Letchworth, Research Study Press, 1988 (also from Wiley)

The role of electrostatic generation as an important ignition source in industrial powder handling operations is discussed in this book.

See DUST EXPLOSION INCIDENTS, ELECTROSTATIC HAZARDS, IGNITION SOURCES

## ORGANOLITHIUM REAGENTS

XArLi

1. Bretherick, L., *Chem. & Ind.*, 1971, 1017
2. Gilman, H., private comm., 1971
3. 'Benzotrifluorides Catalog 6/15', West Chester (Pa.), Marshallton Res. Labs., 1971
4. Coates, 1960, 19
5. *MCA Case History No. 1834*
6. Anderson, R., *Chem. & Ind.*, 1984, 205208
7. Wakefield, B. J., *Organolithium Methods*, London, Academic, 1988

Several halo-aryllithium compounds are explosive in the solid state in absence or near-absence of solvents or diluents, and operations should be designed to avoid their separation from solution. Such compounds include *m*- and *p*-bromo-, *m*-chloro-, *p*-fluoro-, *m*- and *p*-trifluoromethyl-phenyllithiums [1] and 3,4-dichloro-2,5-dilithiothiphenene [2], but *m*-bromo- and *o*-trifluoromethyl-phenyllithium appear to be explosive in presence of solvent also [1,3]. The *m*- and *p*-dilithiobenzenes are also explosively unstable under certain conditions. Most organolithium compounds are pyrophoric when pure (especially those of high lithium content) and are usually handled in solution and under inert atmosphere [4]. A completed preparation of *o*-trifluoromethylphenyllithium refluxing in ether under nitrogen suddenly exploded violently [5]. Equipment and procedures necessary for the safe use of organolithium reagents on the industrial scale have been detailed [6]. Aspects of practical significance (solvents, inert atmospheres, equipment, and handling procedures) related to the safe use of organolithium reagents are included in the volume [7].

Examples of these compounds may be found in the group:

### FLUORINATED ORGANOLITHIUM COMPOUND

and the individual entries:

- 3-Bromophenyllithium, 2129
- 4-Bromophenyllithium, 2130
- 3-Chlorophenyllithium, 2138

4-Chlorophenyllithium, 2139  
3,4-Dichloro-2,5-dilithiothiophene, 1357  
1,3-Dilithiobenzene, 2178  
1,4-Dilithiobenzene, 2179  
4-Fluorophenyllithium, 2166  
2-,3- or 4-Trifluoromethylphenyllithium, 2657

*See other* HALO-ARYLMETALS

### ORGANOMETALLIC NITRATES

These compounds, although not as dangerous as the related perchlorates, have a reducing organic moiety in intimate association with an oxidant nitrate, combined with a metal which may well be an oxidation catalyst. They feature increasingly as explosive compounds in reports too numerous to feature all as individual entries in a handbook. These comments apply equally to the complexed species loosely described as organometallic although lacking a carbon-metal bond. Individual compounds include:

$\eta^6$ -Benzeneruthenium(II) dinitrate, 2320  
Dimethyltin dinitrate, 0914  
2-Hydroxyethylmercury(II) nitrate, 0857  
2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1592

*See* METAL NITRATES, AMMINOMETAL OXOSALTS

### ORGANOMETALLIC PERCHLORATES

The comments on organometallic nitrates, above, apply with redoubled force here. Although becoming fewer as chemists learn caution, reports of explosion are even more numerous than for the nitrates, and the explosions are more powerful. Again far from all reported have been given entries. Individual compounds are :

*See* PERCHLORATES, METAL PERCHLORATES, AMMINOMETAL OXOSALTS

### ORGANOMETALLIC PEROXIDES

### RM-OO, RE-OO

1. Castrantas, 1965, 18
2. Swern, 1970, Vol. 1, 13
3. Sosnovsky, G. *et al.*, *Chem. Rev.*, 1966, **66**, 529
4. Colletti, S. L. *et al.*, *J. Organomet. Chem.*, 1993, **455**(1-2), 99

Available information suggests that both hydroperoxides and peroxides in this extensive group of compounds are in many cases stable to heat at temperatures rather below 100°C, but may decompose explosively at higher temperatures. There are, however, exceptions [1]-[3]. Organoniobium peroxides may be explosive when exposed to air [4]. Individually indexed compounds are:

- \* Bis(methylcyclopentadienyl)peroxoniobium chloride, 3522
- Bis(triethyltin) peroxide, 3581
- Dicyclopentadienylperoxyniobium chloride, 3271
- Diethylhydroxytin hydroperoxide, 1763
- Di(hydroperoxy)trimethylantimony(V), 1333

Methylbis( $\eta^2$ -peroxo)rhenium oxide hydrate, 0497  
Triethyltin hydroperoxide, 2583  
Trimethylsilyl hydroperoxide, 1330  
Triphenyltin hydroperoxide, 3758  
*See also* ALKYL TRIALKYLLEAD PEROXIDES

## ORGANOMETALLICS

## C–M

*High Energy Processes in Organometallic Chemistry*, Suslick, K. S. (ed.), ACS Symp. Ser. No 333, Washington, ACS, 1987

Several of the chapters in this 336 page book are concerned with the preparation, properties and use of very highly reactive materials in organometallic chemistry.

This class of rather miscellaneous organometallic compounds, all with carbon–metal bonding, contains the separately treated groups:

ALKYLMETAL HALIDES, ALKYLMETALS  
ARYLMETALS, 1-ARYL-1-VINYLLITHIUM DERIVATIVES  
GRIGNARD REAGENTS, HALO-ARYLMETALS  
ORGANOLITHIUM REAGENTS

and the individually indexed compounds:

- \* Benzylsodium, 2787
- \* Bis( $\eta$ -benzene)chromium(0), 3511  
Bis(benzene)chromium dichromate, 3851
- \* Bis( $\eta$ -benzene)iron(0), 3512  
Bis(benzeneiron)–fulvalenediyl complex, 3834
- \* Bis( $\eta$ -benzene)molybdenum(0), 3514  
Bis(cyclooctatetraene)uranium(0), 3708  
Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium, 3830  
Bis(cyclopentadienyldinitrosylchromium), 3275  
Bis(cyclopentadienyl)hexafluoro-2-butynechromium, 3636  
Bis(cyclopentadienyl)lead, 3294  
Bis(cyclopentadienyl)magnesium, 3277  
Bis(cyclopentadienyl)manganese, 3278  
Bis(cyclopentadienyl)niobium tetrahydroborate, 3324
- \* Bis(cyclopentadienyl)pentafluorophenylzirconium hydroxide, 3703
- \* Bis(cyclopentadienyl)phenylvanadium, 3705  
Bis(cyclopentadienyl)titanium, 3295  
Bis(cyclopentadienyl)titanium selenate, 3293  
Bis(cyclopentadienyl)zirconium, 3296  
Bis(dicarbonylcyclopentadienyliron)–  
bis(tetrahydrofuran)magnesium, 3835
- \* Bis[dicarbonyl(cyclopentadienyl)tributylphosphinemolybdenum]–tetra-  
kis(tetrahydrofuran)magnesium, 3913  
Bis( $\mu_3$ -methylidyne)triangulo tris(pentamethylcyclopentadienyl)-  
rhodium), 3879  
Bis(pentafluorophenyl)ytterbium, 3423

- \* Bis(2,4-pentanedionato)chromium, 3326
- Chloro( $\eta^8$  1,3,5,7-cyclooctatetraene)(tetrahydrofuran)lutetium, 3536
- \* ( $\eta^8$  1,3,5,7-Cyclooctatetraene)[2-(dimethylaminomethyl)phenyl-*C,N*](tetrahydrofuran)lutetium, 3826
- $\mu$ -Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino) titanium, 3028
- Cyclopentadienylsodium, 1855
- $\mu$ -Cyclopentadienyltrimethyltitanium, 3038
- Diaquabis(cyclopentadienyl)titanium dichromate, 3327
- 1,3-Di[bis(cyclopentadienyl)iron]-2-propen-1-one, 3840
- \* Dicarbonyl- $\pi$ -cycloheptatrienyltungsten azide, 3123
- cis*-Dicarbonyl(cyclopentadienyl)cyclooctenemanganese, 3681
- \* (2,2-Dichloro-1-fluorovinyl)ferrocene, 3470
- Dicumenechromium(0), 3767
- Dicyclopentadienylchromium, 3273
- 4,4-Diferrocenylpentanoyl chloride, 3859
- Dilithium  $\mu$ -cyclooctatetraene, 2948
- Dimethylaminomethylferrocene, 3613
- 2-(Dimethylaminomethyl)fluoroferrocene, 3612
- Dipotassium  $\mu$ -cyclooctatetraene, 2947
- Ferrocene, 3276
- \* Ferrocene-1,1'-dicarboxylic acid, 3479
- \* 1-Ferrocenyl-2-methylpropyl azide, 3661
- \* Methylaluminiumbis(pentamethylcyclopentadienyltrimethyliridium), 3866
- Nickelocene, 3287
- Oxybis[bis(cyclopentadienyl)titanium], 3803
- Pentamethylcyclopentadienyl-bis(thiolatothiazyl)rhodium, 3534
- Poly(cyclopentadienyltitanium dichloride), 1843
- \* Tricyclopentadienyluranium tetrahydroaluminate, 3688
- N,N*,4-Trilithioaniline, 2180
- Triphenylmethylpotassium, 3781
- Tris(cyclopentadienyl)cerium, 3683
- Tris(cyclopentadienyl)plutonium, 3684
- Tris(cyclopentadienyl)uranium, 3685
- \* Tris(2,4-pentanedionato)molybdenum(III), 3690

#### ORGANOSILYL PERCHLORATES

#### $R_3SiClO_4$

Wannagat, U. *et al.*, *Z. Anorg. Chem.*, 1950, **302**, 185–198

Several trialkyl- or triaryl-silyl perchlorates explode on heating, including:

Triethylsilyl perchlorate, 2562

Tri-4-methylphenylsilyl perchlorate, 3823

Trimethylsilyl perchlorate, 1302



Triphenylsilyl perchlorate, 3750

Tripropylsilyl perchlorate, 3218

See related NON-METAL PERCHLORATES

## ORIGINS OF UNWANTED CHEMICAL REACTIONS

Rasmussen, B., *Unwanted Chemical Reactions in Chem. Processing Ind.*, Rept. M-2631, Roskilde (DK), Riso National Lab., 1987

A total of 190 published case histories of chemical processing accidents, selected from the MCA series, *Loss Prevention Bulletin*, *Loss Prevention* and elsewhere have been analysed to determine the underlying reasons for the unwanted chemical reactions. The most common reasons were:- incorrect storage or handling of materials, (24%); contamination or catalytic impurities, (20%); use of wrong chemicals, (19%); incorrect charging or processing conditions, (19%); insufficient agitation, (13%). Accidents in batch reactors were much more frequent than in continuous reactors.

In 55% of the cases, the accidents could have been foreseen by use of risk analysis, and in 35% of the cases by thermal stability testing. Different methods of stability testing were evaluated comparatively during the investigation of a runaway exothermic reaction which occurred during the preparation of a component mixture for a sealing composition in a 1200 l reactor: only DSC was effective in identifying the cause of the hazard.

A series of checklists is proposed to avoid such incidents in chemical processing operations, and an incompatibility chart for groups of reactive chemicals is given.

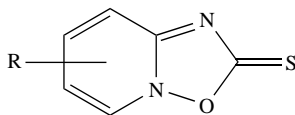
The methods used for the analysis of the case histories are detailed in a separate Appendix A, (Riso-278).

See Lead(IV) oxide: Carbon black, Chlorinated paraffin, Manganese(IV) oxide

See CATALYTIC IMPURITY INCIDENTS, AGITATION INCIDENTS, RUNAWAY REACTIONS

See also ACCELERATING RATE CALORIMETRY, REACTION SAFETY CALORIMETRY

## 2H -1,2,4-OXADIAZOLO[2,3-a]PYRIDINE-2-THIONES



Rousseau, D. *et al.*, *Can. J. Chem.*, 1977, **55**, 3736–3739

The title compounds (R = H, 5-, 6-, 7-, or 8-methyl, or 5,7-dimethyl) explode at 121–137°C.

See other N–O COMPOUNDS

## OXIDANTS

1. *Inorganic High Energy Oxidisers: Synthesis, Structure and Properties*, Lawless, E. W. and Smith, I. C., London, Arnold, 1968
2. *Hazard Classification of Oxidising Materials and Flammable Solids*, King P. V. *et al.*, Rept. PB-220084, Washington, US Dept. Transport, 1972
3. *NFPA 43A*, 1980; *NFPA 43B*, 1986; *NFPA 43C*, 1986, Quincy (Ma), National Fire Protection Association

Developments in inorganic fluorine oxidants, largely for rocketry, are covered [1]. A method of rating the potency of oxidants involves heating a carefully prepared and blended mixture of the solid oxidant with size-graded dried sawdust at 38.5°C/10 min to assess gross self-heating and ignition capability. Then a rectangular bed 2.5 cm deep x 5 x 17.5 cm is ignited at one end and the time taken for the combustion front to traverse 12.5 cm is taken as an inverse measure of oxidising power [2]. Three recent US fire codes cover the storage requirements for liquid or solid oxidants; for formulated organic peroxides; and for gaseous oxidants, respectively [3].

Members of this class of materials have been involved in the majority of the two-component reactive systems included in this Handbook, and the whole class is extremely large. Most oxidants have been treated collectively in the structurally based entries:

ACETYLENIC PEROXIDES, ACYL HYPOHALITES  
ALKYL HYDROPEROXIDES, ALKYL TRIALKYLLLEAD PEROXIDES  
AMINIUM IODATES AND PERIODATES, AMMINECHROMIUM PEROXOCOMPLEXES  
BIS(FUOROXY)PERHALOALKANES, BLEACHING POWDER, CHLORITE SALTS  
COMMERCIAL ORGANIC PEROXIDES, CRYSTALLINE HYDROGEN PEROXIDATES  
CYCLIC PEROXIDES, DIACYL PEROXIDES  
DIALKYL PEROXIDES, *1,1*-DI(BENZOYLPEROXY)ARYLIODINES  
DIFLUOROAMINO COMPOUNDS, DIFLUOROAMINOPOLYNITROAROMATIC COMPOUNDS  
DIFLUOROPERCHLORYL SALTS, DIOXETANES  
DIOXYGENYL POLYFLUOROSALTS, FLUORINATED PEROXIDES AND SALTS  
FLUORODINITRO COMPOUNDS, *N*-HALOGEN COMPOUNDS  
HALOGEN OXIDES, HALOGENS  
N-HALOIMIDES, HEXAFLUOROCHLORONIUM SALTS  
HYDROXOXODIPEROXOCHROMATE SALTS, HYPOHALITES  
INORGANIC PEROXIDES, INTERHALOGENS  
KETONE PEROXIDES, LIQUID AIR  
METAL CHLORATES, METAL HALOGENATES  
METAL HYPOCHLORITES, METAL NITRATES  
METAL NITRITES, METAL OXOHALOGENATES  
METAL OXOMETALLATES, METAL OXONON-METALLATES  
METAL OXIDES, METAL PERCHLORATES  
METAL PEROXIDES, METAL PEROXOMOLYBDATES

METAL POLYHALOHALOGENATES, MOLTEN SALT BATHS  
NITROALKANES, NON-METAL PERCHLORATES  
OXIDES OF NITROGEN  
OXOHALOGEN ACIDS, OXYGEN ENRICHMENT  
1-OXYPEROXY COMPOUNDS, OZONIDES  
PERCHLORYL COMPOUNDS, PEROXOACIDS  
PEROXOACID SALTS, PEROXYACIDS  
PEROXYCARBONATE ESTERS, PEROXYESTERS  
POLYNITROALKYL COMPOUNDS, POLYPEROXIDES  
QUATERNARY OXIDANTS, TRINITROETHYL ORTHOESTERS  
XENON COMPOUNDS

Other individually indexed compounds are:

- Acetyl hypofluorite, 0751
- \* Ammonium hexanitrocerate, 3964
- \* Ammonium nitrate, 4522
- Ammonium permanganate, 4518
- Ammonium peroxodisulfate, 4576
- Antimony pentachloride, 4184
- Barium chlorite, 0204
- Barium peroxide, 0216
- \* Bismuthic acid, 0228
- Bromine, 0261
- 4-*tert*-Butyliodiybenzene, 3319
- Caesium fluoroxysulfate, 4256
- Calcium chromate, 3926
- \* Calcium hypochlorite, 3924
- Calcium nitrate, 3935
- Calcium permanganate, 3934
- Calcium peroxide, 3938
- Calcium peroxodisulfate, 3940
- Calcium triperoxochromate, 3945
- Chlorine, 4047
- Chlorine dioxide, 4042
- Chlorosulfuric acid, 3997
- Chloryl perchlorate, 4104
- Chromic acid, 4229
- Chromium pentafluoride, 4226
- Chromium trioxide, 4242
- Chromyl acetate, 1494
- \* Chromyl chloride, 4054
- \* Chromyl fluorosulfate, 4225
- \* Chromyl perchlorate, 4055
- Cobalt(II) nitrate, 4215
- Di-*tert*-butyl chromate, 3066
- Dichlorine oxide, 4095

Dilead(II)lead(IV) oxide, 4861  
Dinitrogen oxide, 4744  
Dinitrogen pentaoxide, 4748  
Dinitrogen tetraoxide, 4747  
Dinitrogen trioxide, 4746  
Dioxonium hexamanganato(VII)manganate, 4553  
Dioxygen difluoride, 4320  
Dioxygenyl tetrafluoroborate, 0132  
Dipyridinium dichromate, 3304  
Fluorine, 4310  
Fluorine fluorosulfate, 4324  
Fluoroselenic acid, 4295  
Graphite hexafluorogermanate, 3422  
1,1,1,3,5,5,5-Heptanitropentane, 1854  
Hydrogen peroxide, 4477  
Iodic acid, 4424  
Iodine, 4625  
Iodine dioxide trifluoride, 4334  
Iodine(V) oxide, 4627  
Iodine(VII) oxide, 4628  
Iridium hexafluoride, 4362  
Lead chromate, 4243  
Lead(II) nitrate, 4749  
Lead(II) oxide, 4824  
Lead(IV) oxide, 4834  
Lithium chlorite, 4020  
Magnesium nitrite, 4692  
Magnesium nitrate, 4693  
Magnesium permanganate, 4691  
\* Manganese fluoride trioxide, 4301  
Manganese(IV) oxide, 4705  
Manganese(VII) oxide, 4709  
Manganese tetrafluoride, 4343  
Mercury(II) bromate, 0270  
Mercury(II) nitrate, 4603  
Mercury(II) oxide, 4605  
Monofluoroxonium hexafluoroarsenate, 0097  
Neptunium hexafluoride, 4366  
Nickel(II) nitrate, 4743  
Nitric acid, 4436  
Nitrogen dioxide, 4725  
Nitrogen oxide, 4724  
Nitrosyl chloride, 4023  
Nitrosyl fluoride, 4302  
Nitrosyl perchlorate, 4027  
Nitrosylsulfuric acid, 4438

Nitrosyl tetrafluorochlorate, 3985  
Nitrous acid, 4435  
Nitryl chloride, 4025  
Nitryl fluoride, 4303  
Nitryl hypochlorite, 4026  
Nitryl hypofluorite, 4304  
Nitryl perchlorate, 4029  
Osmium hexafluoride, 4370  
Osmium(VIII) oxide, 4858  
Oxygen (Gas), 4831  
Oxygen (Liquid), 4832  
Oxygen difluoride, 4317  
Ozone, 4846  
Palladium(II) oxide, 4825  
Palladium(IV) oxide, 4835  
Perchloric acid, 3998  
Periodic acid, 4425  
Permanganic acid, 4434  
Peroxodisulfuric acid, 4482  
Peroxodisulfuryl difluoride, 4328  
Peroxomonosulfuric acid, 4481  
Peroxytrifluoroacetic acid, 0666  
Platinum hexafluoride, 4371  
Platinum(IV) oxide, 4836  
Plutonium hexafluoride, 4372  
Potassium bromate, 0255  
Potassium chlorate, 4017  
Potassium dichromate, 4248  
Potassium iodate, 4619  
Potassium nitrate, 4650  
Potassium nitrite, 4649  
Potassium perchlorate, 4018  
Potassium periodate, 4620  
Potassium permanganate, 4647  
Rhenium hexafluoride, 4373  
Rubidium fluoroxysulfate, 4309  
Ruthenium(VIII) oxide, 4862  
Selenium dioxide, 4838  
\* Selenium dioxide, 4838  
Silver permanganate, 0021  
Sodium chlorate, 4039  
Sodium chlorite, 4038  
Sodium dichromate, 4250  
Sodium iodate, 4624  
Sodium nitrate, 4721  
Sodium nitrite, 4720

Sodium perchlorate, 4040  
 Sodium permanganate, 4703  
 Sodium peroxide, 4803  
 Sodium peroxodisulfate, 4809  
 † Sulfur, 4897  
   Sulfuric acid, 4479  
   Sulfur trioxide, 4849  
   Tetrafluoroammonium hexafluoromanganate, 4384  
   Tetrafluoroammonium hexafluoronickelate, 4385  
   Tetrafluoroammonium hexafluoroxenate  
   Tetranitromethane, 0546  
   Titanium tetraperchlorate, 4170  
   1,1,1-Triacetoxy-1,2-benziodoxol-3-one, 3610  
   Trifluoromethyl hypofluorite, 0353  
   Trimethylsilyl chlorochromate, 1301  
   ‘Trioxygen difluoride’, 4323  
   Uranium hexafluoride, 4375  
   Vanadium(V) oxide, 4866  
 \* Vanadium trinitrate oxide, 4763  
   Vanadyl perchlorate, 4152  
   Xenon hexafluoride, 4377  
   Xenon(II) pentafluoroorthoselenate, 4382  
   Xenon(II) pentafluoroorthotellurate, 4383  
   Xenon tetrafluoride, 4353  
   Xenon tetrafluoride oxide, 4346  
   Xenon tetraoxide, 4863  
   Xenon trioxide, 4857  
   Zinc permanganate, 4710

### **OXIDANTS AS HERBICIDES**

Cook, W. H., *Can. J. Res.*, 1933, **8**, 509

The effect of humidity on combustibility of various mixtures of organic matter and sodium chlorate was studied. Addition of a proportion of hygroscopic material (calcium or magnesium chlorides) effectively reduces the hazard. Similar effects were found for sodium dichromate and barium chlorate.

*See* Sodium chlorate: Organic matter

### **OXIDATION INCIDENTS**

Since the vast majority of the hazardous occurrences described in this volume involve oxidation reactions, it is not feasible to provide a comprehensive listing of the individual incidents. However, it may be noted that nitric acid and hydrogen peroxide are the two common oxidants most frequently involved in accidents.

*See* MICROWAVE OVEN HEATING, OXIDANTS, OXIDATION PROCESSES, SAMPLE DISSOLUTION

*See other* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## OXIDATION PROCESSES

Kletz, T. A., *Plant/Oper. Progr.*, 1988, **7**, 226–230

Fire and explosion hazards of processes involving the oxidation of hydrocarbons are reviewed, including oxidation of cyclohexane to cyclohexanone/cyclohexanol, ethylene to ethylene oxide, of cumene to its hydroperoxide, and of *p*-xylene to terephthalic acid.

## N-OXIDES

N → O

Baumgarten, H. E. *et al.*, *J. Amer. Chem. Soc.*, 1957, **79**, 3145

A procedure for preparing *N*-oxides is described which avoids formation of peroxoacetic acid. After prolonged treatment of the amine at 35–40°C with excess 30% hydrogen peroxide, excess of the latter is catalytically decomposed with platinum oxide.

Individually indexed compounds are:

2-Bromo-4-methylpyridine *N*-oxide, 2297

3-Bromopyridine *N*-oxide, 1828

\* Decafluoro-2,5-diazaheptane 2,5-dioxy, 1372

2,3-Diazabicyclo[2.2.2]octa-2,5-diene *N*-oxide, 2374

5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3677

\* Disodium 5,5'-azoxytetrazolide, 1019

Fulminic acid, 0381

4(1-Hydroxyethyl)pyridine *N*-oxide, 2820

1-Hydroxyimidazole *N*-oxide, 1134

*N*-Methylmorpholine oxide, 1997

3-Methyl-4-nitropyridine *N*-oxide, 2317

*N*-Methylpiperidine- $N\frac{1}{2}$ -oxide

2-(*N*-Nitroamino)pyridine *N*-oxide, 1851

4-(*N*-Nitroamino)pyridine *N*-oxide, 1852

2,2'-bipyridyl 1-oxide, 3258

4-Nitropyridine *N*-oxide, 1833

2,2'-Oxybis(iminomethylfuran) mono-*N*-oxide, 3260

Pyridine *N*-oxide, 1849

Tribromamine oxide, 0291

Trimethylamine oxide, 1313

See FURAZAN *N*-OXIDES

## OXIDES OF NITROGEN

NO<sub>n</sub>

The oxides of nitrogen collectively are oxidants with power increasing with oxygen content. Dinitrogen oxide will often support violent combustion, since its oxygen content (36.5%) approaches double that of atmospheric air. Nitrogen oxide and dinitrogen oxide are both endothermic and capable of detonation in the liquid state. Individually indexed oxides are:

Dinitrogen oxide  
Dinitrogen pentaoxide  
Dinitrogen tetraoxide  
Dinitrogen trioxide  
Nitrogen dioxide  
Nitrogen oxide

#### Glyptal resin

Anon., *ABCM Quart Safety Summ.*, 1937, **8**, 31

A new wooden fume cupboard was varnished with glyptal (glyceryl phthalate) resin. After a few weeks' use with 'nitrous fumes', the resin spontaneously and violently ignited. This was attributed to formation and decomposition of glyceryl trinitrate or similar compounds.

Oxides of nitrogen are thought to have been involved in several violent incidents.

*See* Hydrogen (Gas), : Liquid nitrogen, 4453

Nitrogen oxide, : Dienes, Oxygen, 4724

Nitrogen dioxide, : Alkenes, 4725

Dinitrogen tetraoxide, : Unsaturated hydrocarbons, 4747

In this latter context, however, according to Henstock, W. H., *Plant/Oper. Progr.*, 1986, **5**, 232–237, no explosive products from hydrocarbon/oxides of nitrogen contact were found in a cryogenic hydrogen recovery unit processing petroleum refinery gases and cracked gases, and no such hazardous reactions seemed likely.

*See other* OXIDANTS

#### OXIME CARBAMATES

C=NOCO.NHR

Pinnegar, M. A. *et al.*, UK Pat. 2 000 031, 1979

Oxime carbamates may explode on heating, after an induction period of very variable length, dependent upon temperature and impurities present.

*See other* INDUCTION PERIOD INCIDENTS, N–O COMPOUNDS

*See also* OXIMES

#### OXIMES

RC=NOH

1. Horner, L. in *Autoxidation and Antioxidants*, Lundberg, W. O. (Ed.), Vol. 1, 184–186, 197–202, New York, Interscience, 1961

2. Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3

3. Cardillo, P. *et al.*, *J. Loss Prev.*, 1993, **6**(2), 69

Several explosions or violent decompositions during distillation of aldoximes may be attributable to presence of peroxides arising from autoxidation. The peroxides may form on the –C=NOH system (both aldehydes and hydroxylamines peroxidise [1]) or perhaps arise from unreacted aldehyde. Attention has been drawn to an explosion hazard inherent to ketoximes and many of their derivatives (and not limited to them). The hazard is attributed to inadvertent occurrence of acidic conditions leading to highly exothermic Beckmann rearrangement reactions accompanied by potentially catastrophic gas evolution. Presence of acidic salts (iron(III)



chloride, or the ketoxime hydrochloride) markedly lowers decomposition temperatures [2].

A nickel catalysed aldoxime rearrangement, to an amide, went out of control after changing the solvent employed. This was found to be due to a slow start and consequent accumulation of unreacted substrate. Changing to a higher operating temperature restored control to the process [3].

Individually indexed compounds are:

- † Acetaldehyde oxime, 0865
- Acetone oxime, 1258
- Azoformaldoxime, 0815
- Benzaldehyde oxime, 2760
- Bromoacetone oxime, 1201
- Butane-2,3-dione dioxime, 1595
- 2,3-Butanedione monoxime, 1570
- 2-Butanone oxime, 1654
- \* 2-Butanone oxime hydrochloride, 1678
- Butyraldehyde oxime, 1655
- '10-Carbon oxime', 3362
- Chloroacetaldehyde oxime, 0787
- \* 2-Chloro-*N*-hydroxyacetamidine, 0849
- 1,2,3-Cyclohexanetrione trioxime, 2400
- 1,3,5-Cyclohexanetrione trioxime, 2401
- Cyclohexanone oxime, 2452
- Cyclopentanone oxime, 1932
- 2,3-Epoxypropionaldehyde oxime, 1182
- 2-Ethylacrylaldehyde oxime, 1933
- Ethyl 2-formylpropionate oxime, 2454
- Furan-2-amidoxime, 1872
- \* Hydroxycopper(II) glyoximate, 0799
- 1-Hydroxyimidazole-2-carboxaldoxime 3-oxide, 1477
- 2-Isopropylacrylaldehyde oxime, 2453
- \* *N*-Methoxy-*N*-methylbenzylidenimmonium methylsulfate, 3334
- 2-Methyl-2-[4-(2-methylpropyl)phenyl]oximinoethane, 3614
- 2-Nitroacetaldehyde oxime, 0809
- 1-Nitro-1-oximinoethane, 0810
- \* Nitrooximinomethane, 0409
- 3-(2-Nitrophenyl)-2-hydroxyiminopropanoic acid, 3131
- 2-Nitrosophenol (1,2-Benzoquinone monoxime), 2263
- \* 4-Nitrosophenol (1,4-Benzoquinone monoxime), 2264
- 4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2357
- \* Potassium cyclohexanone 1,3,5-trioximate, 2625
- \* Potassium 1-nitroethane-1-oximate, 0756
- \* Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1409
- Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3505
- \* Sodium 4-chloroacetophenone oximate, 2927

- \* Sodium 3-methylisoxazolin-4,5-dione-4-oximate, 1419
  - \* Sodium 3-phenylisoxazolin-4,5-dione-4-oximate, 3114
  - \* Sodium tris(*O,O'*-1-oximatonaphthalene-1,2-dione)ferrate, 3871  
Trichloroacetaldehyde oxime, 0698
  - \* Trinitrosophloroglucinol, 2117
- See KETOXIMINOSILANES

## OXOHALOGEN ACIDS

## HOXO<sub>n</sub>

1. Bretherick, L., Comments, 1970
2. Alazard, J-P. *et al.*, *Actual. Chim.*, 1995, (1), 49

The oxidising power of the group of oxohalogen acids increases directly with oxygen content, though the high stability of the perchlorate ion at ambient temperature must be taken into account. The corresponding 'anhydrides' (halogen oxides) are also powerful oxidants, several being explosively unstable [1]. A review has been published on the instability of, and consequent safety considerations for, oxygen derivatives of chlorine; oxides, acids and salts thereof, used in organic synthesis [2].

Individual compounds are:

- Bromic acid, 0248
- Chloric acid, 3996
- Hypochlorous acid, 3995
- Iodic acid, 4424
- Orthoperiodic acid, 4542
- Perchloric acid, 3998
- Periodic acid, 4425

See also HALOGEN OXIDES

## OXOSALTS OF NITROGENOUS BASES

## N<sup>+</sup> EO<sub>n</sub><sup>-</sup>

1. Fogel'zang, A. G. *et al.*, *Chem. Abs.*, 1971, **75**, 142412
2. Mikhailova, T. A. *et al.*, *Chem. Abs.*, 1976, **85**, 201766

Burning rates of ammonium salts were investigated at various constant pressures. Ammonium permanganate burns faster than ammonium bromate, chlorate, dichromate, iodate, nitrite, perchlorate, periodate or triperchromate [1]. When submitting explosive nitrogenous bases or their salts to elemental nitrogen determination, it is advantageous to pre-treat the samples with phosphoric acid which allows the more stable pyro- and meta-phosphates (formed at 260° and 300°C, respectively) to be fully oxidised without explosion in the Dumas nitrogen procedure [2].

Many of the salts of nitrogenous bases (particularly of high nitrogen content) with oxoacids are unstable or explosive. There are separate group entries for:

AMINIUM IODATES AND PERIODATES, AMINIUM PERCHLORATES  
 DIAZONIUM PERCHLORATES, DICHROMATE SALTS OF NITROGENOUS BASES  
 1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES  
 HYDRAZINIUM SALTS, HYDROXYLAMINIUM SALTS

PERCHLORATE SALTS OF NITROGENOUS BASES  
POLY(AMINIUM) PERCHLORATES, NITRITE SALTS OF NITROGENOUS BASES

Individually indexed compounds are:

- \* Ammonium amidoselenate, 4557  
Ammonium amidosulfate, 4556  
Ammonium bromate, 0252  
Ammonium chlorate, 4003
- \* Ammonium fluorochromate, 4224
- \* Ammonium nitrate, 4522  
Ammonium permanganate, 4518  
Ammonium tetrachromate(2-), 4253  
Ammonium tetranitroplatinate(II), 4578  
Ammonium trichromate(2-), 4252  
Anilinium nitrate, 2379  
2,2'-Azobis(2-amidiniopropane) peroxodisulfate, 3091  
3-Azoniabicyclo[3.2.2]nonane nitrate, 3048  
Chloroformamidinium nitrate, 0467  
4-Chloro-1-methylimidazolium nitrate, 1453  
1-(4-Chlorophenyl)biguanidinium hydrogen dichromate, 3005  
Diaminoguanidinium nitrate, 0514  
1,2-Diammonioethane nitrate, 0966
- \* 2-Diethylammonioethyl nitrate nitrate, 2571  
Guanidinium nitrate, 0509  
Hydrazinium chlorate, 4010  
Hydrazinium dinitrate, 4561  
Hydrazinium hydrogen selenate, 4558  
Hydrazinium nitrate, 4549  
Hydroxylaminium nitrate, 4524  
2-Methoxyanilinium nitrate, 2829  
Methylammonium chlorite, 0500  
Methylammonium nitrate, 0506  
Methylammonium nitrite, 0505  
Methylhydrazinium nitrate, 0511  
1-Methyl-3-nitroguanidinium nitrate, 0947  
1-Phenylbiguanidinium hydrogen dichromate, 3019  
Pyridinium nitrate, 1873  
1,3,6,8-Tetraazoniatricyclo[6.2.1.1<sup>3,6</sup>]dodecane tetranitrate, 3092  
Tetraethylammonium periodate, 3090  
Tetrafluoroammonium perbromate, 0242
- \* Tetrakis(hydroxymethyl)phosphonium nitrate, 1754  
Tetramethylammonium chlorite, 1742  
Tetramethylammonium pentaperoxodichromate, 3103  
Triaminoguanidinium nitrate, 0517

Triethylammonium nitrate, 2580

Uronium nitrate, 0494

*See also* CHLORITE SALTS

## OXYGEN BALANCE

1. Kirk-Othmer, 1965, Vol. 8, 581

2. Slack, R., private comm., 1957

The oxygen balance of a compound is the difference between the oxygen content of the compound and that required fully to oxidise the carbon, hydrogen and other oxidisable elements present to carbon dioxide, water, etc. The concept is of particular importance in the design of explosive compounds or compositions, since the explosive power (energy release) is maximal at equivalence, or zero oxygen balance. If there is a deficiency of oxygen present, the balance is negative, while an excess of oxygen gives a positive balance, and such compounds can function as oxidants. The balance is usually expressed as a percentage. The nitrogen content of a compound is not considered as oxidisable, as it is usually liberated as the gaseous element in explosive decomposition [1].

While it is, then, possible to recognise highly explosive materials by consideration of their molecular formulae and oxygen balance (e.g. ethylene dinitrate,  $C_2H_4N_2O_6$  is zero balanced, tetranitromethane,  $CN_4O_8$  has +300% balance), the tendency to instability and high energy release becomes apparent well below the balance point. Trinitrotoluene has an oxygen balance of -64%. The empirical statement that the stability of any organic compound is doubtful when the oxygen content approaches that necessary to convert the other elements present to their lowest state of oxidation forms a useful guide [2] in the absence of more specific information. Some examples of oxygen balances may be found in the entries:

Bis(hydrazine)diperchloratochromium(III) perchlorate, 4128

Bis(triperchloratosilicon) oxide, 4190

5-Chloro-1,2,3-thiadiazole, 0655

Hexaamminechromium(III) perchlorate, 4129

Hexaamminecobalt(III) perchlorate, 4126

Mercury(II) oxalate, 0982

Pentaammineaquacobalt(III) chlorate, 4124

Tetraperchloratosilicon, 4169

Titanium tetraperchlorate, 4170

Trinitromethane, 0385

## OXYGEN BOMB CALORIMETRY

Plewinsky, B. *et al.*, *Thermochim. Acta*, 1985, **94**, 33–43

Safety aspects of the combustion of various materials in an atmosphere of pure oxygen under the conditions prevailing in oxygen bomb calorimetry were investigated experimentally. The combustion of a stable substance (benzoic acid, used to calibrate bomb calorimeters) in oxygen gives a relatively slow combustion, with a low rate of pressure increase of 17 bar/s to a maximum of 64 bar in 2.3 s, for

an initial oxygen pressure of 40 bar, and largely independent of the size of the sample. On the other hand, unstable (or explosive) solids may deflagrate or detonate, leading to very high rates of pressure increase and high maximum pressures, with values very dependent on sample size. Thus, under 40 bar oxygen pressure 0.5 g of picric acid gave values of 3.6 kbar/s to a maximum 98 bar, while 1.5 g gave 54 kbar/s to maximum 216 bar.

In the case of liquid non-explosive samples, three distinct situations can be discerned. First is where the gas phase composition lies outside the explosive range, and rates of pressure rise and maximum pressures attained are both modest and independent of sample size. Examples are benzene and hexamethyldisiloxane, which at 40 bar initial pressure of oxygen gave 36 bar/s to maximum 84 bar, and 63 bar/s to maximum 67 bar, respectively. Second is where the composition of the gas phase lies within the explosive range, as is observed with highly volatile liquids which give a single homogeneous phase, but the explosion pressure and rate of rise strongly depend on the sample size and the initial pressure of oxygen. For a fixed sample size of tetramethyldisiloxane, at an initial oxygen pressure of 10, 15, or 30 bar, rates of rise of 265, 60 and zero kbar/s to maxima of 113, 145 and zero (no reaction), respectively, were measured. The third case is where the composition of the gas phase is outside the explosive range and the system is heterogeneous (relatively non-volatile liquids), and this has been observed using low initial oxygen pressures with tetramethyldisiloxane and pentamethyldisiloxane.

The former, at 15 bar initial oxygen pressure gave 1 kbar/s rise to 75 bar maximum, but at 20 bar a transition to 21 kbar/s to 121 bar maximum occurs, and at 30 bar to 90 kbar/s and 160 bar maximum is observed, the latter almost certainly involving heterogeneous detonation on the wick and shattering of the containing crucible. Pentamethyldisiloxane at 25 bar initial oxygen pressure shows a rate of rise of 60 bar/s to maximum 49 bar, but at 30 bar initial pressure the rate increases to 38 kbar/s to 205 bar maximum.

*See* Oxygen (Gas), : Sodium hydroxide, Tetramethyldisiloxane

*See other* CALORIMETRY

## OXYGEN ENRICHMENT

1. *Oxygen Enrichment of Confined Areas*, Information Sheet, Inst. of Welding, 1966
2. Wilk, I. J., *J. Chem. Educ.*, 1968, **45**, A547–551
3. Johnson, J. E. *et al.*, *NRL Rept. 6470*, Washington, Nav. Res. Lab., 1966
4. Woods, F. J. *et al.*, *NRL Rept. 6606*, Washington, Nav. Res. Lab., 1967
5. Denison, D. M. *et al.*, *Nature*, 1968, **218**, 1111–1113
6. Jones, D. A., *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 1, I13–I22, Rugby, IChE, 1983
7. *NFPA 53M*, Quincy (Na), Natl. Fire Prot. Assocn., 1985
8. ASTM, *STP 1319 (Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres)*, 1997

With the widening availability and industrial use of oxygen, accidents caused by atmospheric enrichment have increased. Most materials, especially clothing, burn

fiercely in an atmosphere containing more than the usual 21 vol% of oxygen. In presence of petroleum products, fire and explosion can be spontaneous. Equipment which may emit or leak oxygen should be used sparingly, and never stored, in confined spaces [1]. Fourteen case histories of accidents caused by oxygen enrichment of the atmosphere are discussed and safety precautions detailed [2]. The flammability of textiles and other solids was studied under the unusual conditions which occur in deep diving operations. The greatest effect on ease of ignition and linear burning rate was caused by oxygen enrichment; increase in pressure had a similar effect [3].

Ignition and flame spread of fabrics and paper were measured at pressures from 21 bar down to the limiting pressure for ignition to occur. Increase in oxygen concentration above 21% in mixtures with nitrogen caused rapid decrease of minimum pressure for ignition. In general, but not invariably, materials ignite less readily but burn faster in helium mixtures than in nitrogen mixtures. The nature of the material has a marked influence on the effect of variables on the rate of burning. At oxygen concentrations of 41% all materials examined would burn except for glass and polytetrafluoroethylene, which resisted ignition attempts in pure oxygen. Flame retardants become ineffective on cotton in atmospheres containing above 32% oxygen [4]. A brief summary of known hazards and information in this general area was published [5]. A method of assessing off-site hazards in the vicinity of bulk liquid oxygen storage installations is presented [6]. The US Fire Protection Association manual covers materials and system design to reduce fire hazards in enriched atmospheres, and includes detail on fire experiences in such systems [7]. The American Society for Testing and Materials has produced an even more comprehensive work [8].

*See* Oxygen (Gas)

## **OXYGEN FLUORIDES**

## **O<sub>2</sub>F, FOF, FOOF, O<sub>2</sub>FOF, (O<sub>2</sub>F)<sub>2</sub>**

Streng, A. G., *Chem. Rev.*, 1963, **63**, 607

In the series oxygen difluoride, dioxygen difluoride, trioxygen difluoride and tetraoxygen difluoride, as the oxygen content increases, the stability decreases and the oxidising power increases, tetraoxygen difluoride, even at  $-200^{\circ}\text{C}$ , being one of the most potent oxidants known. Applications to both chemical reaction and rocket propulsion systems are covered in some detail.

Individual compounds are:

Dioxygen difluoride, 4320

Hexaoxygen difluoride, 4327

Oxygen difluoride, 4317

'Trioxygen difluoride', 4323

*See other* HALOGEN OXIDES

## **OXYGEN INDEX**

1. *Oxygen Index Test*, ASTM D2863, 1970
2. Isaacs, J. S., *J. Fire Flamm.*, 1970, **1**, 36–47

3. Kamp, A. C. F. *et al.*, *Proc. 1st Euro. Symp. Therm. Anal.*, 1976, 440–443
4. Redfern, J. P., *Intern. Lab.*, 1979, **9**, 57
5. Kishore, K. *et al.*, *J. Haz. Mat.*, 1980, **3**, 349–356

The flammability properties of volatile materials are readily gauged from the values of the figures for flash point and limits of flammability in air. For involatile flammable materials, a range of empirical tests provides a measure of flammability properties under various circumstances. One of the tests, originally developed to measure the minimum concentration of oxygen in which a sample of a plastics material will continue to burn candle-like, is simple, accurate and reproducible [1]. Results are expressed as an Oxygen Index (O. I.), which is the minimum proportion of oxygen in a mixture with nitrogen to just sustain combustion of a sample of standard size in a chimney-like apparatus. The method has been applied to textile materials [2], and may well be applicable to a much wider range of materials. Determination of the Oxygen Index over a wide temperature range gives a better understanding of flammability parameters, and the Temperature Index (T. I., the temperature at which O. I. is 20.8) will rank flammability of materials. The O. I. at ambient temperature indicates potential hazard at the primary ignition stage, while the T. I. and the O. I.–temperature relation is related to practical fire situations [3]. The mathematical relationships between O. I. and various fire parameters have been reviewed [4]. A new (dimensionless) parameter for flammability of materials, the Flammability Index, is defined in terms of specific heat, flash or autoignition temperature and heat of combustion. It correlates well with the Oxygen Index [5].

## 1-OXYPEROXY COMPOUNDS

## O–C–OO–

Swern, 1970., Vol. 1, 29, 33

This group of compounds includes those monomers with one or more carbon atoms carrying a hydroperoxy or peroxy group, and also singly bonded to an oxygen atom present as hydroxyl, ether or cyclic ether functions. While the group of compounds is, in general, moderately stable, the lower 1-hydroxy and 1,1'-dihydroxy-alkyl peroxides or hydroperoxides are explosive. Individually indexed compounds are:

- 1-Acetoxy-1-hydroperoxy-6-cyclodecanone, 3669
- \* 1-Acetoxy-6-oxo-cyclodecyl hydroperoxide, 3547
- Bis(1-hydroperoxycyclohexyl) peroxide, 3556
- Bis(1-hydroxycyclohexyl) peroxide, 3553
- Bis(hydroxymethyl) peroxide, 0928
- 1-Hydroperoxy-1'-hydroxydicyclohexyl peroxide, 3555
- \* 1-Hydroxy-3-butyl hydroperoxide, 1706
- Hydroxymethyl hydroperoxide, 0487
- Hydroxymethyl methyl peroxide, 0926
- \* 2-Methoxyprop-2-yl hydroperoxide, 1707

## OZONIDES

1. Rieche, *Angew. Chem.*, 1958, **70**, 251
2. Swern, 1970, Vol. 1, 39

3. Bailey, P. S., *Chem. Rev.*, 1958, **58**, 928
4. Greenwood, F. L. *et al.*, *J. Org. Chem.*, 1967, **32**, 3373
5. Rieche, A. *et al.*, *Ann.*, 1942, **553**, 187, 224

The preparation, properties and uses of ozonides have been reviewed comprehensively [1]. Many pure ozonides (trioxolanes) are generally stable to storage; some may be distilled under reduced pressure. The presence of other peroxidic impurities is thought to cause the violently explosive decomposition often observed in this group [2]. Use of ozone is not essential for their formation, as they are also produced by dehydration of  $\alpha,\alpha'$ -dihydroxy peroxides [3]. A very few isomeric linear trioxides (ROOOR) are known, they are also explosively unstable. Inorganic ozonides, salts of the radical  $O_3^-$  anion, are also hazardous.

Polymeric alkene ozonides are shock-sensitive; that of *trans*-2-butene exploded when exposed to friction in a ground glass joint. The use of GLC to analyse crude ozonisation products is questionable because of the heat-sensitivity of some constituents [4]. Ozonides are decomposed, sometimes explosively, by finely divided palladium, platinum or silver, or by iron(II) salts [5]. Individually indexed compounds are:

- Benzene triozone, 2343
- trans*-2-Butene ozonide, 1623
- † 1,1-Dichloroethylene, Ozone, 0695
- 1,1-Difluoroethylene ozonide, 0703
- 1,2-Dimethylcyclopentene ozonide, 2845
- \* 2,5-Dimethyl-2,5-dihydrothiophene-2,5-endoperoxide, 2387
- 2,6-Dimethyl-2,5-heptadien-4-one diozonide, 3176
- 2,5-Diphenyl-3,4-benzofuran-2,5-endoperoxide, 3798
- Ethylene ozonide, 0836
- Fluoroethylene ozonide, 0752
- trans*-2-Hexene ozonide, 2513
- 4-Hydroxy-4-methyl-1,6-heptadiene diozonide, 3036
- Isoprene diozonide, 1920
- Maleic anhydride ozonide, 1406
- † 2-Methyl-1,3-butadiene, : Ozone, 1893
- 3-Methyl-1,2,4-trioxolane, 1235
- trans*-2-Pentene ozonide, 1982
- Pyrocatecholato(2-)(quinolin-8-olato-*N,O*)-trioxygenido(2-)-phosphorus, 3678
- 3,3,5-Trifluoro-1,2,4-trioxolane, 0667
- Vinyl acetate ozonide, 1543

See also JOJOBA WAX: OZONE

## PACKAGING INCIDENTS

Tobias, B. I., *Chem. Eng. News*, 1991, **69**(10), 2

A 500 ml bottle of peracetic acid (ethaneperoxoic acid), provided with a vented cap, was received packed within a tin padded with what appeared to be paper. The metal was distinctly hot to the touch on opening. Peroxyacetic acid is capable of runaway decomposition from 65°C. The heat is thought to have resulted from



seepage through the vent, the bottle having been on its side, followed by reaction with the paper. The importance of inert packing materials is emphasised. Other packaging incidents are:

Acetyl chloride: Water, 0735

Benzenesulfinyl chloride, 2234

Benzenesulfonyl chloride, 2235

Borane–Tetrahydrofuran, 0138

Calcium oxide: Water (reference 5), 3937

Diethyl dicarbonate, 2444

Ethyl oxalyl chloride, 1456

Formic acid, 0418

Nitric acid: Polyalkenes, 4436

Nitric acid: Wood, 4436

Peroxyacetic acid, 0837

Potassium (reference 3), 4645

Pyruvic acid, 1150

Sodium sulfide: Glass, 4811

Trichloromethyl carbonate, 1040

*See also* INSULATION, PAPER TOWELS

## PAINT TAILINGS

*See* 9,12,15-Octadecatrienoic acid: Cobalt naphthenate

## PAPER TOWELS

Unpublished observations, 1970

The increasing use of disposable paper towels and wipes in chemical laboratories accentuates the potential fire hazards arising from the disposal of solid oxidising agents or reactive residues into a bin containing such towels or wipes. The partially wet paper, necessarily of high surface area and absorbency, presents favourable conditions for a fire to be initiated and spread. Separate bins for paper towels etc., and chemical residues seem advisable.

*See* Zinc: Sodium hydroxide (reference 3)

SODA-LIME

ALDEHYDES, INSULATION, PACKAGING INCIDENTS

## PEAT

1. Sansonov, L. N. *et al.*, *Chem. Abs.*, 1988, **109**, 173306

2. Kashinskaya, I. Ya. *et al.*, *Chem. Abs.*, 1989, **110**, 26472

Stockpiles of milled peat are prevented from self heating and ignition by sprayed application of bitumen emulsion to form a 2–2.5 mm protective permeable film [1]. The mechanism of self heating and ignition first involves aerobic microbiological processes, then chemical transformation of iron-containing minerals in the peat into pyrophoric iron compounds which later ignite the peat mound [2].

PYROPHORIC IRON-SULFUR COMPOUNDS  
DUST EXPLOSION INCIDENTS (reference 21)

**PENTAAZADIENES**



See Bis[1,5-bis(4-methylphenyl)-1,3-pentazadienato-N3,N5]-(T-4) cobalt

See TRIAZENES (reference 3) See other HIGH-NITROGEN COMPOUNDS

**N-PENTAFLUROSULFUR COMPOUNDS**



1. Sitzmann, E., *Chem. Abs.*, 1992, **116**, 132303z
2. De Yong, L. V. *et al.*, *Chem. Abs.*, 1993, **119**, 142309g

A series of carbonimidate esters bearing a pentafluorosulfur group on the nitrogen are described as explosives. The SF<sub>5</sub> is unlikely to be ornamental although most of the alkoxy groups involved also carry nitro groups [1]. However, another study of explosives which bore a pentafluorothio group, probably on carbon, suggested it was equivalent to an hydrogen [2].

**PERCHLORATE-DOPED CONDUCTING POLYMERS**

1. Eisenbaumer, R. L. *et al.*, *Chem. & Eng. News*, 1985, **63**(22), 4
2. Young, X.-Z. *et al.*, *J. Polymer Sci. (Polymer Chem. Edn.)*, 1985, **23**, 859
3. Varyu, M. E. *et al.*, *Chem. & Eng. News*, 1985, **63**(24), 4
4. Österholm, J.-E. *et al.*, *Chem. & Eng. News*, 1986, **64**(6), 2
5. Druy, M. A., *Chem. Eng. News*, 1986, **64**(12), 2
6. Julia, L. *et al.*, *Chem. & Ind.*, 1989, 78–79
7. Editor's comments

A piece of poly(acetylene) film doped with perchlorate detonated spontaneously inside an argon-filled dry box. Doping had been effected by contacting the film with a solution of iron(III) perchlorate in toluene-nitromethane, followed by washing and high-vacuum drying. Samples of the doped film had previously been tested and showed no signs of instability under impact, physical stress, or on flame contact. The explosion occurred 2 weeks later when further samples were being taken [1]. A sample of similar material undergoing thermogravimetric analysis had exploded at 160°C [2]. Use of electrochemical (rather than chemical) doping methods is preferred as more controllable, with determination of perchlorate content (as chloride) by oxygen flask combustion analysis. Limitation of analytical sample size to 10 mg and other precautions are recommended [3]. Perchlorate-doped poly(thiophene) film (up to 25–30 mol % of perchlorate in the matrix) has also been prepared and found stable under ambient conditions. However it is extremely unstable at temperatures above 100°C (possibly explosive), and samples of film intensively desiccated over phosphorus pentoxide have exploded on handling with tweezers. Great care is necessary in handling such materials [4]. Perchlorate-doped poly(pyrrole) and poly(thiophene) film in a dry atmosphere tend to explode when handled with tweezers, though such films were stable to heating at above 100°C. Trifluoromethanesulfonate and *p*-toluenesulfonate are more suitable doping

counterions than perchlorate [5]. The use of thallium(III) trifluoroacetate in trifluoroacetic acid as combined oxidant and dopant appears to give stable radical ion salts of poly(thiophene) [6].

Some conducting polymers with a conjugated polyvinyl structure, such as polyacetylene and poly(phenylacetylene), seem likely to be energetic enough, and reactive enough, to give trouble undoped, if they actually have the supposed structure [7].

*See related* NON-METAL PERCHLORATES

*See* Ethylene, Butadiene, Styrene

## PERCHLORATES

—OCIO<sub>3</sub>

1. Schumacher, 1960
2. Burton, H. *et al.*, *Analyst*, 1955, **80**, 4

All perchlorates have some potential for hazard when in contact with other mutually reactive materials, while many are intrinsically hazardous, owing to the high oxygen content.

Existing knowledge on perchloric acid and its salts was reviewed extensively in 1960 in a monograph including the chapters: Perchloric Acid; Alkali Metal, Ammonium and Alkaline Earth Perchlorates; Miscellaneous Perchlorates; Manufacture of Perchloric Acid and Perchlorates; Analytical Chemistry of Perchlorates; Perchlorates in Explosives and Propellants; Miscellaneous Uses of Perchlorates; Safety Considerations in Handling Perchlorates [1]. There is a shorter earlier review, with a detailed treatment of the potentially catastrophic acetic anhydride–acetic acid–perchloric acid system. The violently explosive properties of methyl, ethyl and lower alkyl perchlorate esters, and the likelihood of their formation in alcohol–perchloric acid systems, are stressed. The instability of diazonium perchlorates, some when damp, is discussed [2].

The class has been divided into the separately treated groups:

ALKYL PERCHLORATES, AMMINOMETAL OXOSALTS  
AMINIUM PERCHLORATES, DIAZONIUM PERCHLORATES  
METAL PERCHLORATES, NON-METAL PERCHLORATES  
PERCHLORATE SALTS OF NITROGENOUS BASES

### Glycol, Polymer

*MCA Case History No. 464*

A mixture of an inorganic perchlorate salt, a glycol and a polymer exploded violently after heating at 265–270°C. It was thought that the glycol may have been oxidised, but formation of the glycol perchlorate ester(s) seems a likely alternative cause.

### Organic matter

Schumacher, 1960, 188

Mixtures of perchlorate salts with finely divided or fibrous organic materials are likely to be explosive. Porous or fibrous materials exposed to aqueous solutions and then dried are rendered explosively flammable and are easily ignited.

### Reducants

1. Mellor, 1941, Vol. 2, 387; Vol. 3, 651
2. Schumacher, 1960, 188

Perchlorate salts react explosively when rubbed in a mortar with calcium hydride or with sulfur and charcoal, when melted with reducers, or on contact with glowing charcoal [1]. Mixtures with finely divided aluminium, magnesium, zinc or other metals are explosives [2].

*See other* REDOX REACTIONS

### PERCHLORATE SALTS OF NITROGENOUS BASES



Kozak, G. D. *et al.*, *Chem. Abs.*, 1981, **94**, 86609

In a study of detonation of aqueous solutions of perchlorate salts of hydroxylamine, urea, methylamine and diaminoethane (mono- or di-salts), the former could be detonated in 20–25% solution at 407–587°C.

Many other perchlorate salts of nitrogenous bases have been involved in explosive incidents, individually indexed compounds being:

2-Aminoethylammonium perchlorate, 0958

Ammonium perchlorate, 4004

Anilinium perchlorate, 2367

2-Aza-1,3-dioxolanium perchlorate, 0898

\* 2-Azatricyclo[2.2.1.0<sup>2,6</sup>]hept-7-yl perchlorate, 2368

\* 1,4-Bis(2-chloroethyl)-1,4-bis(azonia)bicyclo[2.2.1]heptane periodate, 3192

1,2-Bis(ethylammonio)ethane perchlorate, 2589

Chloroformamidinium perchlorate, 0469

Dimethylammonium perchlorate, 0950

1,3-Dimethyl-2,1-benzisoxazolium perchlorate, 3148

1,1-Dimethyldiazonium perchlorate, 0938

1-(4,5-Dimethyl-1,3-diselenonylidene)piperidinium perchlorate, 3340

2,2-Dimethyltriazanium perchlorate, 0963

2,4-Dinitrophenylhydrazinium perchlorate, 2351

*N,N*-Diphenyl-3-phenylpropenyldenimmonium perchlorate, 3820

2-(1,3-Diselena-4,5,6,7-tetrahydroindanylidene)piperidinium perchlorate, 3408

1,2-Ethylenebis(ammonium) perchlorate, 0964

Guanidinium perchlorate, 0502

Hydrazinium diperchlorate, 4068

Hydrazinium perchlorate, 4011

2-Hydroxyethylaminium perchlorate, 0951

Hydroxylaminium perchlorate, 4005

Methylammonium perchlorate, 0501

1-(4-Methyl-1,3-diselenonylidene)piperidinium perchlorate, 3174

1-Methyl-3-nitroguanidinium perchlorate, 0939

Morpholinium perchlorate, 1680

4-Nitroanilinium perchlorate, 2350

Perchloric acid, : Nitrogenous epoxides, 3998

\* Phosphonium perchlorate, 4006

Poly(dimercuryimmonium perchlorate), 4012  
Pyridinium perchlorate, 1863  
Tetraethylammonium perchlorate, 3088  
Tetrafluoroammonium perchlorate, 3986  
*N,N,N',N'*-Tetramethylformamidinium perchlorate, 2026  
Triaminoguanidinium perchlorate, 0515  
Trimethylammonium perchlorate, 1322  
Trimethylhydroxylammonium perchlorate, 1323  
Tri(4-tolyl)ammonium perchlorate, 3824  
Uronium perchlorate, 0491

### PERCHLORYLAMIDE SALTS

$M^+ (O_3CINH)^-$

1. *Perchloryl Fluoride*, Booklet DC-1819, Philadelphia, Pennsalt Chem. Corp., 1957
2. Hennrichs, W. *et al.*, *Z. Anorg. Chem.*, 1983, **50** 6, 205  
Ammonium perchlorylamide and the corresponding silver and barium salts are shock-sensitive when dry and may detonate. Extreme care is required when handling such salts [1]. Some *N*-benzylperchlorylamide derivatives are also unstable, and the barium, silver and mercury salts explode on impact, and the two latter on heating to 105 and 120°C, respectively [2].

Individually indexed compounds are:

Ammonium perchlorylamide, 4009  
Barium perchlorylamide, 0203  
Barium *N*-perchlorylbenzylamide, 3649  
Mercury(II) *N*-perchlorylbenzylamide, 3651  
Monopotassium perchlorylamide, 3994  
Potassium perchlorylamide, 4019  
Silver perchlorylamide, 0028  
Silver *N*-perchlorylbenzylamide, 2734

*See other* PERCHLORYL COMPOUNDS, *N*-METAL DERIVATIVES

### PERCHLORYL COMPOUNDS

$RNHClO_3$ ,  $ArClO_3$

1. *Friedel-Crafts and Related Reactions*, Olah, G. A. (Ed.), Vol. 3.2, 1507–1516, New York, Interscience, 1964
2. Baum, K. *et al.*, *J. Amer. Chem. Soc.*, 1974, **96**, 3233–3237
3. Beard, C. D. *et al.*, *J. Amer. Chem. Soc.*, 1974, **96**, 3237–3239

The need for great care to avoid the possibility of detonation of perchloryl compounds by exposure to shock, overheating or sparks is stressed. The compounds are generally more sensitive to impact than mercury fulminate and are of comparable sensitivity to lead azide [1]. A range of highly explosive alkyl perchlorates [2] and perchlorylamines [3] have been prepared by interaction of dichlorine heptaoxide with alcohols or amines in carbon tetrachloride solution. The solutions of the products were not sensitive to mechanical shock and could

be used directly for further reactions. Adequate warning of the explosion hazards involved in isolating perchloryl compounds is given.

Individually indexed compounds are:

2,6-Dinitro-4-perchlorylphenol, 2101

2,6-Diperchloryl-4,4'-diphenoquinone, 3444

3-Nitroperchlorylbenzene, 2143

Perchlorylbenzene, 2236

Perchloryl fluoride, 3974

*N*-Perchlorylpiperidine, 1949

*See also* PERCHLORYLAMIDE SALTS

## PERFLUOROSILANES

$\text{Si}_m\text{F}_n$

Bailar, 1973, Vol. 1, 1385

The compounds in this group ( $\text{Si}_2\text{F}_6$  to  $\text{Si}_4\text{F}_{10}$  are mentioned later) are said to ignite in air and react violently with water.

*See other* HALOSILANES

## PEROXIDATION INCIDENTS

Many incidents involving explosions have been attributed, not always correctly, to peroxide formation and violent decomposition. Individually indexed incidents are:

2-Acetyl-3-methyl-4,5-dihydrothiophen-4-one, 2807

Aluminium dichloride hydride diethyl etherate, : Dibenzyl ether, 0061

† 1,3-Butadiene, 1480

† Diallyl ether, 2431

† Diisopropyl ether, 2542

Lithium tetrahydroaluminate, : Tetrahydrofuran, 0075

Peroxyacetic acid, : Ether solvents, 0837

† 2-Propen-1-ol, : Sulfuric acid 1.42/53, 1223

Sulfinyl chloride, : Diisopropyl malonate, 4096

*See* PEROXIDES IN SOLVENTS, PEROXIDISABLE COMPOUNDS

*See related* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## PEROXIDES

—OO—

This class name covers one of the largest classes of hazardous compounds, with 3 main divisions: these groups are further subdivided for convenience.

INORGANIC PEROXIDES

ORGANIC PEROXIDES

ORGANOMETALLIC PEROXIDES

## PEROXIDES IN SOLVENTS

1. Author's comments, 1984

2. Burfield, D. R., *J. Org. Chem.*, 1982, **47**, 3821–3824

Many laboratory accidents have been ascribed to presence of peroxides in solvents, usually, but not exclusively ethers. Storage of the solvents for over-long periods,

often under poor conditions, is a common feature of the incidents. When peroxides are removed from solvents by chromatographic adsorption on alumina columns, the concentrated band of strongly adsorbed peroxides at the top of the column may become hazardous if the solvent evaporates [1]. The use of self-indicating molecular sieve under nitrogen is described as an effective method of de-peroxidising THF, diethyl and dipropyl ethers, suitable also for bulk-scale operations [2].

See ETHERS

PEROXIDE TEST STRIPS

PEROXIDISABLE COMPOUNDS

2-Butanol, 1695

2-Butanone, 1606

Diethyl ether, 1697

Diisopropyl ether, 2542

1,4-Dioxane, 1617

4-Methyl-2-pentanone, 2495

2-Propanol, 1280

Tetrahydrofuran, 1612

Hydrogen peroxide: Acetone, 4477

Peroxomonosulfuric acid: Acetone, 4481

## PEROXIDE TEST STRIPS

See 1-Allyloxy-2,3-epoxypropane

See also PEROXIDES IN SOLVENTS

## PEROXIDISABLE COMPOUNDS

1. Jackson, H. L. *et al.*, *J. Chem. Educ.*, 1970, **47**, A175
2. Brandsma, 1971, 13
3. *MCA Case History No. 1693*
4. *Recognition and Handling of Peroxidisable Compounds*, Data sheet 1-655, Chicago, National Safety Council, 1982
5. Shanley, E. S., *Chem. Eng. News*, 1979, **57**(21), 43
6. Mirafzal, G. A. *et al.*, *J. Chem. Educ.*, 1988, **65**(9), A226–229
7. Bretherick, L., private comm. to Dr Mirafzal, 1988; *J. Chem. Educ.*, 1990, **67**(9), A230
8. Kelly, R. J., *Chem. Health & Safety*, 1996, **3**(5), 28

An account of a Du Pont safety study of the control of peroxidisable compounds covers examples of peroxidisable structures, handling procedures, distillation of peroxidisable compounds, and detection and elimination of peroxides [1]. Essential organic structural features for a peroxidisable hydrogen atom are recognised as those below. While the two structural types at the end of that list readily peroxidise, in some cases the products are readily degradable and do not accumulate to a hazardous level. A notable exception is acetaldehyde which is converted to peroxyacetic acid. Inorganic compounds which readily peroxidise are listed as potassium (which gives the superoxide) and higher alkali metals, alkali metal alkoxides and amides, and organometallic compounds.

Three lists of specific compounds or compound types indicate different types of potential hazard, and appropriate storage, handling and disposal procedures are detailed for each.

List A, giving examples of compounds which form explosive peroxides while in storage, include diisopropyl ether, divinylacetylene, vinylidene chloride, potassium and sodium amide. Review of stocks and testing for peroxide content by given tested procedures at 3-monthly intervals is recommended, together with safe disposal of any peroxidic samples.

List B, giving examples of liquids where a degree of concentration is necessary before hazardous levels of peroxides will develop, includes several common solvents containing one ether function (diethyl ether, ethyl vinyl ether, tetrahydrofuran), or two ether functions (*p*-dioxane, 1,1-diethoxyethane, the dimethyl ethers of ethylene glycol or 'diethylene glycol'), the secondary alcohols 2-propanol and 2-butanol, as well as the susceptible hydrocarbons propyne, butadiyne, dicyclopentadiene, cyclohexene and tetra- and deca-hydronaphthalenes. Checking stocks at 12 monthly intervals, with peroxidic samples being discarded or repurified, is recommended here [1].

A simple method of effectively preventing accumulation of dangerously high concentrations of peroxidic species in distillation residues is that detailed in an outstanding practical textbook of preparative acetylene chemistry [2]. The material to be distilled is mixed with an equal volume of non-volatile mineral oil. This remains after distillation as an inert diluent for polymeric peroxidic materials.

List C contains peroxidisable monomers, where the presence of peroxide may initiate exothermic polymerisation of the bulk of material. Precautions and procedures for storage and use of monomers with or without the presence of inhibitors are discussed in detail. Examples cited are acrylic acid, acrylonitrile, butadiene, 2-chlorobutadiene, chlorotrifluoroethylene, methyl methacrylate, styrene, tetrafluoroethylene, vinyl acetate, vinylacetylene, vinyl chloride, vinylidene chloride and vinylpyridine [1].

In general terms, the presence of two or more of the structural features indicated above in the same compound will tend to increase the risk. The selection of compound groups and of individually indexed compounds below includes compounds known to have been involved or those with a multiplicity of such structural features which would be expected to be especially susceptible to peroxide formation. A more recent and thorough review of peroxidation risks gives a critical assessment of test methods for peroxides [8].

Subsequent to incidents involving peroxidation of stored bottles of vinylidene chloride, a labelling procedure and list of peroxidisable compounds was prepared [3]. Of the 108 compounds listed, 35 are noted as forming peroxides with ease, and these need particular care in storage and use. A revised data sheet is now available [4], and peroxide-containing residues may often be rendered innocuous by pouring into an excess of sodium carbonate solution [5].

The argument in an addendum to reference 1 above which claims that primary alcohols should also be classed as peroxidisable [6] is flawed. Among the primary alcohols listed as peroxide formers, the structures of those which formed significant levels of peroxide in storage all possessed tertiary H atoms susceptible to



autoxidation by virtue of their position on the branched carbon skeletons of the alcohols, as well as the (insusceptible) primary hydroxyl group. While it is true that secondary alcohols should certainly be added to List B above, it is not necessary for primary alcohols as such, unless the structure is branched, when there may be susceptible hydrogen(s) present to warrant caution. It is the nature of the carbon skeleton, rather than presence of the hydroxyl group, which is the more important factor [7].

<i>BOND GROUPINGS</i>	<i>CLASS ENTRY</i>
$\begin{array}{c} >C-O- \\   \\ H \end{array}$	as in acetals, ethers, oxygen heterocycles
$\begin{array}{c} -CH_2 >C- \\   \\ -CH_2 >C- \\   \\ H \end{array}$	as in isopropyl compounds, decahydronaphthalenes
$\begin{array}{c} >C=C-C- \\   \\ H \end{array}$	as in allyl compounds
$\begin{array}{c} >C=C-X \\   \\ H \end{array}$	as in haloalkenes
$\begin{array}{c} >C=C \\   \\ H \end{array}$	as in other vinyl compounds (Monomeric esters, ethers, etc.)
$\begin{array}{c} >C=C-C=C< \\   \quad   \\ H \quad H \end{array}$	as in dienes
$\begin{array}{c} >C=C-C\equiv C- \\   \\ H \end{array}$	as in vinylacetylenes
$\begin{array}{c} -C-C-Ar \\   \\ H \end{array}$	as in cumenes, tetrahydronaphthalenes, styrenes
$\begin{array}{c} -C=O \\   \\ H \end{array}$	as in aldehydes
$\begin{array}{c} -C-N-C< \\    \quad   \quad   \\ O \quad H \end{array}$	as in <i>N</i> -alkyl-amides or -ureas, lactams

See Indane-2-aldehyde

ACETYLENIC COMPOUNDS, ALKALI METALS

ALKENES, ALKYNES

BENZYL COMPOUNDS, DIENES

HALOALKENES, OXIMES

TETRAHYDROPYRANYL ETHER DERIVATIVES

and individually indexed compounds:

† Acetaldehyde, 0828  
 † Acrylaldehyde, 1145  
 † Allyl ethyl ether, 1955  
   1-Allyloxy-2,3-epoxypropane, 2434  
 † Bis(2-ethoxyethyl) ether, 3076  
   Bis-(2-methoxyethyl) ether, 2549  
 † 1,3-Butadiene, 1480  
 † 1,3-Butadiyne, 1385  
 † 2-Butanol, 1695  
 † Buten-3-yne, 1423  
 † Butyl ethyl ether, 2540  
 † Butyl vinyl ether, 2484  
 † 2-Chloro-1,3-butadiene, 1451  
 † Chloroethylene, 0730  
 † 2-Chloroethyl vinyl ether, 1557  
   Cinnamaldehyde, 3134  
 † Crotonaldehyde, 1516  
 † Cyclopropyl methyl ether, 1608  
 † Diallyl ether, 2431  
   Dibenzyl ether, 3655  
 † Dibutyl ether, 3071  
 † 1,1-Dichloroethylene, 0695  
 † 1,1-Diethoxyethane, 2545  
 † 1,2-Diethoxyethane, 2546  
 † 3,3-Diethoxypropene, 2858  
 † Diethyl ether, 1697  
   Diethylketene, 2430  
 † 2,3-Dihydrofuran, 1517  
 † Diisopropyl ether, 2542  
 † 1,1-Dimethoxyethane, 1700  
 † 1,2-Dimethoxyethane, 1701  
 † Dimethoxymethane, 1281  
 † 3,3-Dimethoxypropene, 1968  
 † 1,3-Dioxane, 1616  
 † 1,4-Dioxane, 1617  
 \* 1,3-Dioxol-4-en-2-one, 1087  
 † Dipropyl ether, 2543  
   Di(2-propynyl) ether, 2327  
 † Divinyl ether, 1519  
   2-Ethoxyethanol, 1702  
   1-Ethoxy-2-propyne, 1909  
   2-Ethylacrylaldehyde oxime, 1933  
 † 2-Ethylbutanal, 2487  
 † 2-Ethylhexanal, 3050  
 † Ethyl isopropyl ether, 2012  
 † Ethyl propenyl ether, 1956

- † Ethyl vinyl ether, 1610
- 2-Furaldehyde, 1836
- † Furan, 1439
- 2,4-Hexadienal, 2383
- 4,5-Hexadien-2-yn-1-ol, 2328
- 2,5-Hexadiyn-1-ol, 2329
- 2-Hexenal, 2432
- 2-Indanecarboxaldehyde, 3288
- † Isobutyraldehyde, 1611
- 2-Isopropylacrylaldehyde oxime, 2453
- † Isopropyl vinyl ether, 1957
- † Isovaleraldehyde, 1958
- Limonene, 3337
- 1,5-*p*-Menthadiene, 3338
- \* Methoxy-1,3,5,7-cyclooctatetraene, 3149
- 2-Methoxyethanol, 1284
- † 2-Methoxyethyl vinyl ether, 1973
- \* 2-(1-Methylheptyl)-4,6-dinitrophenyl crotonate, 3764
- † 2-3-Methyl-2-methylenebutanal, 2433
- † 4-Methyl-2-pentanone, 2495
- † 2-Methyltetrahydrofuran, 1961
- † Methyl vinyl ether, 1221
- $\alpha$  -Pentylcinnamaldehyde, 3663
- † Propionaldehyde, 1224
- Sodium 5,8,11,14-eicosatetraenoate, 3809
- Sodium ethoxyacetylde, 1478
- 1,1,2,3-Tetrachloro-1,3-butadiene, 1389
- † Tetrahydrofuran, 1612
- Tetrahydronaphthalene, 3300
- † Tetrahydropyran, 1965
- Tridecanal, 3619
- † Vinyl acetate, 1532
- † 4-Vinylcyclohexene, 3004

## PEROXOACIDS

## EOOH

Inorganic acids with a peroxide function are given the IUPAC name above, which distinguishes them from the organic PEROXYACIDS. Collectively they are a group of very powerful oxidants, individual compounds being:

- Peroxodisulfuric acid, 4482
- Peroxomonophosphoric acid, 4506
- Peroxomonosulfuric acid, 4481
- Peroxonitric acid, 4437

## PEROXOACID SALTS

## E<sub>OO</sub><sup>-</sup>, MOO<sup>-</sup>

Many of the salts of peroxyacids are unstable or explosive, are capable of initiation by heat, friction or impact, and all are powerful oxidants. Individually indexed compounds are:

Ammonium hydroxyoxodiperoxochromate(1-), 4230  
Ammonium pentaperoxodichromate(2-), 4247  
Ammonium peroxoborate, 0146  
Ammonium peroxodisulfate, 4576  
Ammonium tetraperoxochromate(1-)  
Calcium peroxodisulfate, 3940  
Calcium triperoxochromate, 3945  
Mercury(II) peroxybenzoate, 3637  
Potassium *O-O*-benzoylmonoperoxosulfate, 2684  
Potassium diperoxomolybdate, 4659  
Potassium diperoxoorthovanadate, 4667  
Potassium hydrogen peroxomonosulfate, 4430  
Potassium hydroxyoxodiperoxochromate(1-), 4227  
Potassium pentaperoxodichromate, 4249  
Potassium peroxodisulfate, 4668  
Potassium peroxyferrate(2-), 4396  
Potassium tetraperoxochromate(3-), 4235  
Potassium tetraperoxomolybdate, 4660  
Potassium tetraperoxotungstate, 4669  
Potassium tricyanodiperoxochromate(3-), 1044  
Silver peroxochromate, 0037  
Sodium monoperoxy carbonate, 0554  
Sodium peroxoborate, 0155  
Sodium peroxodisulfate, 4809  
Sodium peroxyacetate, 0780  
Sodium peroxydicarbonate, 1024  
Sodium tetraperoxochromate(3-), 4240  
Sodium tetraperoxomolybdate, 4715  
Sodium tetraperoxotungstate, 4810  
Tetramethylammonium pentaperoxodichromate, 3103  
Thallium hydroxyoxodiperoxochromate(1-), 4228  
Thallium(I) peroxodiborate, 0171  
*See other* OXIDANTS

## PEROXOCHROMIUM COMPOUNDS

1. Pope, M. T. *et al.*, *Chem. Rev.*, 1994, **94**(3), 576
2. Editor's comments

Most solid peroxochromates explode when heated or struck, some are reported to explode spontaneously at room temperature. Few have been isolated and fully characterised. Assigned structures are sometimes doubtful [1], especially when questionable primary sources have been reinterpreted by secondary and tertiary

reviews. A wide and confused selection of peroxochromate salts is to be found in the literature. It seems probable that there are, in fact, only two main series: the red tetraperoxochromate(3-) salts most of which explode only when provoked by heat or strong acid, and those of a more sensitive blue mono-anion, probably hydroxyoxodiperoxychromate(1-) which just explode. The latter series have an anhydride, CrO<sub>5</sub>, which may be isolated as relatively stable complexes with electron donors such as methanol or pyridine. Both series are made by treating chromium(VI) species with hydrogen peroxide, at differing pH, and may be inter-converted [2]. There is also a mostly neutral group, generally shock and heat sensitive, of diperoxochromium compounds with three donor ligands [1]. A great many others will be found in this work, mostly the result of mistaken identity due to poor analysis. For individual peroxochromate salts and neutral complexes:

Diammonium Aquabis(peroxotartratovanadate)(2-), 3079

*See entries* PEROXOACID SALTS, AMMINECHROMIUM PEROXOCOMPLEXES

### PEROXOMOLYBDATES AND TUNGSTATES

Pope, M. T. *et al.*, *Chem. Rev.*, 1994, **94**(3), 576

Most tetraperoxomolybdates(2-) and tetraperoxtungstates(2-) explode when heated or struck. For individual salts:

Diammonium Aquabis(peroxotartratovanadate)(2-)

*See entry* PEROXOACID SALTS

### PEROXYACIDS

### RCO.OOH

1. Castrantas, 1965, 12; Swern, 1970, Vol. 1, 59, 337
2. Isard, A. *et al.*, *Ger. Offen.*, 1 643 158, 1968
3. Isard, A. *et al.*, *Chemical Tech.*, 1974, **4**, 380
4. Swern, D., *Chem. Rev.*, 1945, **45**, 3-16
5. Augustine, 1969, 221, 217
6. Payne, G. B., *J. Org. Chem.*, 1962, **27**, 628
7. Augustine, 1971, 164

The peroxyacids were until relatively recently the most powerful oxidants of all organic peroxides, and it is often unnecessary to isolate them from the mixture of carboxylic acid and hydrogen peroxide used to generate them. The pure lower aliphatic members are explosive (performic, particularly) at high, but not low concentrations, being sensitive to heat but not usually to shock. Dipicolinic acid or phosphates have been used to stabilise these solutions. The detonable limits of peroxyacid solutions can be plotted by extrapolation from known data. Aromatic peroxyacids are generally more stable, particularly if ring substituents are present [1].

The patented preparation of peroxyacids [2] by interaction of carboxylic acids with hydrogen peroxide in presence of metaboric acid needs appropriate safeguards to prevent accidental separation of the conc. peroxyacids [3]. Much descriptive data on stabilities of a wide selection of peroxyacids has been summarised [4]. A general method of preparation of peroxyacids involving addition of e.g. the anhydrides of acetic, maleic, phthalic or trifluoroacetic acids to a suspension of 90%

hydrogen peroxide in dichloromethane with a drop of sulfuric acid, which although it contravenes the rule of adding concentrated hydrogen peroxide to the substrate (rather than the reverse), is nevertheless preferred because it minimises handling of concentrated peroxide, and avoids the possibility of its contact with stopcock grease [5]. However, the mixture of 90% hydrogen peroxide and dichloromethane is reported to be shock-sensitive [6]. In metal-ion catalysed oxidations by peroxyacids, it is necessary to avoid metal catalysed decomposition of the peroxy acid. Traces of transition metal ions (cobalt, iron, manganese, nickel or vanadium) can lead to explosively violent decomposition of lower aliphatic peroxyacids (peroxyformic, -acetic, -pivalic, -trifluoroacetic acids), even at concentrations of 25% in inert solvents. Maintenance of high-dilution conditions will prevent such runaway reactions [7]. Individually indexed peroxyacids are:

Benzeneperoxyseleninic acid, 2337

Benzeneperoxysulfonic acid, 2341

3-Chloroperoxybenzoic acid, 2676

Diperoxyazelaic acid, 3189

Diperoxyterephthalic acid, 2925

Monoperoxysuccinic acid, 1542

Peroxyacetic acid, 0837

Peroxybenzoic acid, 2733

3-Peroxycamphoric acid, 3348

Peroxycrotonic acid, 1535

Peroxyformic acid, 0420

Peroxyfuroic acid, 1837

Peroxyhexanoic acid, 2514

Peroxypropionic acid, 1236

Peroxytrifluoroacetic acid, 0666

Trichloroperoxyacetic acid, 0659

See *1,1-DI(BENZOYLPEROXY)ARYLIODINES*

POLYMERIC PEROXYACIDS

ORGANIC PEROXIDES

## PEROXYCARBONATE ESTERS

—OCO.OOR, —OOCO.OOR

1. Strain, F. *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 1254
2. Kirk-Othmer, 1967, Vol. 14, 803

Of the 3 possible types of peroxycarbonate esters—dialkyl monoperoxycarbonates, dialkyl diperoxycarbonates and dialkyl peroxydicarbonates—, the latter are by far the least stable group. Several of the 16 alkyl and substituted-alkyl esters prepared decomposed violently or explosively at temperatures only slightly above the temperature of preparation (0–10°C), owing to self-accelerating exothermic decomposition. Several were also explosive on exposure to heat, friction or shock [1]. Amines and certain metals cause accelerated decomposition of dialkyl peroxydicarbonates by a true catalytic mechanism [2]. Individually indexed compounds are:

*O*-*O*-*tert*-Butyl isopropyl monoperoxy carbonate, 3051  
 Bis(2-methoxyethyl) peroxydicarbonate, 3037  
 Diallyl peroxydicarbonate, 2989  
 Di-*tert*-butyl diperoxy carbonate, 3194  
 Didodecyl peroxydicarbonate, 3865  
 Diethyl peroxydicarbonate, 2446  
 Diisopropyl peroxydicarbonate, 3034  
 Dimethyl peroxydicarbonate, 1544  
 Dipropyl peroxydicarbonate, 3035  
*See other* PEROXIDES

**PEROXY COMPOUNDS**

**C-OO-**

Castrantas, 1965  
 Detonation theory is used to clarify the explosive characteristics of peroxy compounds. Some typical accidents are described. Hazards involved in the use of a large number of peroxy compounds (including all those then commercially available) are tabulated, with 134 references.

**PEROXYESTERS**

**-CO.OOR**

Castrantas, 1965, 13; Swern, 1970, Vol. 1, 79  
 Although as a group the peroxyesters are noted for instability, there is a fairly wide variation in stability between particular sub-groups and compounds.  
*See tert*-BUTYL PEROXOPHOSPHATE DERIVATIVES  
*1,1*-DI(BENZOYLPEROXY)ARYLIODINES  
 PEROXYCARBONATE ESTERS  
 and the individually indexed compounds:  
 1,1-Bis(benzoylperoxy)cyclohexane, 3804  
 1,1-Bis(4-nitrobenzoylperoxy)cyclohexane, 3800  
 Bis(trimethylsilyl) peroxomonosulfate, 2602  
*tert*-Butyl 1-adamantaneperoxy carboxylate, 3692  
*tert*-Butyl chloroperoxyformate, 1926  
*tert*-Butyl diperoxyoxalate, 3356  
*O*-*O*-*tert*-Butyl hydrogen monoperoxymaleate, 3015  
*tert*-Butyl 4-nitroperoxybenzoate, 3400  
*tert*-Butyl peroxyacetate, 2509  
 † *tert*-Butyl peroxybenzoate, 3401  
 \* Butyryl peroxonitrate, 1574  
*tert*-Butyl peroxy nitrate, 1663  
 Di-*tert*-butyl diperoxy carbonate, 3194  
 Di-*tert*-butyl diperoxyphthalate, 3715  
 † 1,1-Dichloroethyl peroxyacetate, 1491  
 Fluorocarbonylperoxonitrate, 0338  
 1-Hydroxyethyl peroxyacetate, 1626  
 † Isobutyl peroxyacetate, 2512

- \* Pentafluorosulfur peroxyacetate, 0755
- \* Peroxyacetyl nitrate, 0766
- \* Peroxyacetyl perchlorate, 0737
- \* Peroxypropionyl nitrate, 1187
- \* Poly(peroxyisobutyrolactone), 1536
- 1,1,6,6-Tetrakis(acetylperoxy)cyclododecane, 3810
- 7,7,10,10-Tetramethyl-1,2,5,6-tetroxocane-3,4-dione, 3349
- Trichloromethyl peroxyacetate, 1097
- Trifluoromethyl 3-fluorocarbonylhexafluoroperoxybutyrate, 2061
- Trifluoromethyl peroxonitrate, 0346
- Trifluoromethyl peroxyacetate, 1103

## PETROLEUM COKE

1. Hulisz, S., *Chem. Abs.*, 1977, **86**, 19269
2. Statkov, O. P. *et al.*, *Chem. Abs.*, 1989, **110**, 62453

The flammability and explosivity of high-sulfur petroleum coke dust (particle size <75  $\mu\text{m}$ ) were examined. Air-dried powder was non-explosive but fire-prone above 400°C. A 5 mm layer became incandescent at 420–470° and a dust cloud ignited at 520–660°C [1]. The fire and explosion hazards of petroleum coke or anthracite, when used in the manufacture of furnace electrodes, may be reduced by heat treatment [2].

See CARBON, *also* CARBONACEOUS DUSTS

## $\alpha$ -PHENYLAZO HYDROPEROXIDES



1. Swern, 1971, Vol. 2, 19
2. Busch, M. *et al.*, *Ber.*, 1914, **47**, 3277
3. Baumstark, A. L. *et al.*, *J. Org. Chem.*, 1983, **48620**, **69**
4. Tezuka, T. *et al.*, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2509
5. Tezuka, T. *et al.*, *Chem. Lett.*, 1986, 1671–1674

Alkyl- and aryl-hydrazones of aldehydes and ketones readily peroxidise in solution and rearrange to azo hydroperoxides [1], some of which are explosively unstable [2]. Dry samples of the *p*-bromo- and *p*-fluoro-hydroperoxybenzylazobenzenes, prepared by oxygenation of benzene solutions of the phenylhydrazones, exploded while on filter paper in the dark, initiated by vibration of the table or tapping the paper. Samples were later stored moist with benzene at –60°C to prevent explosion [3]. A series of  $\alpha$ -phenylazo hydroperoxides derived from the phenyl- or *p*-bromophenyl-hydrazones of acetone, acetophenone or cyclohexanone, and useful for epoxidation of alkenes, are all explosive [4]. The stability of several substituted phenylazo hydroperoxides was found to be strongly controlled by novel substituent effects [5].

Individually indexed compounds are:

- $\alpha$ -(4-Bromophenylazo)benzyl hydroperoxide, 3606
- $\alpha$ -(4-Bromophenylazo)phenylethyl  $\alpha$ -hydroperoxide, 3648



- 2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3156
- 1,2-Dihydroperoxy-1,2-bis(benzeneazo)cyclohexane, 3762
- $\alpha$ -Phenylazobenzyl hydroperoxide, 3609
- $\alpha$ -Phenylazo-4-bromobenzyl hydroperoxide, 3607
- 1-Phenylazocyclohexyl hydroperoxide, 3539
- $\alpha$ -Phenylazo-4-fluorobenzyl hydroperoxide, 3608
- \* 3,3,5-Triphenyl-4,4-dimethyl-5-hydroperoxy-4,5-dihydro(3H)pyrazole, 3841

## PHOSPHINES

## RPH<sub>2</sub>, R<sub>2</sub>PH

### Halogens

Van Wazer, 1958, Vol. 1, 196

Organic derivatives of phosphine react very vigorously with halogens

Individually indexed (unsubstituted) phosphines are:

- \* Cobalt tris(dihydrogenphosphide), 4203
- \* *N,N'*-Di-*tert*-butyl-*N,N'*-bis(trimethylsilyl)diaminophosphene, 3675
- † Diphosphane, 4538
- \* Potassium dihydrogenphosphide, 4460
- \* Sodium dihydrogen phosphide, 4474
- \* Tetrakis(trimethylsilyl)diaminodiphosphene, 3588
- \* Trimethylgermylphosphine, 1332
- \* Tris(iodomercurio)phosphine, 4614
- \* Trisilylphosphine, 4583
- \* *N,N,N'*-Tris(trimethylsilyl)diaminophosphine, 3232

## PHOSPHORUS COMPOUNDS

Groups falling within this class are:

ALKYLHALOPHOSPHINES, ALKYLPHOSPHINES  
*tert*-BUTYL PEROXOPHOSPHATE ESTERS  
*N*-CHLORINATED PHOSPHORUS AMIDES  
 HALOPHOSPHINES, METAL PHOSPHINATES  
 METAL PHOSPHORUS TRISULFIDES  
 NON-METAL OXIDES, NON-METAL SULFIDES  
 PHOSPHINES, PHOSPHORUS ESTERS

## PHOSPHORUS ESTERS

## (RO)<sub>3</sub>P, (RO)<sub>3</sub>P:O, (RO)<sub>2</sub>P(S)SR' etc.

1. Anon., *Loss Prev. Bull.*, 1979, (030), 159–160
2. *See entry* SELF-ACCELERATING REACTIONS
3. Lhomme, V. *et al.*, *Ind. Eng. Chem., Prod. Res. Dev.*, 1984, **23**, 98–102

Two incidents involving thermal decomposition of an unspecified phosphorus ester insecticide which unintentionally became heated to 150–160°C are described. In one case the overheating arose from a relatively slow exotherm occurring at 90–100°C, and in the second, material at 55°C was heated instead of being cooled

[1]. A number of phosphate and thiophosphate esters are of limited thermal stability and undergo highly exothermic self-accelerating decomposition reactions which may be further catalysed by impurities. The potential hazards can be reduced by appropriate thermal control measures. An example is the substitution of hot water at 60°C for pressurised steam to melt a solid phosphate ester, which on adiabatic calorimetric examination was found to have a time to maximum decomposition rate of 6 h at 110° but 11 h at 100°C [2]. The combined use of vapour phase pyrolysis to decompose various phosphorus esters, and of GLC and mass spectrometry to analyse the pyrolysis products, allowed a thermal degradation scheme to be developed for phosphorus esters [3]. Individually indexed compounds are:

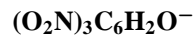
- Allyl phosphorodichloridite, 1169
- Bis(trimethylsilyl) phosphonite, 2611
- O-O-tert*-Butyl diphenyl monoperoxophosphate, 3712
- O-O-tert*-Butyl di(4-tolyl) monoperoxophosphate, 3763
- Diallyl phosphite (Di-2-propenyl phosphonite), 2456
- Dibenzyl phosphite, 3658
- Dibenzyl phosphorochloridate, 3650
- Di(*O-O-tert*-butyl) ethyl diperoxophosphate, 3374
- Dibutyl hydrogen phosphite, 3086
- Diethyl ethanephosphonite, 2572
- Diethyl 4-nitrophenyl phosphate, 3329
- Diethyl 4-nitrophenyl thionophosphate, 3328
- Diethyl phosphite, 1733
- \* Diethyl phosphorochloridate, 1681
- Dimethyl 2-chloro-4-nitrophenyl thionophosphate, 2960
- Dimethyl 3-chloro-4-nitrophenyl thionophosphate, 2961
- Dimethyl *N,N*-dichlorophosphoramidate, 0901
- \* 2,6-Dimethyl-1,3-dioxo-2,6-diphosphacyclooctane, 2548
- Dimethyl ethanephosphonite, 1732
- \* Dimethyl hydrazidophosphate, 0959
- O, O*-Dimethyl *S*-methylcarbamoylmethyl phosphorodithioate, 2009
- Dimethyl 4-nitrophenyl thionophosphate, 2979
- Dimethyl phosphoramidate, 0952
- \* Diphenyl azidophosphate, 3489
- \* Potassium *O,O*-diphenyl dithiophosphate, 3481
- \* Pyrocatecholato(2-)(quinolin-8-olato-*N,O*)-trioxygenido(2-) phosphorus, 3678
- Triallyl phosphate, 3184
- Trimethyl phosphate, 1318
- Trimethyl phosphite, 1315
- Trimethyl thiophosphate, 1316

## PHYTOSTEROLS

(several compounds and isomers)

Dry and finely divided phytosterol materials are a significant dust explosion hazard.  
*See entry* DUST EXPLOSION INCIDENTS (reference 22)

## PICRATES



1. Anon., *Angew. Chem. (Nachr.)*, 1954, **2**, 21
2. Hopper, J. D., *J. Franklin Inst.*, 1938, **225**, 219–225
3. Kast, H., *Chem. Abs.*, 1911, **5**, 2178
4. Nakamura, K. *et al.*, *Bull. Chem. Soc. Japan*, 1987, **60**, 2037–2040

While the m.p. of a picrate was being determined in a silicone oil bath approaching 250°C, an explosion occurred, scattering hot oil. It is recommended that picrates, styphnates and similar derivatives should not be heated above 210°C in a liquid-containing m.p. apparatus [1]. In an investigation of the sensitivity to impact of a range of hydrated and anhydrous metal picrates, anhydrous nickel picrate was found to be particularly sensitive [2]. The explosive characteristics of a range of 13 mono- to tri-valent metal picrates and methylpicrates was determined [3]. The hydrated picrates of the lanthanide (rare-earth) metals were prepared from the carbonates. Dysprosium and ytterbium gave octahydrates, while lanthanum, cerium, praseodymium, neodymium, samarium, europium and gadolinium gave undecahydrates, all being stable to drying in air. Drying under vacuum, by desiccation, or by warming just above 30°C could, however, give the anhydrous picrates, of which the explosion temperatures were all above 300°C [4].

Individually indexed compounds are:

- 2,2,4-Trimethyldecahydroquinolinium picrate, 3765
- Ammonium picrate, 2322
- Calcium picrate, 3430
- \* Cobalt(II) picramate, 3460
- Copper(II) picrate, 3432
- Lanthanum picrate, 3741
- Lead(II) picrate, 3436
- Manganese picrate hydroxide, 3742
- Mercury(II) picrate, 3433
- S-7-Methylnonylthiuronium picrate, 3737
- Nickel picrate, 3435
- Potassium picrate, 2085
- Sodium picrate, 2086
- Zinc picrate, 3437

*See also* ARENECYCLOPENTADIENYLIRON(II) PICRATES

## PLANT CLEANING INCIDENTS

1. Anon., *Loss Prev. Bull.*, 1980, (035), 7–11; 1981, (038), 23–27
2. Peischel, M., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 721–731, Heidelberg, ISSA, 1987

The need to provide both detailed instructions and proper supervision for plant cleaning operations, either before maintenance operations in any plant, or between different product runs in multi-use batch plant, is stressed. Several examples are given of untoward reactions and incidents which occurred when either or both of the above requirements were lacking. The importance of checking the effectiveness

of cleaning operations before restarting plant was highlighted by further examples of incidents [1]. During cleaning of a 6 m<sup>3</sup> tank by pump-recycled solvent mixture, electrostatic sparks ignited the vapour-air mixture and blew off the tank lid [2].

Some individually indexed examples will be found under:

Nitric acid, 4436

Nitric acid, : Alcohols, 4436

Nitric acid, : Polyurethane foam, 4436

Nitric acid, : Resorcinol, 4436

Phosphoryl chloride, : Water, 4149

*See related* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## PLATINUM COMPOUNDS

Cotton, F. A., *Chem. Rev.*, 1955, **55**, 577

Several platinum compounds, including trimethylplatinum derivatives, are explosively unstable. Some compounds of the other platinum group metals are also of limited stability. Individually indexed compounds are:

- Amminedecahydroxydiplatinum
- Amminepentahydroxyplatinum, 4571
- Ammonium hexachloroplatinate, 4186
- Ammonium tetranitroplatinate(II), 4578
- Diacetatoplatinum(II) nitrate, 1510
- Diamminedichloroaminotrichloroplatinum(IV), 4179
- \* Diamminedihydroxyosmium, 4572
- \* Diamminepalladium(II) nitrate, 4562
- \* Diamminepalladium(II) nitrite, 4559
- cis*-Diammineplatinum(II) nitrite, 4560
- \* Dodecamethyltetraplatinum(IV) azide, 3590
- \* Dodecamethyltetraplatinum(IV) perchlorate, 3587
- Hexamethyldiplatinum, 2606
- \* Palladium(II) acetate, 1541
- \* Palladium(III) oxide, 4848
- \* Palladium(IV) oxide, 4835
- \* Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3778
- Platinum(IV) oxide, 4836
- \* Potassium dinitrooxalatoplatinate(2-), 0988
- Potassium hexaazidoplatinate(IV), 4665
- Potassium hexachloroplatinate, 4187
- Sodium hexahydroxyplatinate(IV), 4564
- Tetraamminehydroxynitratoplatinum(IV) nitrate, 4594
- \* Tetraamminepalladium(II) nitrate, 4588
- Tetramethylplatinum, 1768
- Tetraammineplatinum(II) nitrate, 4589
- \* *N,N,N',N'*-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) bromide, 3225

- \* *N,N,N',N'*-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) iodide, 3226
- Triamminenitratoplatinum(II) nitrate, 4582
- Trimethylplatinum hydroxide, 1329

*See also* GOLD COMPOUNDS

*See other* HEAVY METAL DERIVATIVES

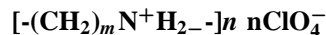
## PLATINUM GROUP METALS

Ullmann, 1992, Vol. A21, 125/6

A section on explosion hazards is included in the monograph on platinum group metals. Most of the hazards are associated with their activity as redox catalysts and are already covered in this work. Warning is given of violent alloy formation with e.g. lithium and titanium, especially by platinum and ruthenium. Alloys, or compounds, with metalloids may also be formed energetically. Absorption and sudden release of hydrogen, which will then be ignited by the catalytic metal (itself pyrophoric if finely divided) is a frequent hazard, worst for ruthenium which can retain more hydrogen than the others. Compounds and complexes incorporating both oxidant anions and oxidisable ligands (ammonia, organic moieties etc.) are likely to prove shock sensitive explosives.

*See* AMMINEMETAL OXOSALTS, ORGANOMETALLIC NITRATES

## POLY(AMINIUM) PERCHLORATES



Thomas, T. J. *et al.*, *Amer. Inst. Aero. Astron. J.*, 1976, **14**, 1334–1335

Ignition temperatures were determined by DTA for the perchlorate salts of ethylamine, isopropylamine, 4-ethylpyridine, poly(ethyleneimine), poly(propyleneimine), and poly(2- or 4-vinylpyridine). In contrast to the low ignition temperatures (175–200°C) of the polymeric salts, mixtures of the polymeric bases with ammonium perchlorate decompose only above 300°C.

*See* AMINIUM PERCHLORATES

*See other* PERCHLORATE SALTS OF NITROGENOUS BASES

## POLYAZACAGED METAL PERCHLORATES

Harrowfield, J. MacB. *et al.*, *Inorg. Synth.*, 1980, **20**, 85–86

A wide range of macrocyclic or multicyclic polynitrogen ‘cage’ ligands have been prepared in recent years and used to study the metal ion shielding and other effects of deep complexing of metal salts. In several cases it is known that the perchlorate salts of such complexes are highly unstable or explosive, and it must be assumed that this is a likely generality for the majority of such perchlorate salts. There are separate entries with specific warnings for the groups CLATHROCHELATED METAL PERCHLORATES, [14] DIENE-N<sub>4</sub> COMPLEXES, TETRAAZAMACROCYCLANEMETAL PERCHLORATES, AND TETRAMETHYL[14]TETRAENE-N<sub>8</sub> METAL PERCHLORATES but the ‘Sepulchrate’ metal complexes (of the reference above, prepared by the reaction

sequence str04 p. S1-S7) of 1,3,6,8,10,13,16,19-octazabicyclo[6.6.6]-eicosane ('Bicyclo[6.6.6]ane-1,3,6,10,13,16,19,-N<sub>8</sub>') are also likely to give unstable perchlorate salts.

CLATHROCHELATED METAL PERCHLORATES

[14] DIENE-N<sub>4</sub> COMPLEXES

TETRAAZAMACROCYCLANEMETAL PERCHLORATES

TETRAMETHYL[14]TETRAENE-N<sub>8</sub> METAL PERCHLORATES

AMMINEMETAL OXOSALTS

## POLYCONDENSATION REACTION INCIDENTS

A number of runaway reaction incidents which have involved the formation of polymeric species differ from usual polymerisation reactions of monomers in that elimination reactions of various types have been involved. Individually indexed examples are:

2-Acetyl-3-methyl-4,5-dihydrothiophen-4-one

Benzyl alcohol, : Hydrogen bromide, Iron

Benzyl bromide, : Molecular sieve

Benzyl chloride, : Catalytic impurities

Benzyl fluoride

1,2-Bis(chloromethyl)benzene

Ethylene oxide, : Contaminants

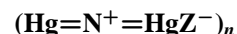
Furoyl chloride

4-Methoxy-3-nitrobenzoyl chloride

*See related* POLYMERISATION INCIDENTS

*See other* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## POLY(DIMERCURYIMMONIUM) COMPOUNDS



1. Ciusa, W., *Chem. Abs.*, 1943, **37**, 3271.9; 1944, 38, 4133.4

2. Sorbe, 1968, 97

3. Bailar, 1973, Vol. 3, 313

Several explosive salts including the acetylide, azide, borate, bromate, chlorate, chromate, iodate (and ammonium iodate double salt), nitrite, perchlorate (and ammonium perchlorate double salt), periodate, permanganate, picrate and trinitrobenzoate were prepared. The 3 latter salts and the acetylide, azide and bromate are impact-sensitive detonators [1]. It appears probable that many of the explosively unstable compounds [2], formed in various ways from interaction of mercury or its compounds with ammonia or its salts, may have the common polymeric structure now recognised for Millon's base [3]. This is a silica-like network of N<sup>+</sup> and Hg in 4- and 2-coordination, respectively, with OH<sup>-</sup> and water in the interstitial spaces. Individually indexed compounds are:

Poly(dimercuryimmonium acetylide)

Poly(dimercuryimmonium azide)

Poly(dimercuryimmonium bromate)

Poly(dimercuryimmonium hydroxide)

Poly(dimercurymmonium iodide hydrate)  
Poly(dimercurymmonium perchlorate)  
Poly(dimercurymmonium permanganate)  
*See other* MERCURY COMPOUNDS, *N*-METAL DERIVATIVES

#### **POLY(DIMETHYLSILYL)CHROMATE**



*See* Bis(trimethylsilyl) chromate

#### **POLYMERIC PEROXYACIDS**

1. Takagi, T. J., *Polymer Sci. (B), Polymer Lett.*, 1967, **5**, 1031–1035
2. Harrison, C. R. *et al.*, *J. Chem. Soc., Chem. Comm.*, 1974, 1009
3. Oshike, Y. *et al.*, *Chem. Abs.*, 1987, **107**, 59502

An ion exchange resin based on poly-acrylic or -methacrylic acids and containing aliphatic peroxyacid groups [1] readily explodes on impact, but a polystyrene resin containing aromatic peroxyacid groups on ~70% of the phenyl residues could not be caused to explode on impact [2]. Polymeric peroxides formed from sodium peroxide and the acid chlorides of dibasic acids show poor solubility in monomers and solvents and poor safety characteristics in handling. However, the polymeric peroxides formed from the acid chlorides derived from oligo-esters of adipic acid and ethylene glycol are better in these respects [3].

*See* 2,2'-Azobis(2-amidiniopropane) peroxodisulfate

*See* PEROXYACIDS

#### **POLYMERISATION INCIDENTS**

1. Anon., *CISHC Chem. Safety Summ.*, 1978, **49**(194), 32, 33
2. Schmidt, C. U. *et al.*, *Chem. Eng. Sci.*, 1988, **43**, 2133–2137
3. King, 1991, 56
4. *Chemical Reaction Hazards.*, Barton, J. & Rogers, R., Rugby, IChE, 1993
5. Rowe, S. M., 1994, personal communication.
6. Frurip, D. J., *et al.*, *Process Safety Progress*, 1995, **14**(2), 79
7. Editor's comments, 1998

In a first full scale attempt at a new polymerisation process, the thermally unstable initiator was charged and heated to reaction temperature, but there was then an unforeseen delay of an hour before monomer addition was started. The rate of polymerisation effected by the depleted initiator was lower than the addition rate of the monomer, and the concentration of the latter reached a level at which an uncontrollable polymerisation set in which eventually led to pressure-failure of the vessel seals. Precautions to prevent such occurrences are detailed. In another incident, operator error led to catalyst, condensing styrene and acrylonitrile being ducted into an unstirred weighing tank instead of a reactor. When the error was recognised, the reacting mixture was dropped into drums containing inhibitor. One of the sealed drums had insufficient inhibitor to stop the reaction, and it slowly heated and eventually burst [1]. The features and use of

a specially developed polymerisation reaction safety calorimeter to study critical polymerisation conditions are described [2]. Conditions and incidents for runaway polymerisation of a number of monomers are given [3]. Polymerisation has latterly overtaken nitration as the leading source of runaway reactions in the British chemical industry [4]. Runaway free-radical polymerisations can be suppressed by injection of a sub-percentage quantity of appropriate free radical traps, such as the anti-oxidants phenothiazine or butylcatechol. Note that this cannot be expected to inhibit condensation polymerisations, such as that of phenol and formaldehyde, which also are a common cause of accident [5]. Procedures for testing monomers for hazardous polymerisation potential have been devised [6].

Stabilisation of unsaturated monomers for storage is a complex phenomenon; acrylates, especially, are partially stabilised by atmospheric oxygen. The anti-oxidants added as stabilisers merely prevent the peroxides produced when oxygen terminates a radical chain from themselves subsequently acting as radical initiators. Acrylates stored with exclusion of air may polymerise violently even though stabilised. Since the core of a crystal will not hold any stabiliser, and probably no oxygen, melting solid monomers produces microdomains well set-up for polymerisation, which may warm the bulk to a temperature where thermal polymerisation becomes unstoppable. Melting frozen monomers, such as acrylamide or acrylic and methacrylic acids, has been a frequent cause of mishap [7].

Other polymerisation incidents are:

- † Acrylaldehyde, 1145
  - Acrylamide, 1180
  - Acrylic acid, 1148
  - Acrylic acid, Initiator, Water, 1148
- † Acrylonitrile, 1107
- † Acrylonitrile, Initiators, 1107
- † Acrylonitrile, Silver nitrate, 1107
- † Acryloyl chloride, 1093
  - Allyl 4-toluenesulfonate, 3315
  - Aluminium chloride, Alkenes, 0062
  - 3-Aminopropionitrile
- † Aziridine, Acids, 0863
  - 2,2'-Azobis(2-amidiniopropane) chloride, 3089
- † 1,3-Butadiene, 1480
- † 1,3-Butadiyne, Arsenic pentafluoride, 1385
- † 1-Buten-3-one, 1515
  - 2-Buten-1-yl benzenesulfonate, 3316
- † 2-Chloro-1,3-butadiene, 1451
- † 1-Chloro-2,3-epoxypropane, Contaminants, 1162
  - 2-Chloroethylamine, 0896
  - 2-Chloroethylammonium chloride, Alkali, 0940
- † Chloroethylene, 0730
  - Chloroperoxytrifluoromethane, Tetrafluoroethylene, 0319



Cyanamide, Water, 0404  
 2-Cyanoethanol, Acids, or Bases, 1181  
 Cyanogen fluoride, Hydrogen fluoride, 4294  
 † Cyclopentadiene, 1857  
 † Cyclopentadiene, : Potassium hydroxide, 1857  
 Diallyl phosphite, 2456  
 Diallyl sulfate, 2443  
 1,2-Di(3-buten-1-ynyl)cyclobutane, 3509  
 † 1,1-Dichloroethylene, 0695  
 1,4-Dicyano-2-butene, 2311  
 Diisocyanatomethane, Dimethylformamide, 1077  
 † Diketene, Acids, or Bases, or Sodium acetate, 1441  
 2,3-Epoxypropionaldehyde oxime, 1182  
 † Ethyl acrylate, 1913  
 † Ethylene oxide, 0829  
 † Formaldehyde, Phenol, 0416  
 6-Fulvenoselone, 2216  
 Furfuryl alcohol, 1880  
 Glycolonitrile, 0760  
 2,4-Hexadienal, 2383  
 † Hydrogen cyanide, 0380  
 4-Hydroxy-*trans*-cinnamic acid, 3136  
*N*-Hydroxymethylacrylamide, 1571  
 Methacrylic acid, 1530  
 † Methyl acrylate, 1531  
 † 2-Methylaziridine, Acids, 1257  
 † Methyl methacrylate, Propionaldehyde, 1915  
 3-Methyl-2-penten-4-yn-1-ol, 2384  
 1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene, 3760  
 † Methyl vinyl ether, Acids, 1221  
 Nitrilotris(oxiranemethane), 3181  
 2-Nitropropene, 1183  
 Octakis(trifluorophosphine)dirhodium, Acetylenic esters, 4387  
 Phenylacetylene, 2912  
 † Propene, Lithium nitrate, Sulfur dioxide, 1198  
 † 2-Propen-1-ol, Sulfuric acid, 1223  
 Propiolaldehyde, 1085  
 † Propylene oxide, Sodium hydroxide, 4445  
 3-Propynethiol, 1152  
 3-Propynol, Mercury(II) sulfate, Sulfuric acid, Water, 4479  
 Styrene, Air, Polymerising styrene, 2945  
 Styrene, Butyllithium, 2945  
 Styrene, Dibenzoyl peroxide, 2945  
 Styrene, Initiators, 2945  
 † Tetrafluoroethylene, 0628  
 2,2,3,3-Tetrafluoropropanol, Potassium hydroxide, or Sodium, 1133

Thiocyanogen, 1001  
1,3,5-Triethynylbenzene, 3443

† Vinyl acetate, 1532  
Vinylpyridine, 2759

See also VIOLENT POLYMERISATION

See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

## POLYNITROALKYL COMPOUNDS

## $C(NO_2)_n$ , $O_2NC-CNO_2$

1. Hammond, G. S. *et al.*, *Tetrahedron*, 1963, **19** (Suppl. 1), 177, 188

2. Grakauskas, V. *et al.*, *J. Org. Chem.*, 1978, **43**, 3485–3488

Trinitromethane ('nitroform'), dinitroacetonitrile, their salts and polynitroalkanes are all potentially dangerous, and must be carefully handled as explosive compounds [1]. Many congeners and derivatives of dinitromethane are explosive and require careful and appropriate handling [2]. Individually indexed compounds are:

*N,N'*-Bis(2,2,2-trinitroethyl)urea, 1875

\* Borane-bis(2,2-dinitropropylhydrazine), 0137

Dichlorodinitromethane, 0328

\* *N*-Dimethylethyl-3,3-dinitroazetidine, 2848

Dinitroacetonitrile, 0676

\* 3,3-Dinitroazetidinium trifluoromethanesulfonate, 1495

1,1-Dinitro-3-butene, 1508

2,3-Dinitro-2-butene, 1509

Dinitrodiazomethane, 0545

5(1,1-Dinitroethyl)-2-methylpyridine, 2965

Dinitromethane, 0410

2,4-Dinitropentane isomers, 1953

2,2-Dinitropropylhydrazine, 1277

3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2403

2-Fluoro-2,2-dinitroethanol, 0750

Fluorodinitromethane, 0374

Fluorodinitromethyl azide, 0341

Fluorotrinitromethane, 0340

1,1,1,3,5,5,5-Heptanitropentane, 1854

Hexanitroethane, 1014

Lithium 1,1,2,2-tetranitroethanediide, 0994

Potassium dinitroacetamide, 0709

Potassium dinitromethanide, 0377

Potassium 1,1-dinitropropanide, 1175

Potassium 1,1,2,2-tetranitroethanediide, 0989

Potassium trinitromethanide, 0530

Silver cyanodinitromethanide, 0567

Silver dinitroacetamide, 0689

Silver trinitromethanide, 0302

Sodium dinitroacetamide, 0712

Sodium dinitromethanide, 0384  
 Sodium 5-(dinitromethyl)tetrazolide, 0681  
 Sodium 1,1,2,2-tetranitroethanediide, 1007  
 Sodium 2,2,2-trinitroethanide, 0713  
 Tetrakis(2,2,2-trinitroethyl) orthocarbonate, 3132  
 \* 1,3,5,7-Tetranitroadamantane, 3310  
 Tetranitromethane, 0546  
 1,1,1-Triazidodinitroethane, 0683  
 Trinitroacetonitrile, 1009  
 1,1,1-Trinitroethane, 0775  
 2,2,2-Trinitroethanol, 0776  
 Trinitromethane, 0385  
 \* 1,3,5-Tris(nitromethyl)benzene, 3145  
 Tris(2,2,2-trinitroethyl) orthoformate, 2786  
*See* FLUORODINITROMETHYL COMPOUNDS, TRINITROETHYL ORTHOESTERS

## POLYNITROARYL COMPOUNDS

$\text{Ar}(\text{NO}_2)_n$

1. Urbanski, 1964, Vol. 1
2. Shipp, K. G. *et al.*, *J. Org. Chem.*, 1972, **37**, 1966
3. Shipp, K. G. *et al.*, US Pat. 3 941 853, 1976
4. Zenor, S., *Thermochim. Acta*, 1979, **31**, 269–283
5. Zhang, H. *et al.*, *Chem. Abs.*, 1988, **109**, 12825
6. Kondrikov, B. N. *et al.*, *Chem. Abs.*, 1996, **125**, 172589

Polynitro derivatives of monocyclic aromatic systems (trinitrobenzene, trinitrotoluene, tetranitro-*N*-methylaniline, trinitrophenol, etc.) have long been used as explosives [1]. It has been found that a series of polynitroderivatives of biphenyl, diphenylmethane and 1,2-diphenylethylene (stilbene) are explosives liable to detonate on grinding or impact [2]. The same may be true of other polynitro derivatives of polycyclic systems not normally used as explosives (e.g. polynitro-fluorenones, -carbazoles, etc. Penta- and hexa-nitrobenzophenones are also high-energy explosives [3]. The thermal stability of 33 polynitroaromatics was studied by DTA [4]. Two empirical equations relating the heat of decomposition to the heat of detonation have been developed and used to calculate the heats of detonation for 47 polynitroaryl compounds [5].

The presence of 2 or more nitro groups (each with 2 oxygen atoms) on an aromatic nucleus often increases the reactivity of other substituents and the tendency towards explosive instability as oxygen balance is approached.

The effect of sulphuric acid, a likely impurity from the usual preparation, in increasing sensitivity to detonation and decomposition has been studied [6].

### Bases, or Salts

Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389–390

In view of previous violent or explosive reactions, heating of di- and tri-nitroaryl compounds with alkalies, ammonia or *O*-ethylsulfuric acid salts in autoclaves should be avoided.

See Diethyl sulfate: 3,8-Dinitro-6-phenylphenanthridine

See also NITROAROMATIC-ALKALI HAZARDS

#### Potassium

Batz, M. L. *et al.*, *J. Org. Chem.*, 1997, **62**, 2045

Potassium salts of the radical anions  $\cdot N^+ (O^-)_2 Ar$  were prepared by treating nitroaromatics (nitrobenzene, o-, m-, & p-dinitrotoluene, 2,4,6-trinitrotoluene and trinitrobenzene with potassium in liquid ammonia and allowing the ammonia to evaporate. All were exceedingly sensitive, exploding on mild agitation of the flask onto which they had been deposited. They decomposed non-explosively in solution to give potassium nitrite and polymers (explosive in the case of TNT) Hydrogen cyanide was among the explosion products of those bearing ortho methyl groups. Presumably other alkali metals would form similar compounds.

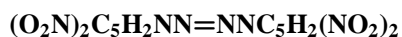
Individually indexed compounds are:

- 2-Acetylamino-3,5-dinitrothiophene, 2280
- 2-Amino-4,6-dinitrophenol, 2278
- 3-Amino-2,5-dinitrotoluene, 2783
- Ammonium 3-methyl-2,4,6-trinitrophenoxide, 2803
- Ammonium picrate, 2322
- \* Ammonium 2,4,5-trinitroimidazolide, 1144
- 2-Azido-3,5-dinitrofuran, 1384
- 2,2'-Azo-3,5-dinitropyridine, 3238
- 2-Benzylideneamino-4,6-dinitrophenol, 3600
- Bis(2,4-dinitrophenyl) disulfide, 3449
- Bis(2-nitrophenyl) disulfide, 3465
- 1,2-Bis(2-nitrophenyl)ethane, 3646
- 6-Bromo-2,4-dinitrobenzenediazonium hydrogen sulfate, 2097
- 5-*tert*-Butyl-2,4,6-trinitro-1,3-xylene, 3532
- Calcium picrate, 3430
- 2-Chloro-4,6-dinitroaniline, 2153
- 4-Chloro-2,6-dinitroaniline, 2154
- 1-Chloro-2,4-dinitrobenzene, 2098
- 6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2102
- 2-Chloro-1,3-dinitro-5-trifluoromethylbenzene, 2637
- \* Cobalt(II) picramate, 3460
- Copper(II) 3,5-dinitroanthranilate, 3627
- Copper(II) picrate, 3432
- 1,5-Dichloro-2,4-dinitrobenzene, 2077
- 1,5-Difluoro-2,4-dinitrobenzene, 2080
- 1,8-Dihydroxy-2,4,5,7-tetranitroanthraquinone, 3621
- miso*-Dimethoxydinitroanthraquinone, 3701
- 2,4-Dinitroaniline, 2277
- 1,2-Dinitrobenzene, 2194
- 1,3-Dinitrobenzene, 2195
- 1,4-Dinitrobenzene, 2196

- 1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3702  
 2,4-Dinitrobenzenediazonium hydrogen sulfate, 2206  
 4,6-Dinitro-1,3-benzenediol, 2198
- \* 2,4-Dinitrobenzenesulfonyl chloride, 2099
  - 2,4-Dinitrobenzenesulfonyl chloride, 2100
  - 4,6-Dinitrobenzofurazan *N*-oxide, 2089
  - 2,6-Dinitrobenzyl bromide, 2672
  - 4,6-Dinitro-2-*sec*-butylphenol, 3306
  - \* 5,6-Dinitro-2-dimethylaminopyrimidinone, 2358
  - 3,5-Dinitro-4-hydroxybenzenediazonium 2-oxide, 2090
  - 3,5-Dinitro-2-methylbenzenediazonium-4-oxide, 2666
  - 3,5-Dinitro-6-methylbenzenediazonium-2-oxide, 2667
  - 2,5-Dinitro-3-methylbenzoic acid, 2919
  - 1,5-Dinitronaphthalene, 3242
  - 2,6-Dinitro-4-perchlorylphenol, 2101
  - 2,4-Dinitrophenol, 2197
  - 2,4-Dinitrophenylhydrazinium perchlorate, 2351
  - O*-(2,4-Dinitrophenyl)hydroxylamine, 2279
  - 3,8-Dinitro-6-phenylphenanthridine, 3780
  - 4,6- or 5,6- or 5,7-Dinitro-1-picrylbenzotriazoles, 3439
  - 3,5-Dinitro-2-toluamide, 2941
  - 2,4-Dinitrotoluene, 2726
  - 2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone, 3130
  - \* 1-Fluoro-2,4-dinitrobenzene, 2108
  - 2-Formylamino-3,5-dinitrothiophene, 1823
  - Hexanitrobenzene, 2632
  - 4-Hydroxy-3,5-dinitrobenzenearsonic acid, 2220
  - 2-Hydroxy-3,5-dinitropyridine, 1822
  - 2-Iodo-3,5-dinitrobiphenyl, 3450
  - Lead 2-amino-4,6-dinitrophenoxide, 3469
  - Lead(II) picrate, 3436
  - Lead 2,4,6-trinitroresorcinoxide, 2071
  - Manganese picrate hydroxide, 3742
  - Mercury(II) picrate, 3433
  - \* 2-(1-Methylheptyl)-4,6-dinitrophenyl crotonate, 3764
  - 3-Methyl-2,4,6-trinitrophenol, 2703
  - Nickel 2,4-dinitrophenoxide hydroxide, 3745
  - Nickel picrate, 3435
  - 1-Nitro-3-(2,4-dinitrophenyl)urea, 2705
  - 5-Nitro-2-picryltetrazole, 2638
  - 4-Nitro-1-picryl-1,2,3-triazole, 2886
  - Pentanitroaniline, 2093
  - Picric acid (2,4,6-Trinitrophenol), 2118
  - Picryl azide, 2092
  - 1-Picryl-1,2,3-triazole, 2893
  - Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide, 2256

Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2114  
 Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienonide, 2722  
 Potassium 6-*aci*-nitro-2,4-dinitro-2,4-cyclohexadieniminide, 2113  
 Silver 2-azido-4,6-dinitrophenoxide, 2075  
 Silver 3,5-dinitroanthranilate, 2642  
 Silver hexanitrodiphenylamide, 3429  
 Sodium 4,4-dimethoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide, 2951  
 Sodium 2,4-dinitrophenoxide, 2115  
 Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2111  
 Sodium 6-*aci*-nitro-4-nitro-2,4-cyclohexadieniminide, 2200  
 2,3,4,6-Tetranitroaniline, 2122  
*N*,2,3,5-Tetranitroaniline, 2121  
*N*,2,4,6-Tetranitroaniline, 2123  
 1,3,6,8-Tetranitrocarbazole, 3442  
*N*,2,4,6-Tetranitro-*N*-methylaniline, 2706  
 1,3,6,8-Tetranitronaphthalene, 3237  
 2,3,4,6-Tetranitrophenol, 2091  
 2,4,6-Tri(2-acetylhydrazino)-1,3,5-trinitrobenzene, 3535  
 1,3,5-Triaminotrinitrobenzene, 2324  
 1,3,5-Trifluorotrinitrobenzene, 2057  
 2,4,6-Trinitrobenzoic acid, 2640  
 Trinitrochloroglucinol, 2120  
 Trinitroresorcinol, 2119  
 2,4,5-Trinitrotoluene, 2702  
 2,4,6-Trinitrotoluene, 2701  
 \* 1,3,5-Tris(nitromethyl)benzene, 3145  
 Zinc picrate, 3437  
*See also* NITROARYL COMPOUNDS

### POLYNITROAZOPYRIDINES



Coburn, M. D., *J. Heterocyclic Chem.*, 1974, **11**, 1099–1100  
 Most of a series of azodinitropyridines and their hydrazine precursors were explosive, with a sensitivity comparable to that of RDX. Individual compounds are:  
 2,2'-Azo-3,5-dinitropyridine, 3238  
 2,6-Bis(2-picrylhydrazino)-3,5-dinitropyridine, 3735  
 2,6-Bis(picrylazo)-3,5-dinitropyridine, 3734  
 3,5-Dinitro-2-(picrylazo)pyridine, 3387  
 1-(3,5-Dinitro-2-pyridyl)-2-picrylhydrazine, 3389  
*See other* HIGH-NITROGEN COMPOUNDS, POLYNITROARYL COMPOUNDS

### POLYPEROXIDES

This group covers polymeric peroxides of indeterminate structure rather than polyfunctional macromolecules of known structure. These usually arise from autoxidation of susceptible monomers and are of very limited stability or

explosive. Polymeric peroxide species described as hazardous include those derived from butadiene (highly explosive); isoprene, dimethylbutadiene (both strongly explosive); 1,5-*p*-menthadiene, 1,3-cyclohexadiene (both explode at 110°C); methyl methacrylate, vinyl acetate, styrene (all explode above 40°C); diethyl ether (extremely explosive even below 100°C); and 1,1-diphenylethylene, cyclopentadiene (both explode on heating).

Individually indexed entries are:

- † Chloroethylene, 0730
  - † 1,3-Cyclohexadiene, 2361
  - † Cyclopentadiene, : Oxygen, 1857
  - † 1,1-Dichloroethylene, 0695
  - † Diethyl ether, 1697
  - 2,4-Diethynyl-5-methylphenol, 3393
  - 2,4-Diethynylphenol, 3244
  - 2,3-Dimethyl-1,3-butadiene, 2407
  - 6,6-Dimethylfulvene, 2967
  - 1,1-Diphenylethylene, : Oxygen, 3642
  - Formaldehyde oxide polymer, 0419
  - † 1,5-Hexadien-3-yne, 2291
  - Hydrogen peroxide, : Poly(hydroxyacrylic acid lactone), etc., 4477
  - 1,5-*p*-Menthadiene, 3338
  - 2-Methylacryaldehyde oxime, 1568
  - † Methyl methacrylate, 1915
  - Oxygen (Gas), : Cyclooctatetraene, 4831
  - Oxygen (Gas), : Tetrafluoroethylene, 4831
  - Poly(1,3-butadiene peroxide), 1533
  - Poly(1,3-cyclohexadiene peroxide), 2386
  - Poly(dimethylketene peroxide), 1536
  - Poly(ethylidene peroxide), 0835
  - \* Poly(peroxyisobutyrolactone), 1536
  - Poly(styrene peroxide), 2957
  - Poly(vinyl acetate peroxide), 1539
  - Styrene, : Oxygen, 2945
  - † Tetrafluoroethylene, 0628
  - † Vinyl acetate, 1532
- See Hydrogen peroxide: Ketones, Nitric acid

## **POLYPROPYLENE POWDER**

Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 91

Polypropylene powder was being conveyed by suction through a duct system as an air dispersion, fines being retained in a filter trap upstream of the centrifugal fans. However, the relatively coarse filter allowed very fine powder to pass and it was eventually retained over a long period of time in a silencer on the fan outlet. The thickening deposit eventually self-heated and ignited, and the fire spread very

rapidly in the air-stream. A second fire, also apparently with polypropylene powder, occurred in a flash-dryer and cyclone system. Washing of the dryer case with water had led to build-up of aggregated powder which had degraded, melted and ignited. Nitrogen purging has been introduced as a preventive measure.

*See other* SELF-HEATING AND IGNITION INCIDENTS

### PRECIOUS METAL DERIVATIVES

Hasenpusch, W., *Chem.-Ztg.*, 1987, **111**(2), 57–60

In a review of explosions involving derivatives of gold, silver and platinum, reactions of ammonia with gold and silver compounds, and of hydrogen in presence of platinum compounds are emphasised.

*See also* FULMINATING METALS, HEAVY METAL DERIVATIVES, HYDROGENATION CATALYSTS, HYDROGENATION INCIDENTS

### PREPARATIVE HAZARDS

Preparative hazards have been noted for the following compounds:

4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3266

Acetyl chloride, 0735

Aluminium copper(I) sulfide, 0084

3-Amino-2,5-dinitrotoluene, 2783

2-Amino-5-nitrothiazole, 1117

6-Aminopenicillanic acid *S*-oxide, 3010

4-Amino-4*H*-1,2,4-triazole, 0812

Azidosilane, 4501

Aziridine, 0863

1,1'-Azo-[2-methyl-1,2-dicarbadeborane(14)], 2624

2-Azoxyanisole, 3653

1,4-Benzenediol–oxygen complex, 2334

Benzeneperoxysulfonic acid, 2341

Benzeneseleninic acid, 2335

Benzeneseleninic anhydride, 3495

Benzenethiol, 2344

2,2'-Bi-1,3-dithiole, 2215

2,2'-Bipyridyl 1-oxide, 3258

Bis(cyclopentadienyl)lead, 3294

Bis-*N*(imidosulfur difluoridato)mercury, 4342

Bismuth trisulfide, 0234

1,2-Bis(2-nitrophenyl)ethane, 3646

1,3-Bis(trifluoromethyl)-5-nitrobenzene, 2885

Bis(trifluoromethyl)sulfur difluoride, 0648

4-Bromocyclopentene, 1884

Bromoethane, 0846

Bromogermane, 0246

4-Bromomethylbenzoic acid, 2926



2-Bromo-4-methylpyridine *N*-oxide, 2297  
3-Bromopyridine, 1827  
3-Bromo-1,1,1-trichloropropane, 1126  
Butylbenzene, 3323  
*tert*-Butyl hydroperoxide, 4477  
*N-tert*-Butylphthalisoimidium tetrafluoroborate, 3521  
Butylsodium, 1667  
Cadmium selenide, 3959  
4-Chloro-2,6-dinitroaniline, 2154  
3-Chloro-1,3-diphenylcyclopropene, 3679  
2-Chloro-5-methylaniline, 2793  
2-Chloro-5-nitrobenzenesulfonic acid, 2144  
Chloronitromethane, 0396  
3-(4-Chlorophenyl)butanoic acid, 3297  
2-(4-Chlorophenyl)-1,1-dimethylethyl hydroperoxide, 3018  
4-Chlorophenyl isocyanate, 2648  
Chlorotetrafluorophosphorane, 3987  
Chlorotrimethylsilane, 1304  
Chromyl acetate, 1494  
Chromyl azide, 4239  
Cyanocyclopropane, 1463  
Cyanogen chloride, 0323  
4-Cyano-3-nitrotoluene, 2917  
*cis*-Cyclododecene, 3351  
1,2-Cyclohexanedione, 2385  
Decafluoro-2,5-diazahexane 2,5-dioxy, 1372  
2-Deuterobicyclo[2.2.1]hept-2-ene, 2811  
Diacetatoplatinum(II) nitrate, 1510  
Diallyl ether, 2431  
2,3-Diazabicyclo[2.2.2]octa-2,5-diene *N*-oxide, 2374  
2,4-Diazido-6-dimethylamino-1,3,5-triazine, 1876  
1,2-Diazido-1-phenylethane, 2954  
Diazomethyldimethylarsine, 1240  
1,5-Dibenzoylnaphthalene, 3845  
Diborane(6), 0166  
Dibromogermane, 0267  
Di-*tert*-butyl peroxide, 3074  
2,4-Di-*tert*-butyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine, 3377  
3,4-Dichloroaniline, 2241  
*cis*-Dichlorobis(2,2'-bipyridyl)cobalt(III) chloride, 3799  
Dichloromaleimide, 1378  
*N,N*-Dichloropentafluorosulfanylamine, 4060  
4-(2,4-Dichlorophenoxy)butyric acid, 3272  
*trans*-Dichlorotetrapyridinecobalt(III) chloride, 3802  
Diethylaminosulfinyl chloride, 1679

Diethyl 4-nitrophenyl phosphate, 3329  
Diethyl trifluoroacetosuccinate, 3320  
1,4-Diethynylbenzene, 3241  
1,5-Difluoro-2,4-dinitrobenzene, 2080  
Difluorotrifluoromethylphosphine oxide, 0360  
4-Dimethylaminoacetophenone, 3321  
2-(Dimethylaminomethyl)ferrocene, 3612  
3,5-Dimethylbenzoic acid, 3152  
3,5-Dimethyl-4-[*I,I*-bis(trifluoroacetoxy)iodo]isoxazole, 3115  
3,3-Dimethyl-1-butyne, 2408  
Dimethyl *N,N*-dichlorophosphoramidate, 0901  
Di- $\mu$ -methylenebis(methylpentamethylcyclopentadienyl)dirhodium, 3855  
3,5-Dimethyl-3-hexyl hydroperoxide, 3075  
3,7-Dimethyl-2,6-octadienal, 3346  
Dimethylphenylphosphine oxide, 3002  
2,2-Dimethylpropane, 1999  
2,5-Dimethylpyrazine 1,4-dioxide, 2378  
2,4-Dinitroaniline, 2277  
3,5-Dinitrobenzenediazonium 2-oxide, 2087  
4,6-Dinitro-1,3-benzenediol, 2198  
2,4-Dinitrobenzenesulfonyl chloride, 2100  
Dinitrogen oxide, 4744  
7,8-Dioxabicyclo[4.2.2]-2,4,7-decatriene, 2955  
Diperoxyazelaic acid, 3189  
Diphenylamine, 3504  
Dipyridinium dichromate, 3304  
Disodium 4-nitrophenylphosphate, 2185  
Dodecamethyltetraplatinum(IV) perchlorate, 3587  
Ethanedial, 0723  
Ethyl cyanoacetate, 1889  
Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2359  
Ethyl iminioformate chloride, 1273  
Ethylphenylthallium(III) acetate perchlorate, 3302  
Fluorobis(trifluoromethyl)phosphine oxide, 0645  
Fluorodiiodomethane, 0373  
5-Fluoro-2-nitrophenol, 2167  
Fluorotrinitromethane, 0340  
Furoyl chloride, 1818  
Hexacarbonyltungsten, 2636  
1,4,7,10,13,16-Hexaoxacyclooctadecane, 3561  
Hydrogen bromide, 0247  
Hydrogen chloride, 3993  
*trans*-4-Hydroperoxy-5-hydroxy-4-methylimidazolin-2-one, 1598  
Hydroxyacetone, 1231  
2-Hydroxy-2-methylglutaric acid, 2445  
Indium bromide, 0289

Iodoethane, 0858  
Iron(II) perchlorate, 4062  
Isophthaloyl chloride, 2888  
Magnesium, 4690  
Mercury peroxide, 4606  
4-Methoxybenzaldehyde, 2956  
2-Methoxy-5-nitroaniline, 2802  
4-Methoxy-3-nitrobenzoyl chloride, 2916  
Methylborylene, 0425  
Methyl iminioformate chloride, 0897  
2-Methyl-5-nitrobenzenesulfonic acid, 2772  
3-Methyl-4-nitropyridine *N*-oxide, 2317  
Methylnitrothiophene, 1850  
*N*-(3-Methylphenyl)-2-nitrobenzimidyl chloride, 3641  
Methyltrifluoromethyltrichlorophosphorane, 0742  
Molybdenum hexamethoxide, 2596  
2-Nitroaniline, 2313  
*tert*-Nitrobutane, 1660  
Nitromesitylene, 3158  
3-Nitrophthalic acid, 2906  
3-Nitropropiophenone, 3141  
*N*-Nitroso-6-hexanelactam, 2424  
Nitrosylsulfuric acid, 4438  
Nitroterephthalic acid, 2907  
1,4-Octadecanolactone, 3773  
1,4,8,11,15,18,22,25-Octamethyl-29*H*,31*H*-tetrabenzob[*b.g.l.q*]porphinato(2-)  
cobalt(II), 3910  
Osmium(IV) oxide, 4833  
4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2357  
Pentaamminedinitrogenruthenium(II) salts, 4596  
Pentafluoroorthoselenic acid, 4354  
Pentanesulfonic acid, 2020  
Perfluoro-*tert*-butanol, 1380  
Peroxomonophosphoric acid, 4506  
2-Phenyl-1,1-dimethylethyl hydroperoxide, 3332  
*N*-Phenylhydroxylamine, 2356  
Phenyllithium, 2259  
Phenylsodium, 2287  
Phosphoryl dichloride isocyanate, 0327  
Phthalic anhydride, 2899  
2-Piperidone, 1934  
Platinum diarsenide, 0107  
Poly(butadiyne), 1386  
Poly(carbon monofluoride), 0337  
Poly(ethylene terephthalate), 3262  
Poly(selenium nitride), 4730

Potassium dithioformate, 0378  
Potassium hexafluoromanganate(IV), 4363  
Propionyl chloride, 2542  
2,5-Pyridinedicarboxylic acid, 2696  
Rhenium chloride trioxide, 4045  
Rhenium hexamethoxide, 2603  
Rhenium nitride tetrafluoride, 4344  
Selenium dioxide, 4838  
Silver tetrafluoroborate, 0005  
Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide, 3924  
Sodium dihydrobis(2-methoxyethoxy)aluminate, 2575  
Sodium hyponitrite, 4736  
Sulfur dioxide, 4837  
Sulfuryl azide chloride, 4031  
Tantalum(IV) sulfide, 4903  
Terephthalic acid, 2924  
Tetraethylammonium periodate, 3090  
Tetrafluorooxathietane-2,2-dioxide, 0635  
Tetrafluorooxirane, 0632  
Tetraiododiphosphane, 4637  
5,10,15,20-Tetrakis(2-nitrophenyl)porphine, 3907  
Tetramethoxyethylene, 2516  
Tetramethylammonium ozonate, 1753  
Tetramethyldiphosphane disulfide, 1766  
Tetramethylsuccinodinitrile, 3007  
7,7,10,10-Tetramethyl-1,2,5,6-tetroxecane-3,4-dione, 3349  
Tetraphosphorus hexaoxide tetrasulfide, 4869  
3-Thietanol-1,1-dioxide, 1238  
3-Thiocresol, 2809  
Titanium diiodide, 4630  
Titanium tetraiodide, 4638  
Triacetyl borate, 2390  
2,4,6-Triallyloxy-1,3,5-triazine, 3530  
2-(Tricarbonylferra)hexaborane(10), 1297  
2,4,5-Trichlorophenol, 2107  
Trifluoromethyl perchlorate, 0321  
Trifluoromethylsulfur trifluoride, 0363  
Trimethyl orthoformate, 1708  
Trimethylsulfonium chloride, 1303  
2,4,6-Trinitrobenzoic acid, 2640  
Triphenylphosphine, 3756  
1,1,1-Tris(aminomethyl)ethane, 2044  
1,1,1-Tris(bromomethyl)methane, 1550  
Tris(cyclopentadienyl)cerium, 3683  
Tris(hydroxymethyl)methylamine, 1731  
Tungsten hexamethoxide, 2604

Tungsten tetrabromide oxide, 0294  
UndecaamminetetRARuthenium dodecaoxide, 4598  
Xenon difluoride dioxide, 4322  
Xenon tetrafluoride oxide, 4346  
Zinc ethylsulfinate, 1711  
*See* 1,2-DIOLS, 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE SALTS

## PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

1. Grewer, T. *et al.*, *Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 657–664, Basle, SSCI, 1980
2. Klais, O. *et al.*, *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, C24–C34, Rugby, IChE, 1983
3. Grewer, T. *et al.*, *Hazards from Pressure*, IChE Symp. Ser. No. 102, 1–9, Oxford, Pergamon, 1987
4. Watanabe, N. *et al.*, *Chem. Abs.*, 1988, **108**, 207227

Equipment was developed to measure the maximum pressure and rate of pressure increase during exothermic decomposition, and the results serve as useful criteria to assess hazards. For each of the 6 compounds examined at a vessel loading of 0.1–0.2 g/cm<sup>3</sup>, the starting temperature, max. pressure (bar) and max. rate of rise (bar/s), respectively, are given below.

Azobenzene, 340/13/6.5; azoformamide, 260/194/925; diketene, 125/140/–; 4-nitroisopropylbenzene, 250/>182/830; 4-nitrophenol, 280/>199/1,030; 4-nitrosophenol, 120/23/5. It is concluded that the first and last compounds are of relatively low hazard [1]. Improved equipment has provided more accurate and detailed results for a further 7 compounds and has shown the effect of variations in the initial stage of decomposition on the final pressure attained, and of the increase in pressure causing a reduction in the rate of pressure rise. At 0.2 g/cm<sup>3</sup> loadings, comparable results are:-

A diazonium salt, 112/200/66; azoisobutyronitrile, 80/130/8,800; 1,3-diphenyltriazene, 140/95/420; 2-nitrobenzaldehyde, 200/945/8,700; 3-nitrobenzaldehyde, 190/830/4,100, 4-nitrobenzaldehyde, 200/960/4,700. Solids which deflagrate give substantially higher rates of pressure rise because the rate of pressure rise is not depressed by increase in pressure, e.g. ammonium dichromate, 227/510/68,000 [2].

Deflagration (progressive exothermic decomposition/combustion) may be rapid, as in propellant explosive compositions, or slow in non-explosive compounds. The high probability of deflagration in this latter type of industrially important materials, as indicated by the number of incidents involving the relatively few deflagrable non-explosives, has led to an investigation of deflagration and the pressure effects which accompany it. Deflagration rates (cm/min) measured by igniting the top of the material in a 5 cm diameter beaker and timing the downward progress were:- ammonium dichromate, 2.2; 1,3-diphenyltriazene, 2.0; hydroxylaminium sulfate, 5.6; 1-nitroso-2-naphthol, 0.74; 1-(2,4-dinitrophenylazo)-2-naphthol, 1.8; 4-nitrosophenol, 8; sodium 3-nitrobenzenesulfonate, 4.5 cm/min.

Most mononitroaryl compounds do not deflagrate, but mixed with an excess of sodium or potassium hydroxide they deflagrate readily. Some rates (cm/min) for such mixtures are:- 4-chloronitrobenzene + KOH (1:1.5 mol), 1.3; 4-nitrobenzoic acid + KOH (1:2 mol), 5.1; 4-nitrophenol + KOH (1:1.5 mol), 30; 2-nitrobenzaldehyde + active carbon (1.5:1 mol), 1.25 cm/min.

Pressure effects measured during deflagration with top-surface ignition in an unheated 200 ml autoclave, or during homogeneous decomposition (no ignition coil, autoclave heated slowly in an oven) led to some problems in interpreting the pressure-time curves in the latter case. Deflagration of 1,3-diphenyltriazene and of hydroxylaminium sulfate showed relatively slow rise of pressure (to 111, 250 bar in 600, 380 ms, respectively), while the results from homogeneous decomposition showed wider variations in the rate of pressure rise. Thus, 1,3-diphenyltriazene and 2-nitrobenzaldehyde showed slow rates of rise (to 132, 940 bar, in 600, 280 ms), while azoisobutyronitrile and ammonium dichromate showed fast rates (to 130, 480 bar during 30, 24 ms, respectively). Log-log plots of deflagration rates of pressure rise vs pressure show that for 1,3-diphenyltriazene, hydroxylaminium sulfate and 1-nitroso-2-naphthol, the rate is approximately proportional to pressure, while for ammonium dichromate it appears proportional to the square of the pressure [3].

In a study of deflagration of inorganic peroxide-combustible mixtures at compositions giving zero oxygen balance (and maximum rates of pressure rise), inorganic peroxides with cellulose give higher rates of rise than peroxyacids or hydrogen peroxide adducts ('sodium percarbonate'), and some of these latter mixtures did not ignite. Mixtures of potassium chlorate with cellulose show high deflagration hazards and exhibit remarkable pressure increase effects [4].

Some incidents of this type may be found under:

- Ammonium dichromate, 4246
- Azoformamide, 0816
- Azoisobutyronitrile, 3011
- Azoisobutyronitrile, 3011
- † *tert*-Butyl peroxybenzoate, 3401
- 4-Chloronitrobenzene, 2142
- † 1,1-Difluoroethylene, 0700
- † Diketene, 1441
- 1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3702
- 1,3-Diphenyltriazene, 3506
- 1,3-Diphenyltriazene, 3506
- † Ethylene oxide, : Sucroglyceride, 0829
- Hydroxylaminium sulfate, 4575
- 3-Methyl-4-nitrophenol, 2766
- 2-Nitrobenzaldehyde, 2686
- 2-Nitrobenzaldehyde, 2686
- 4-Nitrobenzaldehyde, 2688
- 4-Nitrobenzoic acid, : Potassium hydroxide, 2695
- 4-Nitroisopropylbenzene, 3157

4-Nitrophenol, 2267  
4-Nitrophenol, : Potassium hydroxide, 2267  
1-Nitroso-2-naphthol, 3250  
4-Nitrosophenol, 2264  
Sodium 3-nitrobenzenesulfonate, 2184

See ISOXAZOLES

NITROBENZALDEHYDES  
NITROBENZYL COMPOUNDS  
PRESSURE RELIEF  
ZINC BACITRACIN

### PRESSURE RELIEF

1. Huff, J. E., *Proc. Int. Symp. Prev. Major Chem. Accid.*, Washington, 1987, 4.43–4.67, New York, AIChE, 1987
2. Burgoyne, J. H., *Hazards from Pressure*, IChE Symp. Ser. No. 102, 201–213, Oxford, Pergamon, 1987
3. Tippet, J. R. *et al.*, *ibid.*, 358–361
4. Fauske, H. K., *ibid.*, 133–141
5. Bettis, R. J. *et al.*, *ibid.*, 247–263
6. Fauske, H. K., *Plant/Oper. Progr.*, 1988, 7(7), 3

The important role played by pressure relief arrangements to mitigate the effects of runaway exothermic reactions and to prevent catastrophic vessel failure is discussed. For full effectiveness, the pressure relief system must be included in the overall process design, and must be adequately sized to permit discharge of vessel contents at a safe pressure and to a safe location. Methods of achieving these objectives are presented [1], and problems associated with subsequent treatment of the materials from accidental discharges are discussed [2]. Methods of assessing relief requirements for reactive and non-reactive systems are considered, including runaway liquid phase reactions and fire-exposed liquid-filled storage vessels [4]. Special consideration is given to emergency releases involving 2-phase flow [4,5]. The scope of the AIChE design package of the Design Institute for Emergency Relief Systems (DIERS) has been extended to deal with both reactive and non-reactive mixtures being vented [6].

See PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

### PROTEINS

1. Pitts, J. E., *Nature*, 1992, 360, 94

It is suggested that crystalline proteins are explosive, as evidenced by the easily induced shattering of the microcrystals currently available [1]. Except, possibly, where mercuric nitrate is involved, the editor suspects this of being implosive collapse of a metastable ordering of molecules.

See ORGANOMETALLIC NITRATES

## PROPELLANTS

1. Gould, R. F., *Advanced Propellant Chemistry (ACS Monograph 54)*, Washington, Amer. Chem. Soc., 1966
2. Ullmann, 1993, A22, 185

Like other high energy materials deliberately made so (explosives and pyrotechnics) propellants in their proper use do not fall within the scope of this handbook. It is a field of considerable current development [2].

The above book [1] deals, in 26 chapters in 5 sections, with theoretical and practical aspects of the use and safe handling of powerful oxidants and their complementary reactive fuels. Materials include: nitrogen pentaoxide, perfluoroammonium ion and salts, nitronium tetrafluoroborate, hydrazinium mono- and di-perchlorates, nitronium perchlorate, tricyanomethyl compounds, difluoramine and its alkyl derivatives, oxygen difluoride, chlorine trifluoride, dinitrogen tetraoxide, bromine trifluoride nitrogen fluorides, and liquid ozone–fluorine system.

*See also* ROCKET PROPELLANTS

## PYRAZOLONE DYESTUFF PREPARATION

Anon., *Loss Prev. Bull.*, 1979, (030), 160

A 300 g sample of the monoazo product of coupling a diazotised nitroaminophenol onto a pyrazolone exploded violently during vacuum drying at 110°C. Small samples filtered at pH 7.5 had been dried uneventfully, but the large batch had been at pH 8.8 (so may have contained some diazophenoxide, formed as in reaction sequence str05, p. S1-S7). It was further found that parts of the oven were hotter by 20–30°C than the indicated temperature.

*See* ARENEDIAZONIUM OXIDES

## PYROPHORIC ALLOYS

1. Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 163–164
2. Kirk-Othmer, 1982, Vol. 19, 494

Alloys of reactive metals are often more pyrophoric than the parent metals. Examples are alloys of titanium with zirconium; thorium with copper, silver or gold; uranium with tin, lead or gold; magnesium with aluminium; hafnium with iron [1]. Cerium amalgams and thorium–silver alloys are spontaneously flammable when dry [2]. Individually indexed alloys are:

Aluminium–lanthanum–nickel alloy

Cerium: Alone, or Metals, 3961

Lead–zirconium alloys, 4884

Silver–thorium alloy, 0004

Zinc amalgam, 4601

*See other* PYROPHORIC MATERIALS

## PYROPHORIC CATALYSTS

1. *Laboratory Handling of Metal Catalysts*, in *Chem. Safety*, 1949, (2), 5
2. *Catalyst Handbook*, 180–181, London, Wolfe, 1970



A proposed Code of Practice for laboratory handling of potentially pyrophoric catalysts includes: storage in tightly closed containers; extreme care in transfer operations, with provision for immediate cleaning up of spills and copious water flushing; avoidance of air-drying during filtration, and storage of residues under water; use of water-flush in case of ignition [1]. The later reference details precautions to prevent fires in catalysts discharged from industrial reactors [2].

Some examples are:

Dodecacarbonyltetracobalt, 3420

Nickel, : Magnesium silicate, 4820

See COPPER CHROMITE CATALYST HYDROGENATION CATALYSTS

### **PYROPHORIC IRON–SULFUR COMPOUNDS**

1. Schultze, R. *et al.*, *Arbeitsschutz*, 1964, 194–196
2. Dodonov, Ya. Ya. *et al.*, *Chem. Abs.*, 1964, **60**, 5058h –5059a
3. Anon., *Loss Prev. Bull.*, 1977, (012), 1–6
4. Kletz, T. A., *Loss Prev. Bull.*, 1982, (048), 19–20
5. Bitay-Fulop, M. *et al.*, *Chem. Abs.*, 1979, **91**, 94069
6. Gendel, G. L. *et al.*, *Chem. Abs.*, 1982, **96**, 183813
7. Kyazimov, A. M. *et al.*, *Chem. Abs.*, 1982, **97**, 186029
8. Hempel, D. *et al.*, *Chem. Tech. (Leipzig)*, 1983, **35**, 525–529
9. Walker, R. *et al.*, *Surf. Coating Technol.*, 1987, **31**, 163–197
10. Kostur, P. *et al.*, *Chem. Abs.*, 1988, **108** 97651

Iron(III) salts and thiols in alcoholic solution interact to produce highly pyrophoric mixtures containing iron alkylsulfides, iron oxide, hydrates, sulfides and sulfur. Effects of variation in reaction conditions and structure of thiols upon pyrophoricity were examined. Treatment of the pyrophoric mixtures with nitrogen oxide to form nitrosyl complexes effectively deactivates them [1]. Laboratory treatment of hydrated iron oxides with hydrogen sulfide simulated the production of pyrophoric iron sulfides which frequently cause fires in petroleum refining operations. Presence of gasoline during sulfide preparation gave pyrophoric materials which retained their activity longer than when gasoline was absent [2]. Several petroleum refinery fires and incidents are detailed [3]. In the investigation of a petroleum storage tank explosion in 1936, it was noticed that disturbing the sulfide scale in a tank gave several sparks, one of which, trapped in the scale caused incandescence of about 5 seconds duration. This type of occurrence may have been the original ignition source [4]. An apparatus and method for assessing the pyrophoric activity of these deposits is described [5], and their laboratory preparation in presence of amines or polyethylene glycols has been studied [6]. There have been studies of the possibility of suppression of spontaneous ignition of Fe–S deposits by corrosion inhibitors [7] or by other means [8]. The factors affecting the type of pyrophoric deposit produced from rust and petroleum-derived hydrogen sulfide are discussed [9]. Measures to inactivate such deposits call for their slow oxidation with steam–air, or dilute oxygen–inert gas mixtures [10].

Some examples are:

2-Hydroxyethylamine, : Carbon dioxide, etc., 0943

Iron disulfide, 4401

Iron(II) sulfide, 4400

Iron(III) sulfide, 4404

Phthalic anhydride, 2899

## PYROPHORIC MATERIALS

1. Kayser, E. G. *et al.*, *Spontaneously Combustible Solids*—Literature Survey, Rept. 75-159, US Naval Weapons Center, (USNTIS AD-A019919), 1975
  2. Carson, P. A., Mumford, C. J., *Loss Prev. Bull.* 1993, (109), 11; *ibid.*, (110), 9
- Existing information on solids spontaneously combustible in contact with air or water has been reviewed, with 145 references. Data relevant to the causes and prevention of spontaneous ignition are included, as well as the application of mathematical treatments to the problem, and available testing methods for assessing relevant factors in natural and manufactured products are discussed [1]. A two part review of pyrophoric materials and precautions in handling them is given [2].

Separate treatment is given for the relevant groups:

ALKYLALUMINIUM DERIVATIVES, ALKYLBORANES, ALKYLHALOBORANES ■  
ALKYLHALOPHOSPHINES, ALKYLHALOSILANES, ALKYLMETALS  
ALKYLNON-METAL HYDRIDES, ALKYLPHOSPHINES, ALKYLSILANES  
ARYLMETALS, BORANES, CARBONYLMETALS, COMPLEX ACETYLIDES  
COMPLEX HYDRIDES, HALOACETYLENE DERIVATIVES  
HEXAMETHYLNITRATODIALUMINATE SALTS, METAL HYDRIDES  
NON-METAL HYDRIDES, ORGANOMETALLICS, PYROPHORIC ALLOYS  
PYROPHORIC CATALYSTS, PYROPHORIC IRON-SULFUR COMPOUNDS  
PYROPHORIC METALS

Individually indexed compounds are:

- Bis(acrylonitrile)nickel(0), 2312
- \* 1,2-Bis(dichlorophosphino)ethane, 0797
- Bis(trimethylsilyl) phosphonite, 2611
- Bromodimethylborane, 0887
- Calcium silicide, 3943
- Cerium trisulfide, 3967
- Chromium(II) acetate, 1493
- Chromium(II) oxide, 4241
- Cobalt(III) nitride, 4214
- Cobalt(II) sulfide, 4218
- Dicobalt boride, 0128
- Dimethyl ethanephosphonite, 1732
- Europium(II) sulfide, 4293
- 2-Furaldehyde, 1836
- Indium(II) oxide, 4641
- Iron(II) chelate of bis-*N,N'*-(2-pentanone-4-ylidene)-1,3-diamino-2-hydroxypropane, 3616

- Iron(II) hydroxide, 4392
- Iron(II) maleate, 1393
- Lead pentaphosphide, 4881
- Lithium diethylamide, 1686
- Lithium–tin alloys, 4682
- Magnesium hydride, 4463
- Manganese(II) *N,N*-diethyldithiocarbamate, 3358
- Manganese(II) sulfide, 4706
- 5-Methyl-1(1-methylethyl)-1,2,3-azadiphosphole, 2455
- Molybdenum(IV) oxide, 4716
- Osmium(IV) oxide, 4833
- † Phosphorus, 4874
- Plutonium bismuthide, 0231
- Poly(cyclopentadienyltitanium dichloride), 1843
- \* Poly(difluorosilylene), 4330
- Potassium antimonide, 4673
- Potassium *tert*-butoxide, 1650
- Potassium cyclopentadienide, 1846
- Potassium diethylamide, 1685
- Potassium octacyanodicobaltate(8–), 2880
- Potassium–sodium alloy, 4646
- Silicon oxide, 4828
- \* Silver isophthalate, 2887
- Sodium diethylamide, 1688
- Sodium germanide, 4418
- Thorium dihydride, 4489
- \* Thorium oxide sulfide, 4826
- Titanium dibromide, 0284
- Titanium dihydride, 4490
- Titanium diiodide, 4630
- Titanium trichloride, 4158
- \* Tricyclopentadienyluranium tetrahydroaluminate, 3688
- Tris(2,2'-bipyridine)chromium(0), 3875
- Uranium carbide, 0562
- Uranium(III) nitride, 4732
- Uranium(IV) oxide, 4843
- Zinc, 4927
- Zirconium dibromide, 0285
- \* Zirconium oxide sulfide, 4827

*See also* METAL DUSTS (reference 3), THORIUM FURNACE RESIDUES

## PYROPHORIC METALS

1. Feitknecht, W., *Conf. on Finely Divided Solids*, Commis l'Eán. Atom., Saclay, 27–29 Sept., 1967
2. Peer, L. H. *et al.*, *Mill & Factory*, 1959, **65**(2), 79

3. Anon., *Chem. Eng. News*, 1952, **30**, 3210
4. Breidenfeld, J., *Metall.*, 1954, **8**, 94–97
5. Koelman, B. *et al.*, *Metal Progress*, 1953, **63**(2), 77–79
6. Popov, E. L. *et al.*, *Chem. Abs.*, 1975, **83**, 135768
7. Evans, J. D. *et al.*, *Powder Metall.*, 1976, **19**, 17–21
8. Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 157–172
9. Nedin, V. V.; Kostina, E. S., *Chem. Abs.*, 1977, **86**, 157758, 157759
10. Klabunde, K. J. *et al.*, *Inorg. Synth.*, 1979, **19**, 59–86

Finely divided metal powders develop pyrophoricity when a critical specific surface area is exceeded; this is ascribed to high heat of oxide formation on exposure to air. Safe handling is possible in relatively low concentrations of oxygen in an inert gas [1]. Safe handling, storage, disposal, and fire fighting techniques for hafnium, titanium, uranium and thorium, and hazards of machining the 2 latter metals are discussed [2]. Dry finely divided tantalum, thorium, titanium, zirconium metals, or titanium–nickel, zirconium–copper alloys are not normally shock-sensitive. However, if they are enclosed in glass bottles which break on impact, ignition will occur. Storage of these materials moist and in metal containers is recommended [3].

Heat of combustion, thermal conductivity, surface area and other factors influencing pyrophoricity of aluminium, cobalt, iron, magnesium and nickel powders are discussed [4]. The relationship between heat of formation of the metal oxide and particle size of metals in pyrophoric powders is discussed for several metals and alloys including copper [5]. Further work on the relationship of surface area and ignition temperature for copper, manganese and silicon [6], and for iron and titanium [7] was reported. The latter also includes a simple calorimetric test to determine ignition temperature.

In a literature review with 115 references, factors influencing the pyrophoricity of metals are identified as particle size, presence of moisture, nature of the surface of the particle, heat of formation of the oxide or nitride, mass, hydrogen content, stress, purity and presence of oxide, among others. Static charge hazards, fire and explosion incidents, handling procedures and transport considerations are also discussed. References are given to reviews of incidents involving barium, beryllium, magnesium, paper, plutonium, polypropylene, thorium, titanium, zinc-rich coatings and zirconium [8]. Equations to calculate the lower ignition limits for explosive suspensions in air of aluminium, iron, magnesium, manganese, tantalum, tin and titanium powders have been derived. Results for the latter agree well with experimental findings [9]. The reaction residues from various metal atom syntheses (involving vacuum evaporation of cobalt, copper, chromium, iron, magnesium, manganese, nickel, palladium, platinum, tungsten, vanadium or zinc, and co-deposition with a ligand) are often pyrophoric, and suitable precautions are detailed [10].

Individually indexed pyrophoric metals are:

Barium, 0200

Cadmium, 3949

Caesium, 4254

Calcium, 3922  
Cerium, 3961  
Chromium, 4222  
Cobalt, 4199  
Europium, 4292  
Hafnium, 4599  
Iridium, 4643  
Iron, 4388  
Lead, 4882  
Manganese, 4700  
Nickel, 4820  
Palladium, 4885  
Platinum, 4887  
Plutonium, 4888  
Rhodium, 4892  
Rubidium, 4889  
Strontium, 4913  
Tantalum, 4914  
Technetium, 4915  
Thorium, 4917  
Titanium, 4919  
Tungsten, 4925  
Uranium, 4923  
Vanadium, 4924  
Zinc, 4927  
Zirconium, 4928  
*See* Aluminium amalgam, Bismuth plutonide

## **PYROTECHNICS**

1. Hardt, A. P., in Kirk-Othmer, 1982, Vol. 19, 484–499
2. Wharton, R. K., *Proc. Int. Pyrotech. Semin.*, 1991, **16**, 514
3. Ullmann, 1993, A22, 437
4. Kirk Othmer, 1996, Vol. 20, 680
5. Jennings-White, C. *et al.*, *J. Pyrotech.*, 1995, (2), 72
6. Hatanaka, S. *et al.*, *Kayaku Gakkaishi*, 1997, **57**(5), 213 & 220

With the possible exception of delay fuses, any pyrotechnic mixture represents a hazard worthy of report. Although the cause of frequent accidents reviewed in [2], compositions intended to explode or deflagrate are generally outside the field of this work and few are listed. Numerous reviews and specialist texts exist and hundreds of patents appear yearly. The account [1] of the theory and practice of pyrotechnics contains much useful information on the performance and potential hazards of a great variety of oxidant–fuel combinations which burn very rapidly or explosively. Safety measures are found in [2]. Other reviews written from a functional viewpoint are found in [3] and [4]. Some hazardously incompatible pyrotechnic mixes are reported [5]. Detonability of pyrotechnic compositions has

been studied. Whistles and chlorate or perchlorate & aluminium containing noise compositions often show detonability. Most others don't [6].

#### Water

Gu, W. *et al.*, *Kayaku Gakkaishi*, 1996, **57**(5), 204

There is some risk of pyrotechnic mixtures containing powders of magnesium, aluminium, their alloy, or zinc, igniting from exothermic reactions of the metal in damp storage. Some study of inhibitors is undertaken. Titanium seems relatively inactive.

### QUALITATIVE ANALYSIS

*See* Lead(II) picrate, *also* Nitric acid: Metal salicylates

### QUATERNARY OXIDANTS (QUATERNARY PERMANGANATES)

1. Author's comments
2. Leddy, B. P. *et al.*, *Tetrahedron Lett.*, 1980, **21**, 2261–2262
3. Karaman, H. *et al.*, *J. Org. Chem.*, 1984, **49**, 4509–4516
4. Bretherick, L., *J. Chem. Educ.*, 1987, **64**(2), A42–A44

In an attempt to find new oxidants which will function homogeneously in organic substrate/solvent systems, many salts with quaternary organic cations and oxidising anions have been prepared during recent decades. There is however an intrinsic problem associated with this approach in that the compounds so prepared are effectively complete fuel–oxidant systems at the molecular level, with the oxidising anions juxtaposed in the crystal lattice with the organic cations. There have been a number of instances of unheralded and violent decomposition with this type of compound, which taken together suggest that considerable caution is necessary in preparing, storing and using these potentially hazardous salts [1].

Of a series of quaternary permanganate salts examined as organic oxidants, those of the 'unsaturated' cations benzyltrimethylammonium, benzyltriethylammonium, methyltriphenylphosphonium, ethylenebis(triphenylphosphonium) and hexadecylpyridinium all decomposed explosively at ~80–90°C, and of tetraphenylarsonium at 120–130°C. The permanganate salts of the 'saturated' cations tetramethylammonium, tetraethylammonium and hexadecyltrimethylammonium decomposed passively at 80–100°C, and were approximately as effective oxidants as their explosive counterparts. The latter could be considerably stabilised for use by adsorption on alumina [2]. General methods for the preparation and purification of a series of 16 quaternary ammonium permanganates and of 13 quaternary phosphonium permanganates have been developed, and the properties, decomposition temperatures and solubilities in 4 organic solvents and in water are tabulated. Examination of the thermal instability and mode of decomposition of several of the salts leads to the conclusion that thermal stability of these salts is a matter of concern, and that the salts should be held only in small quantity and in cold storage at all times, and that care should be exercised whenever they are handled and transferred from one container to another. Benzyltriethylammonium permanganate appears to be the best choice for long term storage stability,

with dichloromethane as an appropriate reaction solvent [3]. Possible structures for more stable quaternary oxidant salts are discussed [4].

Individually indexed compounds are:

Benzyltriethylammonium permanganate, 3617

Benzyltrimethylammonium permanganate, 3342

1,2-Bis(triphenylphosphonio)ethane permanganate, 3899

*N*-Hexadecylpyridinium permanganate, 3827

Methyltriphenylphosphonium permanganate, 3784

Tetrabutylammonium hydrogen monoperoxysulfate, 3732

Tetrabutylammonium permanganate, 3729

Tetraethylammonium perchlorate, 3088

Tetraethylammonium periodate, 3090

Tetramethylammonium ozonate, 1753

Tetramethylammonium pentaperoxodichromate, 3103

Tetramethylammonium superoxide, 1751

Tetraphenylarsonium permanganate, 3848

Tetramethylammonium periodate, 1749

*See* DICHROMATE SALTS OF NITROGENOUS BASES

*See also* PERCHLORATE SALTS OF NITROGENOUS BASES

*See other* OXOSALTS OF NITROGENOUS BASES

## **RADICAL INITIATORS**

1. Whitmore, M. W. *et al.*, *J. Loss Prev.*, 1993, **6**(2), 95

2. Bravo, S. *et al.*, *Chem. Eng. Progress*, 1994, **90**(7), 62

3. Anon., personal communication, 1999

Apart from their ability to promote reactions beyond control, when used in excess, many polymerisation 'catalysts' of this class are dangerously unstable, to weakly explosive, in their own right. A table of accelerating reaction temperatures, determined by various methods, is given for many of these. The two main classes, azoorganics and peroxides, are likely to destabilise each other and should not be stored together in bulk [1]. A paper treats of safe handling of radical initiators and other polymerisation catalysts [2]. In the aftermath of an incident on a speciality polymer plant, where many different monomers and initiation systems were employed, it came to light that sparks were frequently observed when sweeping the floor. It was recommended that the floor be cleaned wet in future [3].

*See* Ammonium peroxodisulfate

*See also* ACCELERATING RATE CALORIMETRY, SELF-ACCELERATING DECOMPOSITION TEMPERATURE

## **RANEY ALLOYS**

*See* Aluminium–cobalt alloy

Aluminium–nickel alloys, 0055

*See also* HYDROGENATION CATALYSTS

## REACTION SAFETY CALORIMETRY

1. *Proc. Int. Symp. Prev. Risks Chem. Ind.*, Heidelberg, ISSA, 1976
2. Hub, L., *Proc. 6th Symp. Chem. Proc. Haz. Ref. Plant Des.*, 39–46, Rugby, IChE, 1977
3. *See entry* HEAT FLOW CALORIMETRY
4. Grob, B. *et al.*, *Thermochim. Acta*, 1987, **114**, 83–90
5. Singh, J., *Process Safety Progress*, 1997, **16**(1), 43.

One of the sessions of the Symposium was largely devoted to presentation and discussion on the use of various experimental calorimetric methods for use in assessing possible hazards in chemical processing operations. The methods described covered a wide range of sample sizes and degrees of complexity:

Grewer, T. Adiabatic small-scale reaction test in Dewar, simple to operate.

Janin, R. Measurements of heat release by DSC and of pressure development in sealed microcapsules.

Lemke, D. Heat accumulation tests of medium scale samples of thermally unstable technical materials in adiabatic storage.

Schleicher, K. Survey of general hazard testing methods.

Eigenmann, K. Use of micromethods in DTA, DSC.

Hub, L. Medium-small-scale safety calorimeter, usable under isothermal, quasi-isothermal or adiabatic conditions.

Regenass, W. Medium-scale heat flow calorimeter for measurement of heat release and cooling requirements under realistic reaction conditions.

Schofield, F. Use of a range of tests to determine detonation capability, localised thermal decomposition, thermal stability of reaction masses and effects of prolonged storage; translation of these results to industrial-scale processing operations.

Berthold, W. Use of adiabatic autoclave to simulate possibility of thermal explosion in large containers of reactive materials [1].

Use of medium-scale heat flow calorimeter for separate measurement of reaction heat removed via reaction vessel walls and via reflux condenser system, under fully realistic processing conditions, with data processing of the results is reported [2]. More details are given elsewhere [3]. A new computer controlled reaction calorimeter is described which has been developed for the laboratory study of all process aspects on 0.5–2 l scale. It provides precise data on reaction kinetics, thermochemistry, and heat transfer. Its features are exemplified by a study of the (exothermic) nitration of benzaldehyde [4]. A more recent review of reaction safety calorimetry gives some comment on possibly deceptive results. [5].

*See* CHEMICAL STABILITY/REACTIVITY ASSESSMENT

*See also* ACCELERATING RATE CALORIMETRY, ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY, DIFFERENTIAL SCANNING CALORIMETRY

## REACTION SIMULATION

Wright, A. *et al.*, *Chem. & Ind.*, 1988, 114–118

A reaction simulation program, REACTION, which will run on a personal computer, and which is specifically adapted for the non-steady states prevailing in batch reactions, is described and illustrated by a typical reaction model. Among



uses of the program for rapidly studying reaction engineering, process optimisation, control systems, scale-up and staff training requirements, are included thermal stability and process safety studies.

## REACTIVE METALS

Stout, E. L., *Los Alamos Sci. Lab. Rept.*, Washington, USAEC, 1957; *Chem. Eng. News*, 1958, **36**(8), 64–65

Safety considerations in handling plutonium, uranium, thorium, alkali metals, titanium, magnesium, and calcium are discussed.

## REDOX COMPOUNDS

Compounds which contain both oxidising and reducing functions in close proximity on a molecular basis tend towards explosive instability, and usually with low energy of activation. Relevant types are salts of reducing bases with oxidising acids, and metal oxosalts with coordinated nitrogenous reductants.

*See* AMMINOMETAL OXOSALTS, OXOSALTS OF NITROGENOUS BASES

*See also* CHLORITE SALTS, PERCHLORATE SALTS OF NITROGENOUS BASES

and the individually indexed compounds:

(Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614

Bis(hydrazine)diperchloratochromium(III) perchlorate, 4128

\* Borane–bis(2,2-dinitropropylhydrazine), 0137

Copper(I) perchlorate, 4058

Copper(II) phosphinate, 4272

Diamminenitratocobalt(II) nitrate, 4202

Hydrazinium chlorate, 4010

Hydrazinium chlorite, 4008

Hydrazinium nitrate, 4549

Hydrazinium perchlorate, 4011

Hydroxylaminium nitrate, 4524

Hydroxylaminium perchlorate, 4005

Indium(I) perchlorate, 4014

Iron(II) perchlorate, 4062

Iron(III) phosphinate, 4394

Lead(II) nitrate phosphinate, 4468

Manganese(II) chlorate, 4087

Manganese(II) perchlorate, 4088

Mercury(I) chlorite, 4080

Pentaamminephosphinatochromium(III) perchlorate, 4053

Pentaamminephosphinatocobalt(III) perchlorate, 4050

Pentaamminethiocyanatoruthenium(III) perchlorate, 0520

Peroxyformic acid, 0420

\* Phosphonium perchlorate, 4006

- Potassium cyanide–potassium nitrite, 0527
- \* Potassium pentacyanodiperoxochromate(5–), 1810
- Potassium tricyanodiperoxochromate(3–), 1044
- Tetrahydroxotritin(2+) nitrate, 4525
- \* Tetrakis(hydroxymethyl)phosphonium nitrate, 1754
- Tin(II) nitrate, 4750
- Tin(II) perchlorate, 4109
- Trihydrazinealuminium perchlorate, 0064
- Trimethylhydroxylammonium perchlorate, 1323
- \* Triphenylphosphine oxide hydrogen peroxidate, 3755
- OXYGEN BALANCE
- DRUMS

## REDOX REACTIONS

Incidents involving interaction of active oxidants and reducing agents, either by design or accident, are usually extremely energetic, and examples of such redox reactions will be found under the entries:

- \* (Benzenesulfonato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614
- \* Calcium hypochlorite, : Acetic acid, Potassium cyanide, 3924
- Cerium, : Water, 3961
- Copper(II) nitrate, : Ammonium hexacyanoferrate(II), 4279
- Dibenzoyl peroxide, : Lithium tetrahydroaluminate, 3639
- N,N*-Dimethyl-4-nitrosoaniline, : Acetic anhydride, Acetic acid, 2980
- Dinitrogen oxide, 4744
- Dinitrogen tetraoxide, : Formaldehyde, 4747
- Ethyl hydroperoxide, : Hydriodic acid, 0925
- Hydrogen peroxide, : Lithium tetrahydroaluminate, 4477
- Hydroxylamine, 4498
- Hydroxylamine, : Oxidants, 4498
- Lead(IV) oxide, : Carbon black, Chlorinated paraffin, Manganese(IV) oxide, 4834
- Magnesium nitrate, : Tin(II) fluoride, 4693
- Manganese(IV) oxide, : Calcium hydride, 4705
- Molybdenum(VI) oxide, : Graphite, 4717
- Nitric acid, : Formaldehyde, 4436
- Nitric acid, : Formic acid, 4436
- Nitric acid, : Formic acid, Urea, 4436
- Nitric acid, : Metal thiocyanate, 4436
- Oxalic acid, : Urea, 0725
- Ozone, : Acetylene, 4846
- Perchloric acid, : Iron(II) sulfate
- Perchloric acid, : Sodium phosphinate, 3998
- Perchloric acid, : Zinc phosphide, 3998
- $\alpha$ -Phenylazobenzyl hydroperoxide, : Phenylhydrazine, 3609

Phosphinic acid, : Mercury(II) oxide, 4503  
Phosphonium iodide, : Oxidants, 4515  
Potassium nitrate, : Reducants, 4650  
Potassium phosphinate, : Air, or Nitric acid, 4459  
Silver nitrate, : Magnesium, Water, 0022  
Sodium chlorite, : Phosphorus, 4038  
Sodium hypochlorite, : Formic acid, 4037  
Sodium nitrate, : Arsenic trioxide, Iron(II) sulfate, 4721  
Sodium nitrate, : Sodium phosphinate, 4721  
Sodium nitrate, : Sodium thiosulfate, 4721  
Sodium nitrate, : Tris(cyclopentadienyl)cerium, 4721  
Sodium nitrite, : Potassium thiocyanate, 4720  
Sodium nitrite, : Sodium disulfite, 4720  
Sodium nitrite, : Sodium thiocyanate, 4720  
Sodium thiosulfate, : Sodium nitrite, 4804  
1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide, : Lithium tetrahydroaluminate, 3312  
Thallium(III) nitrate, 4762

*See also* METAL NITRATES: Esters, or Phosphorus, or Tin(II) chloride

METAL NITRATES: Metal phosphinates

METAL PERCHLORATES: Calcium hydride

PERCHLORATES: Reducants

*See related* UNIT PROCESS OR UNIT OPERATION INCIDENTS

## REDUCANTS

Most of the compounds showing powerful reducing action have been listed separately under the group headings:

*See also* COMPLEX HYDRIDES, METAL ACETYLIDES, METAL HYDRIDES

The remaining individually indexed compounds are:

Aluminium, 0048  
Ammonium phosphinate, 4554  
Barium phosphinate, 0210  
† Benzaldehyde, 2731  
1,4-Benzenediol, 2333  
\* Bis(hydrazine)tin(II) chloride, 4070  
Calcium acetylide, 0585  
Calcium phosphinate, 3931  
Chromium(II) chloride, 4052  
Chromium(II) oxide, 4241  
Chromium(II) sulfate, 4244  
Copper(I) bromide, 0265  
Diacetatotetraaquocobalt, 1780  
Diisobutylaluminium hydride, 3082  
† 1,2-Dimethylhydrazine, 0955

1,2-Diphenylhydrazine, 3517  
Dipotassium phosphinate, 4431  
† Ethanedial, 0723  
† Formaldehyde, 0416  
Formic acid, 0418  
Gallium(I) oxide, 4411  
Glucose, 2518  
† Hydrazine, 4520  
Hydroxylamine, 4498  
Hydroxylaminium phosphinate, 4555  
Hyponitrous acid, 4470  
Iron(II) chloride, 4061  
Iron(II) hydroxide, 4392  
Iron(II) sulfate, 4399  
Lead(II) phosphinate, 4531  
Lead(II) phosphite, 4535  
Lithium dithionite, 4687  
Magnesium, 4690  
Magnesium phosphinate, 4517  
Manganese(II) phosphinate, 4519  
† Methylhydrazine, 0503  
Phenylhydrazine, 2373  
Phosphinic acid, 4503  
Phosphonic acid, 4504  
Phosponium iodide, 4515  
Potassium, 4645  
Potassium hypoborate, 0163  
Potassium phosphinate, 4459  
Sodium disulfite, 4808  
Sodium dithionite, 4807  
Sodium hydride, 4444  
Sodium hypoborate, 0164  
Sodium phosphinate, 4473  
Sodium thiosulfate, 4804  
Sulfur dioxide, 4837  
Tetraphosphorus hexaoxide, 4867  
Tin(II) chloride, 4116  
Tin(II) fluoride, 4331  
Titanium(II) chloride, 4117  
Titanium trichloride, 4158  
Tungsten dichloride, 4119  
Vanadium dichloride, 4118  
Vanadium trichloride, 4159  
Zinc, 4927  
Zirconium(II) chloride, 4121  
Zirconium trichloride, 4160

## REFRACTORY POWDERS

Krivtsov, V. A. *et al.*, *Chem. Abs.*, 1979, **90**, 125991

Of a series of powdered refractory compounds examined, only lanthanum hexaboride, hafnium carbide, titanium carbide, zirconium carbide, magnesium nitride, zirconium nitride and tin(II) sulfide were dust explosion hazardous, the 2 latter being comparable with metal dusts. Individual entries are:

Hafnium carbide, 0521

Lanthanum hexaboride, 0193

Magnesium nitride, 4698

Tin(II) sulfide, 4900

Titanium carbide, 0561

Zirconium carbide, 0565

Zirconium nitride, 4733

## REFRIGERATORS

Hasenpusch, W., *CLB Chem. Labor, Biotech.*, 1995, 46(5), 212, 214

Explosions in laboratory refrigerators are fairly common, often because volatile solvents such as ether are below their upper flammable limit in a refrigerator, but not in a solvent cabinet. The domestic refrigerators usually employed are far from flame-proofed. This review discusses causes and recommends precautions.

*See also* FLAMMABILITY, FLASH POINTS

## REPAIR AND MAINTENANCE

1. Sanders, R. E., *Management of Change in Chemical Plants*, Oxford, Butterworth-Heinemann, 1993.

2. Anon., *Loss Prev. Bull.*, 1992, **107**, 17

These activities may introduce many hazards, such as contaminants, materials of repair corrodible, combustible or catalytic in the given environment, blocked vents, open valves etc. into the restarted plant, while shutdown and startup are, in any event, the most dangerous periods. Many examples of reactive hazards thus introduced are to be found in [1]. *Mutatis mutandis*, this is also true of the laboratory; this Handbook contains many incidents consequent upon stopping a reaction and/or its agitation to sample, change cooling bath, etc.

If the shutdown for repair is enforced by equipment failure, and thus abnormal, risks are greater; an explosion and fire resulted from failure of the airblower in an operating cracking catalyst regeneration unit, which was then steamed through, vented to the air and allowed to cool for two days prior to opening to replace the catalyst, whereupon the mishap occurred. Investigation suggested that the steam had formed water gas and light hydrocarbons by reaction with coke on the catalyst, and that these had not vented, nor had air penetrated enough to burn off combustibles from the probably still hot catalyst [2].

*See* CATALYTIC IMPURITY INCIDENTS

## ROCKET PROPELLANTS

1. Kirk-Othmer, 1965, Vol. 8, 659
2. Urbanski, 1967, Vol. 3, 291
3. ACS 88, 1969

All of the theoretically possible high-energy (and potentially hazardous) oxidant–fuel systems have been considered for use, and many have been evaluated, in rocket propulsion systems (with apparently the sole exception of the most potent combination, liquid ozone–liquid acetylene). Some of the materials which have been examined are listed below, and it is apparent that any preparative reactions deliberately involving oxidant–fuel pairs must be conducted under controlled conditions with appropriate precautions to limit the rate of energy release.

Many of the possible combinations below are hypergolic (will ignite on contact) or can be made so with additives. A few single compounds have been examined as monopropellants (alkyl nitrates, ethylene oxide, hydrazine, hydrogen peroxide), the two latter being catalytically decomposed in this application. Solid propellant mixtures, which are of necessity long-term storage stable, often contain ammonium or hydrazinium perchlorates as oxidants. The hazardous aspects of rocket propellant technology have been surveyed [3].

OXIDANTS	FUELS
Chlorine trifluoride	Alcohols
Dinitrogen tetroxide	Amines
Fluorine	Ammonia
Fluorine oxides	Beryllium alkyls
Halogen fluorides	Boranes
Methyl nitrate	Dicyanogen
Nitric acid	Hydrazines
Nitrogen trifluoride	Hydrocarbons
Oxygen	Hydrogen
Ozone	Metal hydrides
Perchloric acid	Nitroalkanes
Perchloryl fluoride	Powdered metals
Tetrafluorohydrazine	Silanes
Tetranitromethane	Thiols

*See also* PROPELLANTS

## ROSIN

(complex mixture, mainly resin acids)

Dry finely divided rosin is a significant dust explosion hazard.

*See entry* DUST EXPLOSION INCIDENTS (reference 22)

## ROSINATED PIGMENTS

Twitchett, H. J., *Chem. Brit.*, 1977, **13**, 437

These products, usually calcium or barium 'lakes' of acid azo-dyes co-precipitated with the abietates ('rosinates'), are subject to spontaneous ignition, either in the freshly ground state, or as bulk material in drying ovens while a little moisture remains.

See METAL ABIETATES

## ROTANES



de Meijere, A. *et al.*, *Angewand. Chem. (Int.)*, 1995, **34**(7), 781; *Chem. Eur. J.* 1995, **1**(2), 124

The cyclic oligomers of 3-(1,2-Ethylidene)penta-1,4-diyne-1,5-diyl, ( $n = 5,6,7,8$ ), obtained by oxidative coupling of 1,1-Diethynylcyclopropane, are called 'exploding rotanes'. They live up to the name, being sensitive to heat, friction or shock and having some 6 kJ/g available energy (TNT; 4.3 kJ/g). Higher homologues ( $n = 9,10,12$ ) are probably no more stable, but are not yet reported as exploding; lower would be still less stable but are not known. The pentamer demolished a melting-point apparatus when a melting point was attempted. The permethylated rotanes do not explode similarly, although at most a third of the energy of the spiropropanes would be attributable to the cyclopropane ring. There is no reason to suppose that rotanes which are not polyacetylenic are unstable.

See *other* ALKYNES

## RUBBER

Air, Cotton

Jones, S., *Res. Rept. 137*, Buxton, Safety in Mines Res. Est., 1956

If compressed air leaks from a rubberised cotton hose and causes squealing vibration to occur, enough heat may be generated to cause ignition. Fires have been started by squealing of poorly patched hoses, and ignition sources have been caused by use of rubberised cotton gaskets (cut from used conveyor belting, etc.) in plain flanged joints.

Sodium chlorate

See Sodium chlorate: Aluminium, Rubber

Metal azides

Tanaka, J. *et al.*, *Chem. Abs.*, 1952, **46**, 11743h

During the preparation of cellular rubber by thermal decomposition of calcium, strontium or barium azides, various additives were necessary to prevent explosive decomposition of the azide in the blended mixture.

## RUNAWAY REACTIONS

1. *Runaway Reactions, Unstable Products and Combustible Powders*, Symp. Ser. No 68, Rugby, IChE, 1981
2. Various authors, *J. Loss Prev.*, 1993 **6**(2)

3. *Safety and Runaway Reactions*, Smeder, B & Mitchison, N. (Eds.), EUR 17723 EN, European Commission, 1997

The 22 papers of the symposium [1] were presented under the headings: Theory, Laboratory Studies, Calorimetry (2 sessions), Applications. Several papers are devoted to individual instrumental methods of measuring and assessing potential for exothermic runaway reactions to develop. An issue of the *Journal of Loss Prevention in the Process Industries* is devoted to a variety of, mostly calorimetric, studies of runaway reactions [2]. The proceedings of a European Union Seminar in 1994 appear as a book, including hard data as well as debate about such matters as operator training [3].

Examples of runaway reactions may be found in the entries:

Aluminium chloride, Alkenes, 0062

Butyrolactone, Butanol, 2,4-Dichlorophenol, Sodium hydroxide, 1527

Chlorine, 4047

Dichloronitrobenzene, Aniline, 2103

2,4,-Dichloronitrobenzene, Acetic acid, Potassium fluoride,

Dimethylacetamide, 2104

† Ethylene oxide, Glycerol, 0829

† Ethylene oxide, Ammonia, 0829

† Formaldehyde, Phenol, 0416

Nitric acid, Formic acid, Urea, 4436

Nitric acid, Nitrobenzene, Sulfuric acid, 4436

Nitric acid, 1-Nitronaphthalene, Sulfuric acid, 4436

Sodium molybdate, 4713

1,2,4,5-Tetrachlorobenzene, Sodium hydroxide, Solvent, 2079

2,4,6-Trichloro-1,3,5-triazine, 1038

*See also* CALORIMETRY

## RUST

Rust (a complex hydrated basic iron carbonate) is one of the most common contaminants in non-stainless steel plant, and has been involved, usually catalytically, in many different types of hazardous incident.

*See* FRICTIONAL IGNITION OF GASES AND VAPOURS

*See also* THERMITE REACTIONS

Carbon disulfide: Air, Rust

Hydrogen sulfide: Rust

Hydrazine: Rust

Magnesium: Metal oxides (reference 3)

## SAFE STORAGE OF CHEMICALS

Pipitone, D., (Ed.), *Safe Storage of Laboratory Chemicals*, New York, Wiley, 1984

This book in 2 parts and 9 chapters with 6 appendices covers all aspects of the requirements for safe storage of chemicals for laboratories. The first part consists of 5 chapters:



Steere, N. V. Storage requirements for flammable and hazardous chemicals.  
Bretherick, L. Incompatible chemicals in the storeroom: identification and segregation.  
Nicholls, L. J. Labeling unstable chemicals.  
Pipitone, D. A. Counteracting chemical spills in the storeroom.  
Macenski, A. G. Use and selection of computers for chemical tracking systems.  
The second part of the book contains 4 chapters on case histories and studies relating to chemical storage, and the appendices deal with specific aspects of labeling, purchasing chemicals, microcomputing, safety equipment, flash points of solvents and a safety checklist. A revised second edition is in press.

### SAFETY LITERATURE

Many of the proliferating compendia of chemical safety information are composed in an unthinking, formulaic and plagiaristic manner, by persons or machines knowing no chemistry, giving rise to ramifying errors. These are usually on the side of safety (but not always so). An example in both the major multi-volume English language works was, until recently, the section: 'heating to decomposition'. Thus both reported sodium azide as giving nitrogen oxides, in which case car air-bags, which work by heating sodium azide to decomposition, must be extremely dangerous, both by virtue of the highly poisonous fumes discharged into the passenger compartment and by probable radiation from the nuclear transmutation evidently involved. There is a persistent inability to distinguish between pyrolysis and combustion combined with an automatic assumption that both give rise to the oxides of the elements present (except those of halogens) and to nothing else. Many nitrogenous compounds give much more hydrogen cyanide, even in circumstances of combustion, but this is rarely, if ever, mentioned (nor, apparently, are elemental halogens ever evolved when chlorine and bromine containing materials are burnt). Nitrogen oxides most commonly arise from heating empty air, and air is also omitted from consideration those entries which report common (combustible) solvents exploding on heating. Some of these errors have been copied into safety data sheets issued by supposedly authoritative chemical societies. Even as one source of error is moderated, another hastens to replace it. This handbook, too, may contain errors while certainly holding reports, accident explanations and claims of hazard which the editor does not believe (usually indicated in phraseology or cross-reference). Nor is it automatically to be assumed that all listed and cross-indexed components of complex mixtures contributed to the accidents reported. Accept nothing uncritically!

### SAMPLE DISSOLUTION

1. Bock, R., *Handbook of Decomposition Methods in Analytical Chemistry*, (Marr, L., translator and reviser), Glasgow, International Textbook Co., 1979
2. IUPAC Anal. Chem. Div., *Pure Appl. Chem.*, 1984, **56**, 479–489
3. Kingston, H. M. *et al.*, *Anal. Chem.*, 1986, **58**, 2534–2541
4. Tattersall, P. J., *Lab. Practice*, 1986, **35**(10), 95

5. Bedson, A., *Chem. Brit.*, 1986, **22**, 894
6. Nakashima, S. *et al.*, *Analyst* (London), 1988, **113**, 159–163

Of the 444 pages, 165 deal with oxidising procedures for analytical samples, and the hazards involved are detailed with suitable precautions [1]. The use of acid pressure decomposition methods in trace element analysis is reviewed (61 references). Vessels of high purity materials (PTFE, glassy carbon) within compact metal pressure casings are used. At 170°C, the temperature and considerable autogenous pressure enhance greatly the reaction capacity of acids and oxidising agents, permitting rapid dissolution of a wide range of samples. Critical aspects of vessel design and operational use are detailed [2]. The use of microwave heating to heat closed Teflon PFA vessels containing organic samples and various mineral acids has been investigated, with measurement of temperature profiles in the digestion vessels [3]. The technique has also been applied to other agricultural samples [4]. Use of microwave oven heating to accelerate sample dissolution has been reviewed [5]. Comparative tests on sealed and pressure-relieved digestion vessels with microwave heating have been reported, with nitric–perchloric acid mixtures to digest marine biological samples, and with hydrofluoric–nitric–perchloric acid mixtures to digest marine sediments [6].

Some examples of incidents are detailed under:

Hydrogen peroxide, : Organic materials, Sulfuric acid, 4477

Nitric acid, : Organic matter, Sulfuric acid, 4436

Perchloric acid, : Nitric acid, Organic materials, 3998

Potassium chlorate, : Nitric acid, Organic materials, 4017

*See also* MICROWAVE OVEN HEATING

## SCALE OF WORK

1. Editor's comments
2. Gygax, R. W., *Chem. Eng. Progress*, 1990, (Feb.), 53
3. *Chemical Reaction Hazards*, Barton, J. & Rogers, R., Rugby, IChE, 1993
4. Anon., *Loss Prev. Bull.*, 1992, (105) 15
5. *Org. Proc. Res. Dev.*

Nothing is so explosive that 1 mg is a significant danger. But with 1 tonne of sodium bicarbonate (baking soda), injudiciously mixed with weak acid (vinegar), it is quite possible to blow a reactor apart, with consequent fatalities. This consideration should be held in mind when using this text. Educators might also consider that, though they will have no accidents if they arrange practical work exclusively on the micro-scale, they will create very dangerous graduates who have no idea how to handle danger, nor even where it may lie, should they enter the world of real chemistry.

The problems of scale-up generally arise from the transfer of heat through the walls of a vessel, or the egress of gases and vapours through a hole in the wall. Rates of both of these, being surface phenomena, increase as the square of the linear dimensions of similar vessels. However, the contents, and associated potential energies, increase as the cube. It is also the case that the pressure a

vessel can contain decreases sharply with size if similar materials of construction are used [1].

For a study of methods of assessment of thermal runaway risk from laboratory to industrial scales [2]. A more detailed but eminently clear treatment of this and other needful safety considerations on scaling reactions up to production has since been published [3]. So slight a scale-up as replacing two charcoal filters by one bigger one may cause a fire because heat loss was reduced [4]. A journal largely devoted to scale-up of organic chemical processes has been launched [5].

Heat, and sometimes gas, transfer from the core of a bulk material, also influences auto-ignition and explosion. The concept of critical mass is not limited to nuclear explosives (though shape is also important). Some entries in this text, such as sodium chlorate, ammonium nitrate and ammonium perchlorate, have proved extremely destructive during industrial storage by the tens of tonnes, but are incapable of explosion at the ten gramme scale. Many other entries are for hazards significant only beyond laboratory scale [1].

*See also* ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

### **SELF-ACCELERATING DECOMPOSITION TEMPERATURE (SADT)**

Fisher, H. G. *et al.*, *J. Loss Prev.*, 1993, 6(3), 183

SADTs, a measure of safe storage and drying temperatures for industrial products, are determined by a variety of techniques, often large scale with up to 200 kg samples. Smaller scale calorimetric methods are discussed.

*See also* CALORIMETRY, SELF-HEATING AND IGNITION INCIDENTS

### **SELF-ACCELERATING REACTIONS**

Brogli, F. *et al.*, *Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 665–683, Basle, SSCI, 1980

The general characteristics, contributory factors and potential hazards arising from self-accelerating (sometimes autocatalytic) reactions are discussed, together with the means to identify such reaction systems and appropriate practical precautions. Five product classes showing dangerous self-acceleration tendencies are aromatic nitro compounds, aliphatic *N*-nitroso compounds, thiophosphate esters, acrylates (and acrylonitrile and acrylamide), and sulfones or esters and chlorides of sulfonic acids. Four types of reaction similarly assessed are organic reactions with metals (Béchamp, Grignard), Bucherer amination, Friedel-Crafts with nitro compounds, and condensations with cyanuric chloride. 11 Examples of hazardous chemicals or reaction mixtures discussed in detail are the entries:

Aluminium chloride, : Nitrobenzene, 0062

Ammonium hydrogen sulfite, 4545

Benzyltriethylammonium permanganate, 3617

Bis(4-hydroxyphenyl) sulfone, 3497

2-Chloro-5-nitrobenzenesulfonic acid, 2144

1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione, 1865

† Dimethyl sulfoxide, 0921

- † Methyl acrylate, 1531
- N*-Methyl-*N*-nitrosourea, 0875
- Nitric acid, : 2-Aminothiazole, Sulfuric acid, 4436
- 3-Nitrobenzenesulfonic acid, 2268
- Sodium hydride, : Dimethylformamide, 4444
- Succinodinitrile, 1433
- Sulfuric acid, : 4-Chloronitrobenzene, Sulfur trioxide, 4479
- 2,4,6-Trichloro-1,3,5-triazine, 1038
- 2,4,6-Trichloro-1,3,5-triazine, : Acetone, Water, 1038

### SELF-HEATING AND IGNITION INCIDENTS

1. Virtala, V. *et al.*, *Chem. Abs.*, 1952, **44**, 7770i –7771b
  2. Napier, D. H. *et al.*, *Runaway Reactions*, 1981, Paper 2/F, 1–15
  3. Bishop, R. C., *Runaway Reactions*, 1981, Paper 2/H, 1–4
  4. Duane, T. C. *et al.*, *Runaway Reactions*, 1981, Paper 2/J, 1–8
  5. Kotoyori, T. *et al.*, *Thermochim. Acta*, 1983, **67**, 35–44
  6. Bowes, P. C., *Self-Heating: Evaluation and Control*, London, HMSO, 1984
- Methods for assessing the potential for oxidative self-heating and ignition of a range of 25 organic liquids and solids were described. Case histories are included for ignition of castor oil on peat, mineral oil on iron turnings, and wood shavings as lagging round steam pipes at 100°C, with 56 references [1]. Oxidative self-heating behaviour in mixtures of beech sawdust and raw linseed oil, in presence or absence of water (which accelerates heating) was studied to gain insight into the basic processes involved in ignition of such 2-phase systems [2]. Self-ignition phenomena in powdered grain products, corrugated fibreboards, iron powder, contaminated mineral lagging, and tobacco [3], and also spray drying of milk powder [4] were studied. A new adiabatic self-heating process recorder allows very strictly adiabatic self-heating tests to be carried out accurately and easily on small samples of a wide range of chemical materials [5]. A new book reviews the theoretical background and practical applications of methods of assessing the phenomena [6].

Some self-heating and ignition incidents will be found in the entries:

- Adipic acid, 2441
- 1,4-Benzoquinone, 2214
- † 1,3-Butadiene, 1480
- Cinnamaldehyde, 3134
- Copper iron(II) sulfide, 4269
- Dibromomethylborane, 0426
- † Di-*tert*-butyl peroxide, 3074
- Dichlorine oxide, : Hydrocarbons, 4095
- \* Dimethyl terephthalate, 3292
- † Hydrogen sulfide, : Soda-lime, 4483
- Iron, : Air, Oil, 4388
- Iron disulfide, 4401
- \* Methoxy-1,3,5,7-cyclooctatetraene, 3149

Nitric acid, : Ion exchange resins, 4436  
1-Nitroso-2-naphthol, 3250  
Sodium dichromate, : Sulfuric acid, Trinitrotoluene, 4250  
Sodium nitrite, : Paper, Sulfur, 4720

ALDEHYDES

CELLULOSE NITRATE: Iron red, etc.

MILK POWDER

POLYPROPYLENE POWDER

SOAP POWDER

IGNITION SOURCES, INSULATION

## SILANES

$\text{H}(\text{SiH}_2)_n\text{H}$ ,  $\text{RSiH}_3$ , etc.

1. Stock, A. *et al.*, *Ber.*, 1922, **55**, 3961
2. Kirk-Othmer, 1983, Vol. 20, 888
3. Ullmann, 1993, **A24**, 31 & 35

All the lower silanes are extremely sensitive to oxygen and ignite in air. The liberated hydrogen often ignites explosively [1]. Only under certain critical experimental conditions can they be mixed with oxygen without igniting [2]. Alkyloxysilanes can disproportionate to give silanes under base catalysis. Poly(alkyl)oxasilanes may depolymerise and disproportionate to give alkylsilanes and poly(alkyl)oxosiloxanes [3].

*See* Oxygen: Tetramethyldisiloxane

Chloroform, or Carbon tetrachloride, Oxygen

Stock, A. *et al.*, *Ber.*, 1923, **56**, 1087

The chlorination of the lower silanes by halogenated solvents proceeds explosively in presence of oxygen, but catalytic presence of aluminium chloride controls the reaction.

Halogens

Stock, A. *et al.*, *Ber.*, 1919, **52**, 695

Reaction of silanes with chlorine or bromine is violent.

Olefins, Platinum

Mathias, L. J. *et al.*, *Chem. Abs.*, 1995, **124**, 286890v

Si-H bonds add across olefins over platinum catalysts. This reaction (hydrosilation) is used in silicone polymer manufacture, when the silane is a hydrogen bearing oligo(alkylsiloxane). With some types of olefin there have been reports of runaways to explosion because of unexpectedly fast reaction. Dangerous substrates recorded are 2-allylphenols and ethenylsiloxanes. Very low levels of catalyst (ppm) and good cooling are recommended.

*See also* VINYL-SILOXANES

Individually indexed compounds are:

\* Azidosilane, 4501

† Disilane, 4569

- \* Disilyl oxide, 4565
- \* Disilyl sulfide, 4568
- \* Oxodisilane, 4530
- \* Oxosilane, 4476
- \* Poly(silylene), 4487
- † Silane, 4539
- † Tetramethoxysilane, 1764  
Tetrasilane, 4584
- \* Tetrasilylhydrazine, 4585
- † Trisilane, 4579
- \* 2,4,6-Trisilatirioxane, 4566
- \* Trisilylamine, 4580
- \* Trisilylarsine, 0102
- \* Trisilylphosphine, 4583

*See other* NON-METAL HYDRIDES

## SILICON COMPOUNDS

Groups or substances falling within this class are:

ALKYLHALOSILANES, ALKYL SILANES  
 HALOSILANES, ORGANOSILYL PERCHLORATES  
 SILANES, SILICONE GREASE, SILICONE LIQUID, SILICONE OIL  
 SILYLHYDRAZINES, TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES

## SILICONE GREASE

Bromine trifluoride

*See* Bromine trifluoride: Silicone grease

## SILICONE LIQUID

## Poly(dimethylsiloxane)

Silica powder, Unstated salt

Anon., *Loss Prev. Bull.*, 1987, (078), 9

A cosmetic preparation involved the vigorous dispersion of finely divided silica, and that of an ionically dissociable powder in a volatile silicone fluid. Small scale laboratory tests were uneventful, but in a preliminary 150 l manufacturing run, crackling noises were heard during the dispersion of silica powder, and on heating, the evolved vapour ignited. It was found that surface potentials of 35 kV could be measured 150 mm above the liquid. The static generation problem was completely eliminated by first dispersing the powdered salt component in the silicone liquid which effectively reduced the insulating properties of the silicone liquid.

*See* ELECTROSTATIC HAZARDS

## SILICONE OIL

Yasufuku, S., *Chem. Abs.*, 1982, **96**, 220130

A major factor in ignition of dimethylsilicone oils after heating is the presence of a cyclic trimer. Flash point can be improved by addition of cerium acetylacetonate.

#### Contaminants

D'Onofrio, E. J., *Chem. Eng. News*, 1978, **56**(45), 51

Contamination of silicone oil baths with alkaline or acidic materials may lead to depolymerisation and a marked lowering of the flash point. This happened when the alkaline contents of a beaker heated in a silicone bath at 260°C frothed over into the oil, which itself then frothed and overflowed, exposing the electric immersion heater element which ignited the decomposition products.

#### Nitric acid

*See* Nitric acid: Silicone oil

### SILVER COMPOUNDS

Many silver compounds are explosively unstable and/or powerful oxidants.

*See* METAL ACETYLIDES

Individually indexed compounds are:

- Bis(2-aminoethyl)aminesilver nitrate, 1773
- \* Cyclopentadiene–silver perchlorate, 1859
- Diamminesilver permanganate, 0018
- Dihydrazinesilver nitrate, 0019
- Dipyridinesilver(I) perchlorate, 3267
- Disilver cyanamide, 0305
- Disilver diazomethanide, 0306
- Disilver ketenide, 0570
- Disilver ketenide–silver nitrate, 0571
- Disilver pentatin undecaoxide, 0036
- \* Heptasilver nitrate octaoxide, 0047
- Nitrogen triiodide–silver amide, 4634
- 1,3-Pentadiyn-1-ylsilver, 1815
- Pentasilver diamidophosphate, 0046
- Pentasilver orthodiamidophosphate, 0044
- Phenylsilver, 2217
- Silver acetylide, 0568
- \* Silver acetylide–silver nitrate, 0569
- Silver–aluminium alloy, 0002
- Silver amide, 0015
- Silver 5-aminotetrazolide, 0392
- Silver azide, 0023
- Silver azide chloride, 0009
- Silver 2-azido-4,6-dinitrophenoxide, 2075
- \* Silver azidodithioformate, 0303
- Silver 1-benzeneazothiocarbonyl-2-phenylhydrazide, 3605
- Silver benzo-1,2,3-triazole-1-oxide, 2127

Silver bromate, 0007  
Silver buten-3-ynide, 1408  
Silver chlorate, 0011  
Silver chloride, 0008  
Silver chlorite, 0010  
\* Silver chloroacetylde, 0566  
\* Silver cyanate, 0300  
Silver cyanide, 0299  
Silver cyanodinitromethanide, 0567  
Silver 3-cyano-1-phenyltriazen-3-ide, 2670  
Silver cyclopropylacetylde, 1838  
Silver difluoride, 0014  
Silver dinitroacetamide, 0689  
Silver 3,5-dinitroanthranilate, 2642  
Silver fluoride, 0013  
Silver fulminate, 0301  
Silver hexahydrohexaborate(2-), 0027  
Silver hexanitrodiphenylamide, 3429  
Silver 1,3,5-hexatrienide, 2052  
Silver 3-hydroxypropynide, 1088  
Silver hyponitrite, 0031  
Silver imide, 0030  
Silver iodate, 0020  
\* Silver isophthalate, 2887  
Silver malonate, 1071  
\* Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1409  
Silver nitrate, 0022  
Silver nitride, 0038  
\* Silver 4-nitrophenoxide, 2126  
Silver *N*-nitrosulfuric diamidate, 0016  
Silver osmate, 0034  
Silver oxalate, 0572  
Silver(I) oxide, 0032  
Silver(II) oxide, 0025  
Silver perchlorylamide, 0028  
Silver *N*-perchlorylbenzylamide, 2734  
Silver permanganate, 0021  
Silver peroxochromate, 0037  
Silver phenoxide, 2218  
Silver phenylselenonate  
Silver phosphinate, 0017  
Silver sulfide, 0026  
Silver tetrafluoroborate, 0005  
Silver tetrafluorobromate, 0006  
Silver tetrazolide, 0366  
Silver trichloromethanephosphonate, 0304



- Silver trifluoropropynide, 1030
- Silver trinitromethanide, 0302
- Silver 2,4,6-tris(dioxoselena)perhydrotriazine-1,3,5-triide, 0039
- Silver trisulfurpentanitride, 0024
- Tetrasilber diimidodioxosulfate, 0043
- Tetrasilber diimidotriphosphate, 0042
- Tetrasilber orthodiamidophosphate, 0041
- \* Tetrasulfurtetraimide–silver perchlorate, 0029
- 1,2,4-Triazol[4,3-*a*]pyridine–silver nitrate
- Trisilver tetranitride, 0040

*See other* HEAVY METAL DERIVATIVES

### SILVER-CONTAINING EXPLOSIVES

1. Luchs, J. A., *Photog. Sci. Eng.*, 1966, **10**, 334
2. MacWilliam, E. A. *et al.*, *Photog. Sci. Eng.*, 1977, **21**, 221–224

Silver solutions used in photography can become explosive under a variety of conditions. Ammoniacal silver nitrate solutions, on storage, heating or evaporation eventually deposit silver nitride ('fulminating silver'). Silver nitrate and ethanol may give silver fulminate, and in contact with azides or hydrazine, silver azide. These are all dangerously sensitive explosives and detonators [1]. Addition of ammonia solution to silver containing solutions does not directly produce explosive precipitates, but these are formed at pH values above 12.9, produced by addition of alkali, or by dissolution of silver oxide in ammonia [2].

*See* Silver nitrate: Ammonia, etc.

*See also* FULMINATING METALS, SILVERING SOLUTIONS, TOLLENS' REAGENT

### SILVER-CONTAINING RESIDUES

1. Wakeford, D. H., *School Sci. Rev.*, 1978, **59**(209), 665–666
2. Perman, C. A., *Talanta*, 1979, **26**(7), 603–604

A simple and economical method for recovering silver residues by dissolution in used photographic fixer (thiosulfate) solution, then precipitation by addition of zinc powder, is detailed [1]. After the acid digestion phase of silver recovery operations, addition of ammonia followed immediately by addition of ascorbic acid as reductant gives a near-quantitative recovery of silver metal, and avoids the possibility of formation of silver nitride [2].

### SILVERING SOLUTIONS

1. Smith, I. C. P., *Chem. & Ind.*, 1965, 1070; *J. Brit. Soc. Glassblowers*, 1964, 45
2. Ermes, M., *Diamant*, 1929, **51**, 62, 587
3. Loman, E., and Mylius, W., *Diamant*, 1929, **51**, 526, 42
4. Sivertz, C. *et al.*, Ger. Pat. 2 162 263, 1972

Brashear's silvering solution (alkaline ammoniacal silver oxide containing glucose) or residues therefrom should not be kept for more than 2 hours after preparation, since an explosive precipitate forms on standing [1]. The danger of explosion may

be avoided by working with dilute silver solutions (0.35 M) in the Brashear process, when formation of  $\text{Ag}(\text{NH}_3)_2\text{OH}$  (and explosive  $\text{AgNH}_2$  and  $\text{Ag}_3\text{N}$  therefrom) is minimised. The use of Rochelle salt, rather than caustic alkali, and shielding of solutions from direct sunlight, are also recommended safeguards [2,3]. Addition of sodium gluconate or tartrate to ammoniacal silver salt–base mixtures inhibits the formation of fulminating silver [4].

*See* FULMINATING METALS, TOLLENS' REAGENT

### SILVER–NITROGEN COMPOUND HAZARDS

Anon, *CISHC Chem. Safety Summ.*, 1978, **49**, 29

A silver-containing solution was basified with sodium hydroxide, and after filtration, ammonia solution was used to wash residual silver from the filter. Hydrazine sulfate was then added to precipitate metallic silver and when the mixture was heated it exploded. This may have been caused by formation of silver nitride and/or hydrazine–silver complexes, both of which are explosively unstable.

*See* FULMINATING METALS, SILVER-CONTAINING EXPLOSIVES, TOLLENS' REAGENT

*See also* Silver chloride: Ammonia

*See also* Silver nitrate: Ammonia, Sodium hydroxide

### SILYLHYDRAZINES

$(\text{R}_3\text{Si})_2\text{NNHSiR}_3$ , etc.

#### Oxidants

1. Wannagat, U. *et al.*, *Z. Anorg. Chem.*, 1959, **299**, 341–349

2. Wannagat, U. *et al.*, *Monats.*, 1966, **97**, 1157–1162

During analysis of a series of tris(organosilyl)hydrazines, treatment with 1 : 1 mixtures of nitric and sulfuric acids had caused explosive reactions [1]. Subsequently the hypergolic behaviour of a range of 20 silylhydrazines and congeners in contact with fuming nitric acid was examined. All di- or tri-silyl derivatives showed ignition delays of 10 ms or less, several also exploding after ignition. All the derivatives ignited on dropping into gaseous fluorine, and into conc. liquid ozone–oxygen mixtures, most also exploding in the latter [2].

The most reactive compounds are:

1,2-Bis(triethylsilyl)hydrazine, 3583

1,2-Bis(triethylsilyl)trimethylsilylhydrazine, 3696

1,2-Bis(trimethylsilyl)hydrazine, 2616

1,2-Bis(tripropylsilyl)hydrazine, 3777

Dilithium 1,1-bis(trimethylsilyl)hydrazide, 2595

1,2-Dimethyl-2-trimethylsilylhydrazine, 2047

Lithium 2,2-dimethyltrimethylsilylhydrazide, 2041

3,3,6,6-Tetraphenylhexahydro-3,6-disilatetrazine, 3852

Triethylsilyl-1,2-bis(trimethylsilyl)hydrazine, 3586

Tris(trimethylsilyl)hydrazine, 3230

*See other* N-METAL DERIVATIVES

## SINTERED GLASS

The recent replacement, in many laboratories, of filter papers and Buchner funnels by sintered, or fritted, glass filters when isolating solids has increased explosion hazards in two ways. Firstly, fritted glass is an excellent surface on which to induce detonation by scraping a solid. Secondly, the sinters rapidly clog and are valuable enough to encourage cleaning with powerful oxidant reagents rather than disposal, sometimes resulting in explosions from reaction with solvent or other materials impregnating the frit. The editor also finds it difficult to clean the porous support such that contamination of subsequently filtered solid is avoided and impossible to recover as much product as from a filter paper.

*See* Nitric acid: Glassware, Hydrogen peroxide, 5-Bromo-4-pyrimidinone

*See also* CLEANING BATHS FOR GLASSWARE, FRICTIONAL INITIATION INCIDENTS

## SLAG WOOL

Potassium permanganate

*See* Potassium permanganate: Slag wool

## SMELT

1. Nelson, W., *Chem. Abs.*, 1973, **78**, 126458
2. Morgan, H. W. *et al.*, *Chem. Abs.*, 1967, **66**, 56874t
3. Anon., *Chem. Abs.*, 1967, **66**, 56876v
4. Duda, Z., *Chem. Abs.*, 1976, **84**, 32851
5. Kashtanov, V. S., *Chem. Abs.*, 1979, **91**, 41112
6. Shivgulam, M. *et al.*, *Pulp Pap. Can.*, 1979, **80**(9), 89–92
7. Gardner, H. S., US Pat. 4 194 124, 1980
8. Kohl, A. L. *et al.*, *Tappi J.*, 1986, **63**(9), 82–85
9. Gairns, S. A. *et al.*, *Pulp Pap. Can.*, 1996, **97**(6), 46

‘Smelt’, the residue from ‘burning’ (high temperature combustive evaporation, sometimes with submerged burners) of spent sulfite liquor from wood-pulp treatment and consisting largely of sodium sulfide and sodium carbonate, explodes violently on contact with water while still hot. The mechanism is discussed [1], and operational procedures to avoid the possibility of explosions are recommended [2,3]. A further possible cause of explosions is the generation of hydrogen and/or hydrogen sulfide at the high temperatures involved [4]. Equipment used for processing kraft liquor is classified on the basis of explosion and fire hazards [5]. Addition of sodium or potassium chloride to smelt reduces the eutectic m.p. and the tendency to spout plugging and dissolving tank explosions, but increases the corrosion rate [6]. Smelt–water explosions are suppressed by the radiochemical nucleation of bubbles. No explosions occurred when cold water was dropped into molten sodium chloride at 1000°C under  $\gamma$ -irradiation at 4300 rad/min [7]. The probability and intensity of explosions in smelt–water systems is reduced by increase in pressure and temperature [8]. Experiment shows that pyrolysis of liquors at high temperatures in non-oxidising atmosphere can generate char

particles containing substantial levels of metallic sodium, from reduction of sodium carbonate by carbon. This char may be pyrophoric and will certainly evolve hydrogen on contact with water; this is suggested as the principal cause of explosions [9].

*See* SUPERHEATED LIQUIDS

### **SOAP POWDER**

Anon., *Chem. Abs.*, 1935, **29**, 6759.7

General factors affecting spontaneous ignition of soap powders were discussed.

### **SODA-LIME**

**NaOH.Ca(OH)<sub>2</sub>**

Hydrogen sulfide

Bretherick, L., *Chem. & Ind.*, 1971, 1042

Soda-lime, after absorbing hydrogen sulfide, exhibits a considerable exotherm (100°C) when exposed simultaneously to moisture and air, particularly with carbon dioxide enrichment, and has caused fires in laboratory waste bins containing moist paper wipes. Saturation with water and separate disposal in sealed containers is recommended.

### **SODIUM CARBOXYMETHYLCELLULOSE**

Hydrogen peroxide, Iron(II) sulfate, Nitric acid

*See* Hydrogen peroxide: Iron(II) sulfate, Nitric acid, etc.

### **'SODIUM PERCARBONATE'**

**Various structures, below**

Acetic anhydride

1. Anon., *Lab. Accid. in Higher Educ.*, item 20, HSE, Barking, 1987

2. Author's comment, 1989

Mixing 'sodium percarbonate' with acetic anhydride led to explosive shattering of the flask [1], undoubtedly caused by the formation of acetyl peroxide. The name 'sodium percarbonate' has been used indiscriminately to describe 3 different compounds, all of which would react with acetic anhydride to give extremely explosive acetyl peroxide [2]. These are sodium monoperoxydicarbonate, NaOCO.OONa, [4452-58-8]; sodium peroxydicarbonate, NaOCO.OOCO.ONa, [3313-92-6]; and sodium carbonate sesqui hydrogen peroxidate, NaOCO.ONa.1.5H<sub>2</sub>O<sub>2</sub>, [15630-89-4].

*See other* PEROXOACID SALTS

### **SODIUM PRESS**

Blau, K., private comm., 1965

The jet of a sodium press became blocked during use, and the ram was tightened to free it. It suddenly cleared and a piece of sodium wire was extruded, piercing a finger, which had to be amputated because of severe necrosis. Sodium in a blocked die should be dissolved out in a dry alcohol.

See Potassium: Alcohols

### SOLVATED OXOSALT INCIDENTS

1. Bretherick, L., *Chem. Eng. News*, 1983, **61**(50), 2
2. Raymond, K. N., *Chem. Eng. News*, 1983, **61**(49), 4
3. Wolsey, W. C., *J. Chem. Educ.*, 1973, **50**(6), A335
4. Cotton, F. A. *et al.*, *J. Amer. Chem. Soc.*, 1960, **82**, 2986
5. Sandstrom, M. *et al.*, *Acta Chem. Scand.*, 1978, **A32**, 610
6. Cook, R. E. *et al.*, *J. Chem. Res.*, 1982, (S) 267, (M) 2772
7. Forsberg, J. H., *Chem. Eng. News*, 1984, **62**(6), 33
8. Bretherick, L., *Chem. Eng. News*, 1990, **68**(22), 4

Several instances of apparently stable solvated metal perchlorates being converted by partial desolvation into explosively unstable materials indicate that this may be a more common potential hazard than has been realised [1]. Neodymium perchlorate tetra-solvated with acetonitrile (obtained by vacuum evaporation of the solution at ambient temperature) had not been found to be thermally- or shock-sensitive, but when vacuum dried at 80°C to the di-solvate, it exploded violently on contact [2]. Erbium perchlorate tetrasolvated with acetonitrile had likewise appeared stable, but when vacuum dried at 150°C to a glassy solid which still contained some solvent, it too exploded when scraped with a spatula [3]. Mercury(II) perchlorate hexa-solvated with DMSO appears stable [4], but when dried to the tetrasolvate, it is impact- and friction-sensitive [5]. The fact that the solvating species may also be water suggests that this is not a direct effect of a perchlorate oxidising an organic solvent. Thus, cobalt(II) perchlorate hexahydrate is a common commercial (and stable) chemical, but when overheated during final drying which converted it to a trihydrate, the latter exploded under slight impact, and was later shown to be endothermic [6]. It is suggested that there is a need for closer control and documentation of drying procedures for solvated metal perchlorates [1]. An incident is reported where a solution of a lanthanide metal perchlorate in acetonitrile detonated during heating under reflux [7].

A possible explanation of the reduced stability of the lower organic solvates may be connected with the effect of reduced solvation upon the oxygen balance of the salts. Unsolvated metal perchlorates have an apparent balance of +700%, and solvation with 4 mols of acetonitrile reduces this to -46.3%, and with 4 or 6 mols of DMSO to -43% and -28.6% respectively. Desolvation to 2.18 mols of acetonitrile, or to 2.0 mols of DMSO, would give products of zero oxygen balance, with maximum energy release potential [8].

These and related incidents are detailed under:

- † Acetonitrile, : Lanthanide perchlorate, 0758
- Chromium(III) perchlorate . 6 dimethyl sulfoxide
- Cobalt(II) perchlorate hydrates, 4051

- Erbium perchlorate, 4132
- \* Gallium perchlorate, 4135
- Iron(III) perchlorate, 4134
- Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide
- Neodymium perchlorate . 2 acetonitrile, 4148
- Silver perchlorate, 0012

## **SOLVENT CABINETS**

1. Anon., *Sichere Chemiearbeit*, 1997, **49**, 3
2. Editor's Comments

After standing unopened for about a week, an unventilated solvent cabinet exploded violently, starting a fire which burnt out the laboratory. This was considered to have been a vapour/air explosion, not one caused by peroxide accumulation. The source of ignition was not clear, it might have been reactive drying agents. It is stated that the consequences would not have been as serious had the cabinet been ventilated [1]. To judge by the picture, the cabinet was of thin steel, offering negligible protection against heating by external fire. If it was like most of the solvent cabinets and bins known to the editor, the catch will probably also have been internal and made of sparking metal (although this explosion was not initiated by opening). A slight seepage of flammable solvent vapour seeping past a stopper in an open laboratory will be immediately dispersed by the ventilation. In the unventilated cabinets in which solvents have lately been kept, it is claimed as a safety measure, slight seepages of vapour will accumulate until they can form a substantial, enclosed, volume of explosive gases. A solvent cabinet designed for safety would be ventilated, thermally insulated, of non-sparking construction, and with blow-out panels. The majority of those the editor has met are none of these: they are potential explosive charges waiting to blow their door into the face of some unfortunate who sparks the explosion by turning the (sparking) catch [2].

## **SPILLAGES**

1. *How to Deal with Spillages of Hazardous Chemicals*, Poole, BDH Chemicals Ltd., 5th edn, 1986
2. Melvold, R. W. *et al.*, *J. Haz. Mat.*, 1988, *17*, 329–335

A revised wall chart, with standardised disposal procedures for 396 toxic and hazardous chemicals, which is useful in the storeroom as well as in the laboratory [1]. A guidance manual has been developed by EPA in the US to assist in the selection and use of sorbent materials to control industrial spillages of hazardous liquids [2].

## **STARCH**

*NFPA 61A*, Quincy (Ma), National Fire Protection Association, 1989

The new US fire code covers precautions to prevent fires or dust explosions in handling dried starch.

Energy of exothermic decomposition in range 260–340°C was measured as 0.461 kJ/g.

Cornstarch dust may be a dust explosion hazard.

*See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

*See* DUST EXPLOSION INCIDENTS (reference 33)

Calcium hypochlorite, Sodium hydrogensulfate

*See* Calcium hypochlorite: Sodium hydrogensulfate, etc.

Nickel nitrate

*See* METAL NITRATES: organic matter

### STATIC INITIATION INCIDENTS

1. Krämer, H., *Chem. Ing. Tech.*, 1982, **55**, 419–428

2. Schaperklaus, H., Brit. Pat. 2004 476, 1979

3. Cartwright, P., *Chemtech*, 1991, **21**(11), 682

4. Britton, L. G., *Plant/Oper. Progr.*, 1992, **11**(2), 56

The current state of knowledge of charge generation in flowing or sprayed liquids was reviewed with 20 references, and criteria to allow assessment of ignition hazards were presented [1]. The risk of static sparks from thermoplastic bags or sacks was reduced by printing a grid of conductive ink on the surfaces [2]. A review of static electrical problems in the chemical industry, with further references, is found in [3]. Minimum Ignition Energies, with especial reference to electrostatic ignition, with tables of these and electrical properties of organic materials, are covered in [4].

Ignition by static features in the entries:

\* Bis(2-azidobenzoyl) peroxide, 3628

\* Calcium hypochlorite, 3924

Calcium polysulfide, 3942

Chlorine dioxide, 4042

Chlorine, : Hydrogen(?), Sulfuric acid, 4047

† Chloroethylene, 0730

Ethyl acetate, 1618

Iron, : Polystyrene, 4388

Lead(IV) oxide, : Metals, 4834

Methylmercury perchlorate, 0433

Oxygen (Gas), : Biological material, Ether, 4831

Potassium chlorate, : Metal phosphinates, 4017

Potassium perchlorate, 4018

Sodium chlorate, : Paper, Static electricity, 4039

† Trichlorosilane, 4136

Tris(2,2'-bipyridine)chromium(II) perchlorate, 3874

*See also* ADHESIVE LABELS, IGNITION SOURCES, MINIMUM IGNITION ENERGY

## STEAM EXPLOSIONS

Drumheller, D. S., *TOM MIX: A Computer Code for Calculating Steam Explosion Phenomena*, Rept. SAND-81-2520, Richmond (Va), USNTIS, 1982

A mathematical model of the processes leading to steam explosions has been developed for the contact of hot liquids or molten solids dropping into water.

See MOLTEN METAL EXPLOSIONS, SMELT, SUPERHEATED LIQUIDS, VAPOUR EXPLOSIONS

## STEEL

1. Anon., *Fire Prot. Assoc. J.*, 1953, **21**, 53

2. Karim, G. A. *et al.*, *J. Fire Sci.*, 1987, **5**, 272–285

Ignition can occur if steel wool (or a scouring pad) short-circuits the contacts of even a small dry-cell torch battery [1]. The ignition and combustion characteristics of steel wool, loosely packed in wire crates has been investigated in a heated air stream of 4 m/s. Autoignition temperatures above 377°C were recorded [2]. As a structural material, wet steel vessels can deplete the air within of oxygen by rusting, or by autoxidation of ferrous sulfide formed by contact with sulfur-containing materials. This has caused a number of deaths from asphyxiation and the sulfide has ignited several fires. Hydrogen evolution is possible especially in contact with acids. Iron being a good catalyst for many reactions, trouble can also spring from this cause.

See Magnesium chloride: Air, etc., Sulfur dichloride: Iron

### Apricots

Ontario Ministry of Labour, Internet information alert, 1997

A worker was killed while venting a bulging 45 gallon steel drum of apricot concentrate with a grinder. A grinder, the ultimate sparking tool, is not suitable for cutting into bulging food containers, which are more usually pressurised with hydrogen from interior corrosion than by the products of bacterial decay. However, bulging drums can kill without ignition.

See DRUMS

### Silicon dioxide

See Silicon dioxide: Steel

See also RUST

See other IGNITION SOURCES

## STORAGE OF CHEMICALS

1. See entry SAFE STORAGE OF CHEMICALS

2. Anon., *Loss Prev. Bull.*, 1988, (084), 19–22

3. Armstrong, B. S., *Loss Prev. Bull.*, 1988, (084), 23–31

The book is an amplified version of papers presented at the 1982 ACS CHAS Div. Symposium on safe storage of laboratory chemicals. Chap. 2 deals with the segregation of incompatible reactive chemicals on a logical basis [1]. Two accounts



of chemical warehouse fires emphasise the severe problems which arise from lack of proper segregation in storage of chemicals [2,3].

AMMONIUM PEROXODISULFATE: SODIUM SULFIDE  
EARTHQUAKE, SOLVENT CABINETS

### STRAINED-RING COMPOUNDS

Some molecules with small distorted rings (of high strain energy) are explosively unstable. Individually entries are:

- \* 2-Azatricyclo[2.2.1.0<sup>2,6</sup>]hept-7-yl perchlorate, 2368
- † Azetidine, 1255
- Benzvalene, 2289
- Bicyclo[2.1.0]pent-2-ene, 1856
- 2-*tert*-Butyl-3-phenyloxaziridine, 3406
- 3-Chloro-1,3-diphenylcyclopropene, 3679
- 1-Chloro-2,3-di(2-thienyl)cyclopropenium perchlorate, 3388
- Cyanocyclopropane, 1463
- † Cyclopropane, 1197
- † Cyclopropyl methyl ether, 1608
- 2,3:5,6-Dibenzobicyclo[3.3.0]hexane, 3633
- 3,5-Dibromo-7-bromomethylene-7,7a-dihydro-1,1-dimethyl-1H-azirino[1,2-a]indole, 3474
- 2,2'-Di-*tert*-butyl-3,3'-bioxaziridine, 3359
- Dicyclopropyldiazomethane, 2824
- 1,4-Dihydrodicyclop[*b, g*]naphthalene, 3452
- N*-Dimethylethyl-3,3-dinitroazetidine, 2848
- Dinitrogen pentaoxide, : Strained ring heterocycles, 4748
- † 1,2-Epoxybutane, 1609
- † Ethyl cyclopropanecarboxylate, 2437
- 2,2'-(1,2-Ethylenebis)3-phenyloxaziridine, 3707
- † Methylcyclopropane, 1581
- † Methyl cyclopropanecarboxylate, 1917
- † Oxetane, 1222
- Pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane-1,2-dicarboxylic acid, 3261
- 1,2,3,-4,5, or -5,6-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2070
- Poly([7,8-bis(trifluoromethyl)tetracyclo [4.2.0.0<sup>2,8</sup>.0<sup>5,7</sup>]octane-3,4-diyl]-1,2-ethenediyl), 3463
- Prismane, 2294
- Spiro(homocubane-9,9'-diazirine), 3127
- Tetracyclo[4.3.0<sup>3,5</sup>.0<sup>4,6</sup>]nona-1,7-diene, 3125
- 3,6,9-Triazatetracyclo[6.1.0.0<sup>2,4</sup>.0<sup>5,7</sup>]nonane, 2398

See also FURAZAN *N*-OXIDES

### STYRENE-BUTADIENE RUBBER

Emmons, H. W., *J. Appl. Polym. Sci.*, 1981, **26**, 2447-2457

Plioflex rubber heated to above 300°C may ignite spontaneously. The mechanisms of the thermal reactions involved are discussed.

See also RUBBER

## SUGARS

### Air, Base

1. Young, J. A., *Chem. Health & Safety*, 1998, **5**(1), 4
2. Nicloux, M., *Bull. Soc. Chim. Biol.*, 1928, **10**, 1135
3. Young, J. A., private communication, 1979
4. Bretherick, L, *Chem. & Ind.*, 1980, 164; *Chem. Brit.*, 1980, **16**, 184

A fatality from carbon monoxide poisoning is reported while cleaning out a milk tank with an alkaline cleanser [1]. Apparently autoxidation of reducing sugars, including lactose, can produce up to 3,000 ppm of carbon monoxide under moderately alkaline conditions [2]. This is only likely to be hazardous in confined spaces. Warnings of the possibility of poisoning in such circumstances from this curious, long known but little remembered, reaction had been given earlier [3], [4]. Although alkalis are much used in the sugar industry, sucrose is not a reducing sugar.

### Yeast

Dilute solutions of all sugars are subject to fermentation, either by yeast or by other micro-organism, or enzymes derived from these, producing gases which can pressurise and burst sealed containers. Some micro-organisms will produce hydrogen or methane, adding a fire and explosion hazard

See YEAST, CELLULOSE: Water

## SULFINYL AZIDES



Maricich, T. J. *et al.*, *J. Amer. Chem. Soc.*, 1974, **96**, 7771, 7776

Benzene-, *p*-nitrobenzene-, and *p*-toluene-sulfinyl azides are thermally unstable, decomposing explosively when warmed alone or as conc. solutions. They may be prepared safely and handled as solutions at -20°C or below. The isolated solids may be stored at -80°C, but benzenesulfinyl azide explodes at 11°C, and *p*-toluenesulfinyl azide at 8°C. Individually indexed compounds are:

- Benzenesulfinyl azide, 2273
- 4-Nitrobenzenesulfinyl azide, 2204
- 4-Toluenesulfinyl azide, 2780

See other ACYL AZIDES

## SULFONATION INCIDENTS

1. Anon., *Loss Prev. Bull.*, 1979, (030), 159
2. Brogli, F. *et al.*, *Runaway Reactions*, 1981, Paper 3/M, 4-5, 9
3. Quinn, M. E. *et al.*, *Chem. Abs.*, 1985, **102**, 208618

An unspecified sulfonation mass was being held at 160°C for 24 h to distil out water. After 22 h an exothermic reaction set in, and sulfur dioxide and sulfur trioxide were evolved in quantity. It was later found that catalytic impurities had reduced the decomposition temperature considerably [1]. The use of a bench scale heat flow calorimeter to determine safe operating limits for effective sulfonation (reaction unspecified) is described [2]. During start-up of a reactor for continuous sulfonation of an aromatic compound under conditions close to the region of high decompositional activity, a thermal explosion occurred in a pump and recirculation line. After full thermal investigation of the various contributory factors, it was concluded that the decomposition was too violent for emergency venting procedures to be effective, and alternative quenching and/or dumping systems were proposed [3].

See other GAS EVOLUTION INCIDENTS

Other sulfonation incidents will be found in the entries:

- Chlorosulfuric acid, : Hydrocarbons, 3997
- \* 4-Hydroxy-3-nitrobenzenesulfonyl chloride, 2146
- 2-Methoxyanilinium nitrate, 2829
- 3-Nitrobenzenesulfonic acid, 2268
- 4-Nitrotoluene, 2764
- Sulfuric acid, : Tetramethylbenzenes, 4479

See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

## SULFONIC ACID ESTERS

## RSO<sub>2</sub>OR'

1. Collin, D. T. *et al.*, *Chem. & Ind.*, 1987, 60
2. James, D. M., *Comprehensive Organic Chemistry*, Vol. 3, 342, Oxford, Pergamon, 1979
3. Dauben, W. G. *et al.*, *J. Amer. Chem. Soc.*, 1968, **90**, 3835
4. Anon., private comm., 1989

During the distillation at 81–89°C/0.8 mbar of cyclobutylmethyl methanesulfonate from a bath at 120°C, there was a sudden and violent explosion. Thermal instability of the ester was confirmed by heating a small sample at 0.5°C/min, when rapid autocatalytic and exothermic decomposition occurred at 110°C. In an isothermal test at 65°C a sample decomposed vigorously after 48 h. The decomposition involves rapid elimination of cyclopentene, the residue being methanesulfonic acid and polymer. Promotion of the decomposition by presence of added traces of methanesulfonic acid, and inhibition by the presence of sodium hydrogen carbonate confirms a mechanism involving acid catalysis. The ester is also unstable in toluene at 110°C, and in *N,N*-dimethylacetamide or sulfolane at 120°C. If the ester must be stored, this should be done as a 20 wt% solution in *tert*-butyl methyl ether at 0°C in presence of 5 mol% of sodium hydrogen carbonate. Cyclobutyl 4-toluenesulfonate, cyclopentylmethyl methanesulfonate and 1-pentyl methanesulfonate when heated at 0.5°C/min showed similar but slightly less energetic decomposition at 118, 128, and 185°C, respectively [1]. Instability of sulfonates of secondary alcohols is well documented [2]. A sample (25 g) of cyclobutylmethyl 4-toluenesulfonate was prepared by a literature method [3]. Upon attempted vacuum distillation at

0.27 mbar from a 50 ml flask in an oil bath at ca. 150°C, a violent explosion occurred. A sample from a repeat preparation was examined by DSC and at 2°C/min vigorous exothermic decomposition occurred at 140°C [4]. It is calculated that some 3.9 l of cyclopentene vapour at 140°C would cause a pressure surge to 80 bar in a 50 ml closed vessel.

Individually indexed compounds are:

Cyclobutyl 4-methylbenzenesulfonate, 3404

Cyclobutylmethyl methanesulfonate, 2510

Cyclopentylmethyl methanesulfonate, 2867

1-Pentyl methanesulfonate, 2550

*See also* SULFUR ESTERS

### SULFONYL AZIDES



*See* ACYL AZIDES

### SULFUR BLACK

Anon., *Ind. Eng. Chem.*, 1919, **11**, 892

Twenty-four hours after several barrels of the dyestuff were bulked, blended and repacked, spontaneous heating occurred. This was attributed to aerobic oxidation of excess sodium polysulfide used during manufacture.

*See* Sodium sulfide *See other* SELF-HEATING AND IGNITION INCIDENTS

### SULFUR COMPOUNDS

Groups and substances falling within this class are:

*See also* ALKANETHIOLS, ALKENE BIS(SULFONIUM PERCHLORATES) ALLYL TRIFLUOROMETHANESULFONATES, ARENEDIAZO ARYL SULFIDES BIS(ARENEDIAZO) SULFIDES, BIS(SULFURDIIMIDES DIAZONIUM SULFATES, DIAZONIUM SULFIDES AND DERIVATIVES METAL AMIDOSULFATES, METAL PHOSPHORUS TRISULFIDES METAL SULFATES, METAL SULFIDES, NON-METAL SULFIDES SULFONIC ACID ESTERS, SULFUR BLACK, SULFUR ESTERS THIOPHENOXIDES, 'XANTHATES'

### SULFUR ESTERS



The group name is intended to cover esters derived from sulfenic, sulfinic and sulfonic acids, some of which are thermally unstable. This is especially so for esters of unsaturated alcohols, which are also liable to polymerise, catalysed by the liberated acids. Individually indexed compounds are:

Allyl benzenesulfonate, 3155

Allyl 4-toluenesulfonate, 3315

Bis(trimethylsilyl) peroxomonosulfate, 2602

2-Buten-1-yl benzenesulfonate, 3316

- 3-Butyn-1-yl 4-toluenesulfonate, 3399
  - 2-Chloro-2-propenyl trifluoromethanesulfonate, 1426
  - Cyclobutyl 4-methylbenzenesulfonate, 3404
  - Cyclobutylmethyl methanesulfonate, 2510
  - Cyclopentylmethyl methanesulfonate, 2867
  - Diallyl sulfate, 2443
  - Diethyl sulfate, 1710
  - Diethyl sulfite, 1709
  - 1,10-Di(methanesulfonyloxy)deca-4,6-diyne, 3543
  - \* Dimethyl selenate, 0930
  - † Dimethyl sulfate, 0929
  - Dimethyl sulfite, 0927
  - Ethyl 3,4-dihydroxybenzenesulfonate, 2988
  - Ethyl fluorosulfate, 0856
  - \* 2-Isocyanoethyl benzenesulfonate, 3143
  - \* *N*-Methyl-*p*-nitroanilinium 2(*N*-methyl-*N*-*p*-nitrophenylaminosulfonyl)ethylsulfate, 3713
  - 1-Pentyl methanesulfonate, 2550
  - Prop-2-enyl trifluoromethanesulfonate, 1461
  - \* Silyl trifluoromethanesulfonate, 0444
  - Trifluoroacetyl trifluoromethanesulfonate, 1057
  - 3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2847
  - \* Zinc ethylsulfinate, 1711
- See* ALLYL TRIFLUOROMETHANESULFONATES

## SUNSPOTS

Ye, Y. *et al.*, *Proc. 18th Int. Pyrotech. Semin.*, 1992, 1019

It is claimed that accidents in the Chinese pyrotechnic industry peak with the sunspot cycle

## SUPERHEATED LIQUIDS

1. Reid, R. C., *Superheated Liquids, A Laboratory Curiosity and, Possibly, an Industrial Curse*, *Chem. Eng. Educ.*, 1978, 60–63, 83–87; 108–111, 127–129; 194–196, 203–206

2. Reid, R. C., *Science*, 1979, **203**(4386), 1263–1365

This comprehensive survey of the title topic is in three parts, the first dealing with the theoretical background and laboratory studies, with 29 references. The second part, with 21 references deals with case histories and experimental studies of industrial vapour explosions. These involved the systems molten titanium–water, molten copper–water, molten aluminium–water, smelt–water, water–various cryogenic liquids, molten salt–water and molten uranium dioxide–liquid sodium. In the third part (with a further 26 references) is discussion of the various theories which abound, and the general conclusion that superheated liquids most likely play a major role in all these phenomena [1]. A further related publication covers BLEVES and pressure let-down explosions [2].

*See* LIQUEFIED GASES, LIQUEFIED NATURAL GAS, MOLTEN METAL EXPLOSIONS, SMELT, VAPOUR EXPLOSIONS

### **SUPERIORS/SUPERVISORS**

Can be a source of hazard. Some may react violently to suggestions that they are not omniscient. Suggested reactions should never be undertaken without investigating safety factors, not even if the editor is the superior in question.

### **TETRAAZAMACROCYCLANEMETAL PERCHLORATES**

Hung, Y., *Inorg. Synth.*, 1980, **20**, 112–113

The dichlorocobalt(IV) perchlorate salts complexed with [15] ane-N<sub>4</sub> and [16] ane-N<sub>4</sub> are described as potentially explosive.

*See also* POLYAZACAGED METAL PERCHLORATES, AMMINEMETAL OXOSALTS

### **TETRAHYDROPYRANYL ETHER DERIVATIVES**

Meyers, A. I. *et al.*, *Tetrahedron Lett.*, 1976, 2417–2418

The tetrahydropyranyl group, commonly used in synthetic procedures to protect hydroxyl groups, appears not to be safe when peroxidising reagents are used with tetrahydropyranyl ether derivatives, because explosive peroxides, not destroyed by the usual reagents, are produced.

The hydroboration product of 2-methyl-2-propenyl tetrahydropyranyl ether was routinely oxidised with alkaline hydrogen peroxide, then treated with sodium sulfite solution during work-up. The product gave a negative test for peroxides but exploded violently during attempted distillation at 0.06 mbar from a vessel at 120°C. Epoxidation of 3-methyl-3-butenyl tetrahydropyranyl ether with peroxyacetic acid gave, after sulfite treatment, an apparently peroxide-free product. However, after distillation at 1 mbar, the fore-run (b.p. 40–70°C) exploded violently when the flask was disturbed. The main fractions were found subsequently to give strong positive indications for the presence of peroxides which were only removed after prolonged treatment with sodium thiosulfate. (There is some evidence to suggest that sodium sulfite may under certain circumstances actually promote peroxide formation.)

Other acetal-type protecting groups (tetrahydrofurfuryl ethers, methoxymethyl ethers, 1,3-dioxolanes) are also considered to be incompatible with oxidising agents.

*See other* PEROXIDISABLE COMPOUNDS

### **TETRA(N-METHYLPYRIDYL)PORPHINE PERCHLORATES**

Reid, J. B. *et al.*, *Inorg. Chem.*, 1977, **16**, 968

Variously metallated derivatives of the porphine nitrate were converted to the perchlorate salts, but several exploded during drying. The need for great caution in attempting to prepare the anhydrous perchlorates is stressed.

*See* Tetrakis(4-N-methylpyridinio)porphinecobalt(III)(5+) perchlorate

*See other* AMMINEMETAL OXOSALTS

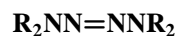
## TETRAMETHYL [14] TETRAENE-N<sub>8</sub> METAL PERCHLORATES

Peng, S.-M. *et al.*, *Inorg. Chem.*, 1978, **17**, 120

The perchlorate salts of the complexes with divalent cobalt, nickel, and particularly iron (analogous to IV, p. S-15) are potentially explosive, and storage for more than 4 weeks is not advised.

See [14] DIENE-N<sub>4</sub> COMPLEXES, AMMINOMETAL OXOSALTS

## TETRAZENES



Houben Weyl, 1967, 10/2, 828

Several compounds of this class explode forcefully on heating, the tetramethyl and tetraallyl derivatives are specifically mentioned.

Individual compounds are:

1-Acetyl-4-(4'-sulfophenyl)-3-tetrazene, 2982

1-Ethyl-1,1,3,3-tetramethyltetrazenium tetrafluoroborate, 2586

3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2804

Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide, 2256

Tetraallyl-2-tetrazene, 3545

Tetramethyl-2-tetrazene, 1759

See HIGH NITROGEN COMPOUNDS

## TETRAZOLES



1. Benson, F. R., *Chem. Rev.*, 1947, **41**, 4–5
2. Morisson, H., *Util. Elem. Pyrotech. Explos. Syst. Spatiaux, Colloq. Int. 1968* (publ. 1969), 111–120
3. Schroeder, M. A., *Rept. AD-A018652*, Richmond (Va.), USNTIS, 1975
4. Grimmett, M. R.; *Barton & Ollis*, 1979, Vol. 4, 364
5. Matsuzawa, T. *et al.*, *Loss Prevention and Safety Promotion in the Process Industries*, (Mewis, Pasman and De Rademaker: Eds), Vol II, 315, Amsterdam, Elsevier, 1995

There is a wide variation in thermal stability in derivatives of this high-nitrogen nucleus, and several show explosive properties [1]. The characteristics of explosive tetrazole salts have been summarised [2], and the relationship between structure and reactivity of isomeric 1- and 2-tetrazole derivatives has been reviewed in a ballistics context [3]. It is claimed that tetrazole diazonium salts detonate, in water, at concentrations little above 2%, at 0°C [4]. A sensitivity study has been made of numerous tetrazoles, their salts, and compositions thereof with oxidants, as gas generators for airbags. Salts are less sensitive than the parent tetrazoles. Mixtures with potassium perchlorate are both more energetic and more sensitive, those with potassium nitrate are usually similar, though some are less sensitive to electric discharge. In the absence of oxidants, hydrogen cyanide is a frequent decomposition product [5]. Individually indexed compounds are:

5-Amino-2-ethyl-2*H*-tetrazole, 1268

5-Aminotetrazole, 0461

5-Azidotetrazole, 0388  
 Barium 5,5'-azotetrazolide, 0577  
 1,6-Bis(5-tetrazolyl)hexaaza-1,5-diene, 0827  
*N*-Chloro-5-phenyltetrazole, 2674  
 Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1429  
 5-Cyano-2-methyltetrazole, 1120  
 2(5-Cyanotetrazole)pentaamminecobalt(III) perchlorate, 0974  
 5-(Diazomethylazo)tetrazole, 0719  
 5-Diazoniotetrazolide, 0548  
 1-Dichloroaminotetrazole, 0371  
 1,2-Dihydropyrido[2,1-*e*]tetrazole, 1834  
 5-(4-Dimethylaminobenzeneazo)tetrazole, 3161  
 Disodium 5,5'-azotetrazolide, 1018  
 \* Disodium 5,5'-azoxytetrazolide, 1019  
 Disodium 5-tetrazolazocarboxylate, 1012  
 Disodium tetrazole-5-diazoate, 0549  
 1,3-Di(5-tetrazolyl)triazene, 0778  
 Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2359  
 2-Ethyltetrazole, 1213  
 5-Ethyltetrazole, 1214  
 5,5'-Hydrazotetrazole, 0826  
 Lead 5,5'-azotetrazolide, 1020  
 Mercury 5,5'-azotetrazolide, 0980  
 Mercury(II) 5-nitrotetrazolide, 0981  
 2-Methyltetrazole, 0814  
 2-Methyl-5-vinyltetrazole, 1511  
 1-(2-Naphthyl)-3-(5-tetrazolyl)triazene, 3394  
 5-*N*-Nitroaminotetrazole, 0415  
 1-(2-Nitrophenyl)-5-phenyltetrazole, 3602  
 5-Nitro-2-picryltetrazole, 2638  
 5-Nitrotetrazole, 0387  
 \* Pentazole, 4443  
 5-Phenyltetrazole, 2727  
 3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2804  
 Potassium 1-tetrazolacetate, 1106  
 Silver 5-aminotetrazolide, 0392  
 Silver 1,3-di(5-tetrazolyl)triazenide, 0690  
 Silver tetrazolide, 0366  
 Sodium 5-azidotetrazolide, 0551  
 Sodium 5-(dinitromethyl)tetrazolide, 0681  
 Sodium 5(5'-hydroxytetrazol-3'-ylazo)tetrazolide, 0682  
 Sodium 5-nitrotetrazolide, 0547  
 Sodium 1-tetrazolacetate, 1119  
 1,3,4,6-Tetrakis(2-methyltetrazol-5-yl)-hexaaza-1,5-diene, 3013  
 Tetrazole, 0411  
 Tetrazole-5-diazonium chloride, 0370



5-Trichloromethyltetrazole, 0657  
5-Trichloromethyl-1-trimethylsilyltetrazole, 1927  
*See other* HIGH-NITROGEN COMPOUNDS

### TEXTILE CLOTHING STATIC CHARGES

Wilson, N., *J. Electrostat.*, 1977, **4**, 67–84

The clothing worn by a process operator insulated from earth may develop static charges far higher (up to 100-fold) than the minimum ignition energies for various flammable gas–air mixtures. This is true for a wide range of clothing materials including cotton. Dangerous levels of charge may be avoided by ensuring a low resistivity of the surface material worn outermost.

*See other* IGNITION SOURCES

### THERMAL EXPLOSIONS

Verhoeff, J., *Experimental Study of the Thermal Explosion of Liquids*, Doctoral Thesis, University of Delft, 1983

In a study of the course of thermal explosions in low, high and constant pressure autoclave experiments, 3 stages of thermal runaway, initiation and explosion were identified and studied in detail. Most of the work was done with *tert*-butyl peroxybenzoate, but limited comparative examinations were carried out on 8 other energetic substances.

### THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

1. Grewer, T., *Chem. Ing. Tech.*, 1975, **47**, 230–235
2. Hartgerink, J. W., *Proc. 3rd Symp. Chem. Probl. Connected Stab. Explos.* 1973, (publ. 1974), 220–230
3. Grewer, T., *Chem. Abs.*, 1980, **93**, 210923
4. Tyler, B. J., *Chem. Brit.*, 1981, **17**, 274, 276
5. O'Brien, G. J., *Chem. Eng. Progr.*, 1982, 78(1), 46–49
6. Fierz, H. *et al.*, *Chem. Engr.*, 1984, **400**, 9–10
7. Gibson, N., *Chem. & Ind.*, 1984, 209–211
8. Smith, C. D., *Chem. Eng. Progress*, 1994, **90**(9), 67

The importance of gaining knowledge on the reaction parameters of exothermic reaction systems to assess potential processing hazards is discussed in detail. The roles of DTA, adiabatic storage tests and adiabatic reaction tests were discussed, and suitable techniques described with reference to practical examples of thermally unstable systems [1]. Two storage tests (adiabatic storage and isothermal heat generation) were described which give information on the induction period of instability. An exothermal decomposition meter, with 100-fold higher sensitivity than DTA is described [2]. The importance of the relationship between reaction energy and reaction rate for batch reactions, and of the factors which may lead to reaction delays and instability, and of secondary reactions, are discussed and exemplified [3].

The safety margin between reaction stability and runaway may be as little as 10–20°C, and this may be diminished or eliminated by apparently minor changes (higher initial temperature or concentration, better catalysts, less stirring or cooling capacity) in processing conditions [4]. A standardised review procedure to identify and eliminate factors likely to lead to reaction instability is described [5]. Application of the bench scale heat flow calorimeter to the overall problems of ensuring stability in chemical processing operations is discussed with examples [6]. The advantages to be gained by using a range of tests to identify potential processing hazards are outlined [7]. Considerations of explosion and detonation are expounded. A quick simple scanning procedure for detecting self-heating to explosion is detailed, much cheaper than Accelerating Rate Calorimetry. There is also a test for transition from deflagration to detonation (though this will only detect materials of greater detonability than most explosives) [8].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

### THERMITE REACTIONS

1. Bond, 1991, 63
2. Gibson, N. *et al.*, *Proc. 3rd Symp. Chem. Proc. Haz. Ref. Plant Des.*, 26–35, London, IChE, 1968
3. Britten, G. C., *School Sci. Rev.*, 1976, **57**(201), 732
4. Hadfield, J. M., *School Sci. Rev.*, 1980, **62**(219), 394
5. Bozzelli, J. W. *et al.*, *J. Chem. Educ.*, 1979, **54**, 675–676
6. Roebuck, P. J., *Educ. Chem.*, 1979, **16**, 178–179
7. Ivanov, G. V. *et al.*, *Chem. Abs.*, 1979, **91**, 76323
8. Billinge, K., *Fire Prev. Sci. Technol.*, 1981, (24), 13–19
9. Shidlovskii, A. A. *et al.*, *Chem. Abs.*, 1983, **98**, 18942
10. Eastland, G. W., *J. Chem. Educ.*, 1984, **61**, 723
11. Zumdahl, S. S., *Chem. Eng. News*, 1990, **68**(20), 2  
Fawcett, H. *et al.*, *CHAS Notes*, 1990, **VIII**(3), 2
12. Ismailov, M. B., *et al.*, *Fizika Goreniya i Vzryva*, 1992, **28**(1), 46  
Filatov, B. M., *et al.*, *ibid.* 53
13. Wright, S. W., *J. Chem. Educ.*, 1994, **71**(3), 251

The name given to reaction of a very electropositive metal with the oxide of a less active one, producing the less electropositive metal, usually incandescent. Archetypally a reaction between aluminium and iron oxide, now applied to a variety of similar combinations. Thermite reactions of rusty iron falling on other metals, especially magnesium protective electrodes, are a source of ignition of fires on oil tankers. Aluminium paint is only a danger if it has previously been to 150°C, the risk remains on cooling, bulk aluminium and alloys do spark fires, as can titanium [1]. The conditions under which incendive sparks are generated by impact of a striker with an aluminium smear on rusted steel were investigated. This was part of a comprehensive series of experiments to assess the importance of the variables and the mechanism of the process which leads to ignition of flammable materials in chemical plant environments [2]. Further to an earlier publication on the use of transition metal oxides in school demonstrations of thermite reactions [3], it was

stressed that use of manganese dioxide with aluminium may lead to explosion [4]. The use of potassium permanganate–glycerol mixture to ignite thermite mixture is more reliable than the magnesium ribbon/barium oxide:aluminium igniter [5].

Safety aspects are detailed for practical demonstrations of thermite reactions of aluminium with various oxides of chromium, cobalt, copper, iron, manganese, and nickel. The molar heat of reaction is maximal for  $\text{Fe}_3\text{O}_4$ , but the exotherm on a weight basis is maximal for the stoichiometric mixture with  $\text{MnO}_2$  at 4.8 kJ/g [6]. The dependence of the burning rate on pressure (1–80 kbar) was studied for mixtures of magnesium, zinc or zirconium with barium dioxide, chromium(III) oxide, iron(III) oxide, manganese dioxide, molybdenum trioxide, lead dioxide or vanadium pentoxide [7]. Combustion mechanisms for aluminium thermites with chromium(III) and Ni(II) oxides, also with silica, have been studied [12]. Five incidents in a survey of frictional ignition hazards probably involved thermite reactions [8], and the combustion rate of nickel oxide–aluminium mixtures is 2.5-fold greater than iron oxide mixtures [9]. Precautions necessary to activate large-scale (6 kg of mixture!) spectacular demonstrations are detailed [10]. Caution is given against conducting thermite demonstrations over water, or wet sand, after a lecture/demonstration audience were showered with hot iron [11]. A second-hand report of what is almost certainly the same incident claims that the front row of seats was pulverised—tales seldom lessen in the telling. Not only metal oxides but some halides undergo thermite type reactions with aluminium or magnesium [13]. Individually indexed examples are:

Aluminium, : Metal oxides, etc., 0048

Aluminium, : Sodium sulfate, 0048

Aluminium–magnesium alloy, : Iron(III) oxide, Water, 0053

Calcium acetylide, : Iron(III) chloride, Iron(III) oxide, 0585

Copper(I) oxide, : Aluminium, 4288

Iron(II,III) oxide, : Aluminium, Sulfur, 4405

Magnesium, : Metal oxides, 4690

Magnesium, : Metal oxosalts, 4690

Magnesium, : Rusty steel, 4690

Manganese(IV) oxide, : Aluminium, 4705

*See other* REDOX REACTIONS

*See also* VAPOUR EXPLOSIONS

## THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

1. Grever, T. *et al.*, *Proc. 4th Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, A1–A11, Rugby, IChE, 1983
2. Grever, T. *et al.*, *Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

The difficulties in relating the calculated thermodynamic energy of decomposition ( $-\Delta U$ ) to that occurring in practice are discussed, and values of the experimentally observed energies of decomposition for some characteristic molecular structures are tabulated in comparison with the calculated values. A second table gives the range of decomposition energies which have been measured by DSC for

10 series of compounds each containing the same characteristic molecular structural group(s). These values are:— nitro, 220–410 kJ/mol (in 30 nitro compounds, with dinitro towards the top of the range); nitroso, 90–290 (4); oxime, 170–230 (2); isocyanate, 20–30 (3); azo, 100–180 (5); hydrazo, 65–80 (3); diazonium, 130–165 (5); peroxide, 200–340 (20); epoxide, 45–80 (3); double bond, 40–90 (6). The reasons for the observed variation in these energies of decomposition are discussed.

The relationships between energy of decomposition and processing hazards are then considered, and the practical importance of using values of energy released per unit mass, rather than on a molar basis is stressed, and the decomposition energies in J/g are given in a further table. Finally it is suggested that in ‘open vessel’ processes (with man-hole sized opening), substances with exothermic decomposition energies below 500 J/g are not likely to be hazardous, but that in ‘closed vessel’ processes (opening is a safety valve or bursting disk), an upper limit of 150 J/g might be appropriate [1]. (Some of the alkali chlorate decomposition explosions experienced in, effectively open, bulk storage must have been of lower energy than 500 J/g — editor’s comment.)

In a comprehensive investigation of exothermic decomposition, the thermal behaviour of a further 105 reactive compounds (included below) in 18 classes was investigated by DSC, and the heats of decomposition so determined were tabulated. Of these compounds, 39, together with 21 other compounds, were investigated in detail in a series of adiabatic Dewar tests to examine the relationship between adiabatic temperature and induction time to exothermic decomposition. The adiabatic holding temperature which gives a time to exothermic decomposition of 24 hours has been proposed as a new practical characteristic for the particular compound. This temperature ‘ $T_{ait24}$ ’ can be calculated from isothermal DTA diagrams [2], and this temperature is given in the text entries in this volume for the 60 compounds investigated.

Some other examples may be found in the entries:

- Acetohydrazide, 0912
- Acetone oxime, 1258
- Acetylenedicarboxylic acid, 1405
- † Acrylaldehyde, 1145
- † Allyl acetate, 1912
- N*-Allylthiourea, 1600
- 4-Aminophenylazobenzene, 3487
- Ammonium dichromate, 4246
- Ammonium peroxodisulfate, 4576
- 4-Azidobenzaldehyde, 2697
- 2-Azido-2-phenylpropane, 3159
- † Aziridine, 0863
- Azobenzene, 3483
- Azoformamide, 0816
- Azoisobutyronitrile, 3011
- Azoxybenzene, 3485
- Benzaldehyde oxime, 2760

Benzyl chloride, 2738  
4-Bromoaniline, 2296  
2-Bromocyclohexanone, 2392  
Butane-2,3-dione dioxime, 1595  
† Butyl isocyanate, 1931  
Chloroacetamide, 0788  
4-Chloro-2-aminophenol, 2303  
2-Chloroaniline, 2300  
3-Chloroaniline, 2301  
4-Chloroaniline, 2302  
4-Chloro-1,2-benzenediamine, 2347  
4-Chloro-1,3-benzenediamine, 2348  
4-Chloro-2,6-diamino-*N*-methylaniline, 2822  
1-Chloro-2,4-dinitrobenzene, 2098  
† 1-Chloro-2,3-epoxypropane, 1162  
3-Chloro-4-methoxyaniline, 2795  
2-Chloronitrobenzene, 2141  
4-Chloronitrobenzene, 2142  
2(3-Chlorophenoxy)ethylamine, 2976  
*N*-Chlorosuccinimide, 1427  
*N*-Chlorotoluene-4-sulfonamide, 2797  
Dibenzoyl peroxide, 3639  
2,4-Dibromoaniline, 2226  
2,3-Dichloroaniline, 2237  
2,4-Dichloroaniline, 2238  
2,5-Dichloroaniline, 2239  
3,4-Dichloroaniline, 2241  
*N,N*-Dichlorobenzenesulfonamide, 2244  
2,4-Dimethoxyaniline, 2998  
3,5-Dimethoxyaniline, 2999  
Dimethyl acetylenedicarboxylate, 2340  
*N,N*-Dimethyl-2-chloroacetamide, 1585  
† 1,1-Dimethylhydrazine, 0954  
*N,N*-Dimethyl-4-nitrosoaniline, 2980  
† Dimethyl sulfoxide, 1588  
2,4-Dinitroaniline, 2277  
1,3-Dinitrobenzene, 2195  
2,4-Dinitrophenol, 2197  
3,5-Dinitro-2-toluamide, 2941  
2,4-Dinitrotoluene, 2726  
† 1,4-Dioxane, 1617  
1,2-Diphenylhydrazine, 3517  
1,1-Diphenylhydrazinium chloride, 3519  
1,3-Diphenyltriazene, 3506  
2,3-Epoxypropanol, 1229  
† Ethylene oxide, 0829

Fumaric acid, 1446  
Fumarodinitrile, 1397  
Glucose, 2518  
Glutarodinitrile, 1870  
Hydroxylaminium sulfate, 4575  
*N*-Hydroxysuccinimide, 1469  
Maleic anhydride, 1404  
Maleimide, 1418  
Malononitrile, 1078  
2-Methoxyaniline, 2816  
3-Methoxyaniline, 2817  
4-Methoxyaniline, 2818  
3-Methoxybenzylamine, 2997  
† 2-Methoxyethylamine, 1312  
4-Methoxy-1,3-phenylenediamine, 2826  
3-Methoxypropylamine, 1730  
1-Naphthyl isocyanate, 3390  
2-Nitroaniline, 2313  
3-Nitroaniline, 2314  
4-Nitroaniline, 2315  
2-Nitrobenzaldehyde, 2686  
3-Nitrobenzaldehyde, 2687  
4-Nitrobenzaldehyde, 2688  
Nitrobenzene, 2262  
2-Nitrobenzoic acid, 2693  
3-Nitrobenzoic acid, 2694  
4-Nitrobenzoic acid, 2695  
4-Nitrobenzyl chloride, 2714  
4-Nitrodiphenyl ether, 3472  
2-Nitrophenol, 2265  
3-Nitrophenol, 2266  
4-Nitrophenol, 2267  
Nitrosobenzene, 2261  
*N*-Nitrosodiphenylamine, 3486  
1-Nitroso-2-naphthol, 3250  
2-Nitrosophenol (1,2-Benzoquinone monoxime), 2263  
4-Nitrosophenol (1,4-Benzoquinone monoxime), 2264  
2-Nitrotoluene, 2763  
4-Nitrotoluene, 2764  
3-Phenoxy-1,2-epoxypropane, 3150  
Phenyl azide, 2271  
2-Phenylethyl isocyanate, 3139  
Phenylhydrazine, 2373  
Phenyl isocyanate, 2685  
Poly(vinyl alcohol), 0831  
Potassium hydrogen acetylenedicarboxylate, 1382

Potassium peroxodisulfate, 4668  
† 2-Propen-1-ol, 1223  
† Propylene oxide, 1225  
Pyridine *N*-oxide, 1849  
Sodium azide, 4758  
Sodium chloroacetate, 0694  
Sodium methoxide, 0464  
Sodium 3-nitrobenzenesulfonate, 2184  
Sodium peroxodisulfate, 4809  
Sodium trichloroacetate, 0608  
Styrene, 2945  
Sucrose, 3558  
1,2,4-Triazole, 0769  
2,3,4-Trichloroaniline, 2163  
Trimethylamine oxide, 1313  
2,4,6-Trinitrotoluene, 2701

*See also* CELLULOSE

*See* CALORIMETRY, THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

*See also* EXOTHERMICITY

## THIOPHENOXIDES

ArS<sup>-</sup>

Diazonium salts

*See* DIAZONIUM SULFIDES AND DERIVATIVES (reference 9)

## THORIUM FURNACE RESIDUES

Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 163

Many furnace residues (fine powders and salts) deposited in the upper parts of furnaces used for thorium melting operations, are highly pyrophoric and often ignite as the furnace is opened. Such residues may be rendered safe by storage under water for 60–90 days. If the water is drained off early, ignition may occur.

*See other* PYROPHORIC MATERIALS

## TOLLENS' REAGENT

1. Green, E., *Chem. & Ind.*, 1965, 943
2. Waldman, H., *Chimia*, 1959, **13**, 297–298
3. Coltoff, W., *Chem. Weekblad*, 1932, **29**, 737
4. MCA Guide, 1972, 319
5. Breedlove, C. H. *et al.*, *J. Coll. Sci. Teach.*, 1983, **12**, 281
6. Klinger, G. S., *et al.*, *Chem. Eng. News* 1996, **74**(2), 2

This mixture of ammoniacal silver oxide and sodium hydroxide solution is potentially dangerous, because if kept for a few hours it deposits an explosive precipitate. This danger was described by Tollens in 1882 but is not generally known now. Prepare the reagent just before use, in the tube to be used for the test, and discard

immediately after use, **NOT** into a container for silver residues [1]. Several earlier references to hazards of storing the reagent before or after use are discussed [2]. On one occasion a violent explosion of the reagent occurred 1 h after preparation and before a precipitate had formed [3], and on another, an empty but unrinsed test tube exploded when picked up [4]. Attempts to recover silver from a batch of the reagent of indeterminate age (!) caused explosions [5].

*See* FULMINATING METALS, SILVERING SOLUTIONS

### TOXIC HAZARDS

While toxic hazards have been specifically excluded from consideration in this Handbook, such hazards are at least as important as reactive ones, and particularly on a long-term basis. Due account of toxic hazards must therefore be taken in planning and executing laboratory work, particularly if unfamiliar materials are being brought into use.

It is perhaps appropriate to point out that many of the elements or compounds listed in this Handbook are here because of a high degree of reactivity towards other materials. It may therefore broadly be anticipated that under suitable circumstances of contact with animal organisms (including readers), a high degree of interaction will ensue, with possible subsequent onset of toxic or other deleterious effects.

*See* APROTIC SOLVENTS

### TRIALKYLALUMINIUMS

**R<sub>3</sub>Al**

Basyrov, Z. B. *et al.*, *Chem. Abs.*, 1988, **109**, 215294

In a review of the fire and explosibility hazards of this group, data on 15–50% solutions of trimethyl- and triisobutyl-aluminium in isopentane and in hexane are given.

A highly reactive group of compounds, of which the lower members are extremely pyrophoric, with very short ignition delays of use in rocket- or jet-fuel ignition systems. Storage stability is generally high (decomposition with alkene and hydrogen evolution begins above about 170–180°C), but branched alkylaluminiums (notably triisobutylaluminium) decompose above 50°C. Individually indexed compounds, many commercially available in bulk, are:

3-Buten-1-ynyldiethylaluminium, 3017

3-Buten-1-ynyldiisobutylaluminium, 3549

\* Diethyl-3-diethylaminopropylaluminium, 3414

† Triethylaluminium, 2553

† Triisobutylaluminium, 3568

Triisopropylaluminium, 3214

Trimethylaluminium, 1291

Tripopylaluminium, 3215

\* Tris(trimethylsilylmethyl)aluminium, 3584

\* Tris(trimethylsilylmethyl)indium, 3585

### TRIALKYLANTIMONY HALIDES

**R<sub>3</sub>SbX**

Leleu, *Cahiers*, 1977, (88), 361



These ignite spontaneously in air.  
*See other* ALKYL METAL HALIDES

### TRIALKYL BISMUTHS

**R<sub>3</sub>Bi**

#### Oxidants

Gilman, H. *et al.*, *Chem. Rev.*, 1942, **30**, 291

The lower alkylbismuths ignite in air, and explode in contact with oxygen, or concentrated nitric or sulfuric acids. Individually indexed compounds are:

Tributylbismuth, 3571

Triethylbismuth, 2561

\* Trivinylbismuth, 2391

*See other* ALKYL METALS

### TRIALKYL SILILOXY ORGANOLEAD DERIVATIVES

**R<sub>3</sub>SiOPbR'<sub>3</sub>**

Houben-Weyl, 1975, Vol. 13.7, 118

Compounds containing Si–O–Pb bonds may interact explosively with oxygen at about 140°C, or with aluminium chlorides, acyl halides or anhydrides.

*See related* ALKYL METALS, ALKYL NON-METALS

### TRIAZENES

**RN=N–NR'R''**

1. Houben Weyl, 1967, 10/2, 827

2. Houben-Weyl, 1965, Vol. 10.3, 700, 717, 722, 731

3. Vaughan, K. *et al.*, *Chem. Soc. Rev.*, 1978, **7**, 378–379

4. White, E. H. *et al.*, *Org. Synth.*, 1973, Coll. Vol. 5, 797

5. Rondevstedt, C. S. *et al.*, *J. Org. Chem.*, 1957, **22**, 200

Care is required with these compounds since many explode on heating [1]. A number of triazene derivatives bearing hydrogen, or cyano, hydroxy or nitroso groups on the terminal nitrogen of the chain are unstable, mainly to heat [2]. Purification of triazenes by vacuum sublimation carries the risk of explosion [3]. Further examples of unstable triazenes and precautions are given [4,5].

Individually indexed compounds are:

\* 1-Acetyl-4-(4'-sulfophenyl)-3-tetrazene, 2982

1-Benzyl-3-(4-tolyl)triazene, 3657

1,3-Bis(phenyltriazeno)benzene, 3757

Copper(II) 1,3-di(5-tetrazolyl)triazene, 1429

3,3-Dimethyl-1-phenyltriazene, 2996

3,3-Dimethyl-1-(3-quinolyl)triazene, 3398

1,3-Dimethyltriazene, 0945

\* 1,5-Diphenylpentaazadiene, 3507

1,3-Diphenyltriazene, 3506

1,3-Di(5-tetrazolyl)triazene, 0778

3-Ethyl-1(4-methylphenyl)triazene, 3171

1-(4-Methoxyphenyl)-3-methyltriazene, 3000

1-(2-Naphthyl)-3-(5-tetrazolyl)triazene, 3394

N-Phenylazopiperidine, 3407

1-Phenyl-3-*tert*-butyltriazene, 3335  
Silver 3-cyano-1-phenyltriazene-3-ide, 2670  
Silver 1,3-di(5-tetrazolyl)triazene, 0690

See 3-CYANOTRIAZENES

3-HYDROXYTRIAZENES

3-NITROSOTRIAZENES

See other HIGH-NITROGEN COMPOUNDS

## TRIAZOLES

1. Wilson, W. S. *et al.*, *Austr. J. Chem.*, 1992, **45**(3), 513, 525
2. Grimmett, M. R.; *Barton & Ollis*, 1979, Vol. 4, 364

For a study of nitrophenylbenzotriazoles as explosives, the triazole ring conferring impact sensitivity, see [1]. Simpler nitro- and azido-triazoles also find explosive use. On heating to above 260°C, 1,2,3-triazole halides explode violently [2]. Several examples of instability among this group of relatively high-nitrogen compounds may be found under the entries:

- 4-Amino-4*H*-1,2,4-triazole, 0812
- 5-Amino-3-phenyl-1,2,4-triazole, 2952
- Ammonium 3,5-dinitro-1,2,4-triazolide, 0823
- 3-Azido-1,2,4-triazole, 0717
- 3,3'-Azo-(1-nitro-1,2,4-triazole), 1401
- Benzotriazole, 2269
- 1,3-Bis(5-amino-1,3,4-triazol-2-yl)triazene, 1576
- Bis(1-benzo[*d*]triazolyl) carbonate, 3598
- Bis(1-benzo[*d*]triazolyl) oxalate, 3629
- \* Bis(1-methylbenzotriazole)cobalt(II) nitrate, 3652
- N*-Chloro-4,5-dimethyltriazole, 1490
- 5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1345
- 4-Diazo-5-phenyl-1,2,3-triazole, 2910
- 3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2909
- 4-Diazo-1,2,3-triazole, 0678
- 3-Diazo-3*H*-1,2,4-triazole, 0677
- 4,6- or 5,6- or 5,7-Dinitro-1-picrylbenzotriazoles, 3439
- Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1853
- \* 5-Hydrazino-1,2,3,4-thiatriazole, 0462
- 1-Hydroxybenzotriazole, 2272
- 4-Hydroxy-3,5-dimethyl-1,2,4-triazole, 1575
- 1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0817
- \* 5-Methoxy-1,2,3,4-thiatriazole, 0773
- 1-Methyl-1,2,3-triazole, 1189
- 4-Nitroamino-1,2,4-triazole, 0777
- 4-Nitro-1-picryl-1,2,3-triazole, 2886
- 3-Nitro-1,2,4-triazolone, 0716
- 1-Picryl-1,2,3-triazole, 2893
- Silver benzo-1,2,3-triazole-1-oxide, 2127

1,2,3-Triazole, 0768

1,2,4-Triazole, 0769

1,2,4-Triazole-3-diazonium nitrate, 0680

*See other* HIGH-NITROGEN COMPOUNDS

### TRICARBONYL(CYCLOPENTADIENYL)SILYLMETAL COMPLEXES

Hagen, A. P. *et al.*, *Inorg. Synth.*, 1972, **17**, 104

During the preparation of the complexes of chromium, molybdenum and tungsten from  $K[M(CO)_3C_5H_5]$  and bromosilane, the residues from sublimation of the products are all pyrophoric.

*See related* CARBONYLMETALS, ORGANOMETALLICS

### *N,N,N''*-TRIFLUOROAMIDINES

—C(NF)NF<sub>2</sub>

Ross, D. L. *et al.*, *J. Org. Chem.*, 1970, **35**, 3093

This group of compounds, (which combines the structural features of both the separately treated *N*-HALOIMIDES and DIFLUOROAMINO COMPOUNDS, each of high reactivity) is explosively unstable.

All the N—F compounds involved in the synthesis of a group of C<sub>3</sub>—C<sub>7</sub>N-trifluoroalkylamidines were shock-sensitive explosives in varying degrees. Several were only stable in solution, and others exploded during analytical combustion. Individually indexed compounds are:

2-Chloro-*N,N,N'*-trifluoropropionamidine, 1128

Decafluorobutyramidine, 1371

\* Pentafluoroguanidine, 0359

Perfluoro-1-aminomethylguanidine, 0647

Perfluoroformamidine, 0350

*N,N,N'*-Trifluorohexanamidine, 2448

*N,N,N'*-Trifluoropropionamidine, 1172

*See other* *N*-HALOGEN COMPOUNDS

### TRINITROETHYL ORTHOESTERS    HC[OCH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>]<sub>3</sub>, C[OCH<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>]<sub>4</sub>

Nitromethane

Shimio, K. *et al.*, *Chem. Abs.*, 1976, **85**, 194924

Both tris(2,2,2-trinitroethyl)orthoformate and tetrakis(2,2,2-trinitroethyl)-orthocarbonate form powerfully explosive solutions in nitromethane. The oxygen balance of the esters are +154 and +182%, respectively. The compounds are:

Tetrakis(2,2,2-trinitroethyl)orthocarbonate, 3132

Tris(2,2,2-trinitroethyl) orthoformate, 2786

*See* OXYGEN BALANCE, POLYNITROALKYL COMPOUNDS

### TURPENTINE

*NSC* 367, 1968;

*HCS* 1980, 948

Paulin, M. S., *Tappi J.*, 1983, **66**(4), 91–92

A 45 kl tank of sulfate turpentine from a paper mill became dangerously heated, owing to oxidation arising from local high temperature and an air-purging procedure.

#### Diatomaceous earth

Anon., *Ind. Eng. Chem.*, 1950, **42**(7), 77A

A large quantity of discoloured (and peroxidised) turpentine was heated with fuller's earth to decolourise it, and it subsequently exploded. Fuller's earth causes exothermic catalytic decomposition of peroxides and rearrangement of the terpene molecule.

#### Halogens, or Oxidants, or Tin(IV) chloride

Mellor, 1941, Vol. 2, 11, 90; 1941, Vol. 7, 446; 1943, Vol. 11, 395

Turpentine ignites in contact with fluorine (at  $-210^{\circ}\text{C}$ ), chlorine, iodine, chromium trioxide, and chromyl chloride, and usually with tin(IV) chloride. Other highly unsaturated hydrocarbons may be expected to react similarly.

#### Other reactants

Yoshida, 1980, 290

MRH values calculated for 13 combinations with oxidants are given.

See Calcium hypochlorite: Turpentine

Nitric acid: Hydrocarbons (reference 16)

MRH 6.03/82

### UNIT PROCESS OR UNIT OPERATION INCIDENTS

1. Shabica, A. C., *Chem. Eng. Progr.*, 1963, **59**(9), 57–66
2. *Organic chemical manufacturing hazards*, Goldfarb, A. S. et al., Zurich, Technomic Publishing, 1981
3. *Control of industrial chemical hazards*, Carson, P. A. et al., Harlow UK, Longmans, (2 Vols) 1989
4. *Hazards of commercial chemical reactions; Hazards of commercial chemical operations*, Austin, G. T., Chs. 4, 5 in *Safety and accident prevention in chemical operations*, Fawcett, H. H. and Wood, W. S. (eds), New York, Wiley, 2nd edn., 1982

In a paper on the qualitative evaluation of hazards in organic batch chemical processing operations, the following types of reaction are rated for hazard on a scale of A–E. Reduction (13 methods); oxidation (13 methods); alkylation, C–C (13 methods), C–O (5 methods), C–N (5 methods); condensation (16 methods); amination (3 methods); esterification (9 methods); hydrolysis; substitution; peroxide preparations (2 methods); pyrolysis (2 methods); Schmidt reaction; Mannich reaction; halogenation (3 methods); nitration (2 methods). Some 200 common reagents and solvents are also hazard-rated, and general precautions and techniques to avoid batch processing hazards are listed [1]. Three more recent texts deal with the hazards of specific industrial processes or groups of products [2,3], or with unit processes or operations [4].

Incidents have been grouped for each of the unit process or unit operation headings:

AGITATION INCIDENTS, AMINATION INCIDENTS, CATALYTIC NITRO REDUCTION PROCESSES

DIAZOTISATION, DRYING, EPOXIDATION, GAS EVOLUTION INCIDENTS  
GRIGNARD REAGENTS, HALOGENATION INCIDENTS, HYDROGENATION INCIDENTS  
IRRADIATION DECOMPOSITION INCIDENTS, MIXING, NEUTRALISATION INCIDENTS, NITRATION INCIDENTS  
OXIDATION INCIDENTS, PEROXIDATION INCIDENTS, PLANT CLEANING INCIDENTS  
POLYCONDENSATION REACTION INCIDENTS, POLYMERISATION INCIDENTS, REDOX REACTIONS, SULFONATION INCIDENTS

### UNSATURATED OILS

*See* Linseed oil

Carbon: Unsaturated oils, 0298

### URANYL MACROCYCLIC PERCHLORATE LIGANDS

Vidali, M. *et al.*, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1715–1719

A series of uranyl complexes of macrocyclic azomethines were used as ligands for transition metal ions, with perchlorate anions. Raman spectra of the uranyl–metal complexes could not be recorded because the samples exploded during attempted measurements.

*See other* AMMINEMETAL OXOSALTS, IRRADIATION DECOMPOSITION INCIDENTS

### VACUUM DISTILLATION RESIDUES

1. Editor's comments, 1995
2. Cardillo, P. *et al.*, *Chem. Abs.*, 1998, **128**, 118814h

Explosions shortly after the completion of vacuum distillations are common. There are two causes, firstly that the residues are unstable and, heat removal declining with the cessation of agitation and evaporation, there is unaided thermal runaway from the elevated temperature at which such distillations commonly finish. The second is that the still very hot vessel has been repressurised with air, and residues are usually combustible. Cooling of such residues should be checked, if not assisted, and air not admitted to the vessel until it is below 100°C [1]. An account of the investigation of an industrial accident of the first type is available [2].

Some examples: 4-Chloro-2-methylaniline 2-Chloro-4-nitrotoluene: Sodium hydroxide 2-Nitrobenzaldehyde (reference 4) 4-Nitrophenylacetic acid: Acetic anhydride, Pyridine 4-Nitrotoluene (reference 3)

*See also* COOL FLAMES

### VACUUM PUMPS

1. Ripper, L. J., *Vak. Praxis*, 1994, **6**(2), 91; *Chem. Abs.*, 1995, **122**, 87800v
2. Oliver, G., *Chemical Engineer*, 1996, (619), s21
3. Grabs, E., *PTB-Mitt.*, 1996, **106**(5), 345

Some reviews on explosion prevention measures for vacuum pumps have been published, including consideration of possible sources of ignition [1]. The second is a discussion of how to prevent and contain explosions in the various cavities of dry vacuum pumps where fuel/oxygen mixes may be present. In view of the ability of oil pumps to generate mists, they may be an even greater danger than dry ones [2]. Another review of vac. pumps pumping potentially explosive mixtures, e.g. in fuel recovery at filling stations, has been written [3].

*See* Oxygen: Plastic tubes

## VAPOUR CLOUD EXPLOSIONS

1. van Wingerden, C. J. M. *et al.*, *Plant/Oper. Progr.*, 1989, **8**(4), 234
2. Johnson, D. M. *et al.*, *Hazards XI*, 67, Symp. Ser. **124**, Rugby (UK), IChE, 1991
3. Abou Arab, *et al.*, *J. Loss Prev. Process Ind.*, 1991, **4**(3), 202
4. Mercx, W. P. M., *Trans. Inst. Chem. Eng.*, 1992, **70** (B4), 197
5. Anon., *Loss Prev. Bull.*, 1991, **099**
6. Davenport, J. A. *et al.*, *Process Safety Progr.*, 1993, **12**(1), 12
7. Mancini, R. A., *Plant/Oper. Progr.*, 1992, **11**(1), 27; Bull, D. C., *ibid.*, 33
8. Mercx, W. P. M. *et al.*, *Process Safety Progr.*, 1993, **12**(4), 222
9. Mercx, W. P. M. *et al.*, *Process Safety Progr.*, 1995, **14**(2), 121
10. Bjerketvedt, D. *et al.*, *J. Hazard Mat.*, 1997, **52**(1), 1

This term (or, confusingly, Vapour Explosion) is used for releases of superheated flammable liquids, or gases, followed by ignition after a delay, which may be of some minutes. Overpressures are slight and deflagration slow in open, unobstructed spaces. Obstruction and partial confinement accelerate the flame front and produce blasts such as Flixborough; a predictive model is described and demonstrated on Flixborough, understanding is not yet complete [1]. There may be substantial delay between ignition and significant overpressure. Experiments and their results with large-scale natural gas release are described [2]. Smaller scale experiment is described [3]. A comparison of large scale experiments with small (even these of several m<sup>3</sup>) is given; high energy fuels, especially ethene, show transition to detonation in obstructed spaces [4]. The most damaging industrial explosions of the last few decades have been of this nature [5,6]. For reviews of both the theory and experiment: [7]. The development of methods to predict the blast risks is described [8]. Techniques for experimental vapour cloud explosion studies are evaluated [9]. A handbook on (natural) gas explosion safety has been published [10].

*See also* BLEVE, GEOMETRY OF VESSELS AND PIPEWORK, DEFLAGRATION TO DETONATION

## VAPOUR EXPLOSIONS

1. Fröhlich, G., *Chem. Ing. Tech.*, 1978, **50**, 861–866
2. Ogiso, C. *et al.*, *Chem. Abs.*, 1985, **102**, 190161
3. Iida, Y. *et al.*, *JSME Int. J.*, 1987, **30**, 1972–1981

4. Fletcher, D. F. *et al.*, *J. Loss Prev.*, 1994, **7**(6), 457
5. Theofanous, T. G. *et al.*, *Phys. Fluids*, 1994, **6**(11), 3513

A vapour explosion can occur on contact between 2 liquids of differing temperatures if the temperature of the hotter liquid is above the b.p. of the cooler, and the explosion is due to extremely rapid vapour generation (phase transition) of the cooler liquid. Vapour generation must be preceded by very good heat transfer by a fragmentation process leading to enormous heat transfer coefficients. Experimental results are discussed for water as the cooler liquid and melts of glass, aluminium, copper, iron, gallium or lead as the hotter liquid. The probability of steam explosions depends on the materials of the melt, the temperatures of the 2 liquids (not only the temperature difference), the reacting masses, the shape of the container and external triggering (by impact, etc.) [1]. An experimental study of vapour explosions of water in contact with sodium carbonate–sodium chloride hot melts is reported [2]. The mechanism of vapour explosions caused by drops of molten lithium nitrate falling into ethanol has been studied by high-speed photography and pressure trace measurements [3]. Recent work in the area is reviewed, with a description of the processes involved. It is suggested that the Krakatoa eruption was the largest incident on record [4]. Interaction of molten aluminium and water is studied, in particular the conditions in which vapour explosion can initiate chemical reaction [5].

*See* LIQUEFIED GASES, MOLTEN METAL EXPLOSIONS, SMELT, SUPERHEATED LIQUIDS

## VEGETABLE OILS

Catalysts, Hydrogen

*See* Hydrogen: Catalysts, Vegetable oils

## VINYLSILOXANES

Schilling, C. L., *et al.*, *Chem. Eng. News*, 1994, **72**(37), 2

Vinyl siloxanes are prone to uncontrolled exotherm and explosion without other than thermal assistance. There is extremely rapid pressure generation in closed containers from about 200°C.

*See* SILANES

## VINYL SULFOXIDES

**C=C.SO<sub>2</sub>–**

Nikonov, V. A. *et al.*, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**(7,1), 1374; *Chem. Abs.* 1990, **112**, 29847

Complexes of butyl vinyl sulfoxide and iron, chromium and cobalt (III) nitrates were found to be unstable, the ferric salt (the least stable) exploding even as a 40 mol% solution in benzene. It is considered that other vinyl sulfoxide ligands will behave similarly.

*See* METAL NITRATES

## VIOLENT POLYMERISATION

1. Harmon, M. *et al.*, *A Review of Violent Monomer Polymerisation*, Rept. AD-017443, Richmond (Va.), USNTIS, 1974
2. Bond, J., *Loss Prev. Bull.*, 1985 (065), 21–28
3. Frurip, D. J. *et al.*, *Process Safety Progr.*, 1995, **14**(2), 79
4. Ogiso, C. *et al.*, *Chem. Abs.*, 1986, **105**, 29100
5. *Encyclop. Polym. Sci. Eng.*, Mark, H. F. *et al.* (eds), Vol. 14, 805–827, New York, Wiley, 1988
6. Thomas, I. F. in *Integrated Risk Management* (Eds: Melchers & Stewart), 177, Rotterdam, Balkema, 1995

Radical polymerisations, in particular, are liable to run out of control. There are three reasons for this; firstly monomers may contain traces of inhibitors, in which case the rate of polymerisation will rise when these are exhausted, secondly the physics of polymer solution cause the termination rate of radical chains to decline as the reaction proceeds, meaning acceleration and increased heat evolution exactly when increasing viscosity makes it difficult to remove (the Norrish–Tromsdorff effect). The third possibility is ‘popcorn polymerisation’ (so called from the appearance of the product) which is a spontaneous event, usually during storage, in which polymer gel particles are thought to be osmotically swollen by penetrating monomer to the degree of rupturing bonds: more radicals and, effectively, a branched chain process.

Literature related to the possibility of violent polymerisation of the 10 monomers most significant industrially has been classified and reviewed, and 209 annotated references are given. The compounds covered are acrylic acid, acrylonitrile, 1,3-butadiene, ethylene, ethylene oxide, methyl acrylate, methyl methacrylate, propiolactone, styrene, vinyl acetate, vinyl chloride and vinylidene chloride. Almost all have been involved in explosive polymerisation incidents. For each compound, data and selected references on physical properties, reactivity, inhibition and handling procedures are given [1]. Mechanisms of initiation, inhibition, and de-inhibition of polymerisation are reviewed briefly, with 8 case histories of incidents involving violent polymerisation of 6 common monomers [2]. A procedure is given for assessing monomers for risk of runaway polymerisation [3]. Conditions for runaway reactions in suspension polymerisation when stirring is stopped were determined experimentally. A vapour explosion was observed in a closed system under runaway conditions [4]. A 22-page section devoted to safety aspects of the production and uses of polymeric materials covers a wide range of relevant topics in polymerisation and processing plant management, including a comprehensive reference list [5].

Acrylic monomers, in particular, are inclined to polymerisation in the absence of oxygen which serves as a chain-breaker in their radical polymerisation. Most such monomers are also flammable and may therefore be directed to be stored under a nitrogen blanket. If nitrogen purging is complete, the risk of fire within vessels may be zero, but the risk of explosive polymerisation, tank-rupture and external fire is increased. Some suspect that accidents of this type have occurred already [6].



Detailed examples may be found in the entries:

- † Acrylonitrile, : Initiators, 1107
- † 1,2-Butadiene, 1479
- † 1,3-Butadiene, 1480
- † 1,1-Dichloroethylene, 0695
- † Ethylene, 0781
- † Ethylene oxide, : Ammonia, 0829
- † Methyl acrylate, 1531

*See* ACRYLIC MONOMERS

*See also* POLYMERISATION INCIDENTS

## WASTE DISPOSAL

*See* DISPOSAL

## WATER-REACTIVE COMPOUNDS

A large number of individual compounds react exothermally and violently with water, particularly with restricted amounts of the latter. Many such compounds come within the groups:

ACID ANHYDRIDES, ACYL HALIDES, ALKALI METALS  
ALKYLALUMINIUM DERIVATIVES, ALKYLNON-METAL HALIDES  
COMPLEX HYDRIDES, METAL HALIDES, METAL HYDRIDES  
METAL OXIDES, NON-METAL HALIDES (AND THEIR OXIDES)  
NON-METAL OXIDES

## WAX FIRE

Carbon tetrachloride

1. Gilmont, R., *Chem. Eng. News*, 1947, **25**, 2853
2. Author's comment, 1989

Use of carbon tetrachloride to extinguish a wax fire caused an explosion. This was attributed to a violent reaction between unsaturated wax components and carbon tetrachloride initiated by radicals from decomposing peroxides [1]. Perhaps a more likely explanation could be that contact of the cold low-boiling liquid with the hot molten wax led to the physical effect of a vapour explosion, rather than the chemical explosion postulated [2].

*See* Dibenzoyl peroxide: Carbon tetrachloride

## WOOD PULP

Eidsan, G. *et al.*, *Biotechnol. Lett.*, 1979, **1**, 31–34

Semi-chemical pulp contaminated with micro-organisms and incubated at 60°C produces a hydrogen-containing gas. A gas-phase explosion in a pulp storage tower was attributed to static ignition of this gas admixed with air.

*See other* STATIC INITIATION INCIDENTS

## WOOL

Lee, P. R., *J. Appl. Chem.*, 1969, **19**, 345–351

The self-heating and ignition of baled or loose wool in bulk storage is discussed and analysed, and steady state thermal explosion theory is applied to the prediction of critical masses and induction periods for storage and transportation situations in relation to ambient temperature. Results obtained were consistent with current safety practices.

## WORKERS AT THE NEXT BENCH

Are almost as dangerous as are you, dear reader. Make sure you know what he is doing and expect her to return the compliment.

## ‘XANTHATES’

## ROC(S)S<sup>-</sup>

1. Sorbe, 1968, 74
2. Anon., Private communication, 1990
3. Kirk-Othmer, 1984, 3rd Edn., Vol. 24, 646

Salts of *O*-alkyldithiocarbonates (‘xanthates’) are hazardous as dusts, forming explosive suspensions in air. The lower-alkyl salts are claimed to be explosive in the solid state when dry [1]. Explosions reported when drying hydrated xanthate salts are probably the consequence of release of carbon disulphide to form an inflammable atmosphere of very low autoignition temperature in the oven [2]. Xanthate esters are thermally unstable by a variety of eliminations and rearrangements, all distinctly exothermic and many evolving extremely flammable gases and vapours. Free xanthic acids, which may be isolated on acidification, decompose autocatalytically and perhaps explosively [3].

See Potassium *O*-ethyl dithiocarbonate

See also Carbon disulfide

Diazonium salts

See DIAZONIUM SULFIDES AND DERIVATIVES (reference 8)

## XENON COMPOUNDS

## Xe–F, Xe–O

1. Jha, N. K., *RIC Rev.*, 1971, **4**, 16765168
2. Kirk-Othmer, 3rd Edn., 1980, Vol. 12, 293; 4th Edn, 1995, Vol. 13, 9

For convenience, the even rarer and less stable krypton compounds are also covered in this entry. All xenon compounds are very strong oxidants and many are also explosively unstable. For a now obsolete review, see [1]. A recent compact review of noble gas chemistry is found in [2]. A series of alkali xenates,  $\text{MHOXeO}_3 \cdot 1.5\text{H}_2\text{O}$  are unstable explosive solids. The equivalent fluoroxenates  $\text{MFXeO}_3$  are far more stable. Individually indexed compounds are:

Caesium bromoxenate, 0237

Caesium chloroxenate, 3970

Caesium hydrogen xenate, 4259

- \* Krypton difluoride, 4313
- Potassium hexaoxoxenonate–xenon trioxide, 4674
- Tetrafluoroammonium hexafluoroxenate, 4386
- Xenon difluoride dioxide, 4322
- Xenon difluoride oxide, 4319
- Xenon difluoride, 4332
- Xenon hexafluoride, 4377
- Xenon tetrafluoride, 4353
- Xenon tetrafluoride oxide, 4346
- Xenon tetraoxide, 4863
- Xenon trioxide, 4857
- Xenon(II) fluoride methanesulfonate, 0443
- Xenon(II) fluoride perchlorate, 3977
- Xenon(II) fluoride trifluoroacetate, 0634
- Xenon(II) fluoride trifluoromethanesulfonate, 0356
- Xenon(IV) hydroxide, 4533
- Xenon(II) pentafluoroorthoselenate, 4382
- Xenon(II) pentafluoroorthotellurate, 4383
- Xenon(II) perchlorate, 4110

*See other* NON-METAL HALIDES, NON-METAL OXIDES

## YEAST

1. Anon., *The Daily Telegraph* (London), Jan. 30th 1996, 6
2. Editor's comments

A package of brewers' yeast exploded, slightly injuring three postal workers [1]. Fermentations in sealed containers can easily generate sufficient pressure of carbon dioxide to rupture the container. The problem is well known to home ginger beer makers and Champagne houses; now that yeast is sometimes used as a reducing agent it is appearing in the chemical world [2].

*See* SUGARS

## ZINC BACITRACIN

Piotrowski, T., *Chem. Abs.*, 1984, **101**, 60040

In a study of explosive potential of 20 pharmaceutical products, zinc bacitracin was identified as unusual, in that though not normally explosive, when it does explode it produces relatively high pressures.

*See entry* PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

# Source Title Abbreviations used in Handbook References

The abbreviations used in the references for titles of journals and periodicals are those used in BP publications practice and conform closely to the recommendations of the *Chemical Abstracts* system. Abbreviations which have been used to indicate textbook and reference book sources of information are set out below with the full titles and publication details.

<i>ABCM Quart. Safety Summ.</i> ,	<i>Quarterly Safety Summaries</i> , London, Association of British Chemical Manufacturers, 1930–1964
<i>ACS 54</i> , 1966	<i>Advanced Propellant Chemistry</i> , ACS 54, Washington, American Chemical Society, 1966
<i>ACS 88</i> , 1969	<i>Propellants Manufacture, Hazards and Testing</i> , ACS 88, Washington, American Chemical Society, 1969
Albright, Hanson, 1976	<i>Industrial and Laboratory Nitrations</i> , ACS Symposium Series 22, Albright, L. F., Hanson, C., (Eds.), Washington, American Chemical Society, 1976
<i>Alkali Metals</i> , 1957	<i>Alkali Metals</i> , ACS 19, Washington, American Chemical Society, 1957
<i>ASHRAE. J.</i>	<i>American Society of Heating, Refrigeration and Air-conditioning Engineers Journal</i> , New York.
Augustine, 1968	<i>Reduction, Techniques and Applications in Organic Chemistry</i> , Augustine, R. L., London, Edward Arnold, 1968

- Augustine, 1969, 1971 *Oxidation, Techniques and Applications in Organic Synthesis*, Augustine, R. L., (Ed.), New York, Marcel Dekker, Vol. 1, 1968, Vol. 2 (with Trecker, D. J.), 1971
- Bahme, 1972 *Fire Officer's Guide to Dangerous Chemicals*, FSP-36, Bahme, C. W., Boston, National Fire Protection Association, 1972
- Bailar, 1973 *Comprehensive Inorganic Chemistry*, Bailar, J. C., Emeléus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., (Eds.), Oxford, Pergamon, 5 vols., 1973
- BCISC Quart. Safety Summ.*, *Quarterly Safety Summaries*, London, British Chemical Industries Safety Council, 1965–1973
- Barton & Ollis, 1979 *Comprehensive Organic Chemistry*, Barton, D. H. R., Ollis, W. D., (Eds), Oxford, Pergamon, 1979.
- Biasutti, 1981 *History of Accidents in the Explosives Industry*, Biasutti, G. S. (Author and publisher), Vevey, 1981
- Bond, 1991 *Sources of Ignition*, Bond, J., Oxford, Butterworth-Heinemann, 1991
- Braker, 1981 *Matheson Gas Data Book*, Braker, W., Mossman, A. L., Lyndhurst (NJ), Matheson Div. Searle, 6th edn. 1981
- Brandsma, 1971 *Preparative Acetylenic Chemistry*, Brandsma, L., Barking, Elsevier, 1971
- Brauer, 1961, 1965 *Handbook of Preparative Inorganic Chemistry*, Brauer, G., (Translation Ed. Riley, R. F.), London, Academic Press, 2nd edn. Vol. 1, 1963; Vol. 2, 1965
- Bretherick, 1986 *Hazards in the Chemical Laboratory*, Bretherick, L. (Ed.), London, Royal Society of Chemistry, 4th edn., 1986
- Castrantas, 1965 *Fire and Explosion Hazards of Peroxy Compounds*, Special Publication No. 394, Castrantas, H. M., Banerjee, D. K., Noller, D. C., Philadelphia, ASTM, 1965
- Castrantas, 1970 *Laboratory Handling and Storage of Peroxy Compounds*, Special Publication No. 491, Castrantas, H. M., Banerjee, D. K., Philadelphia, ASTM, 1970

- CHAS Notes* *Chemical Health and Safety Notes*, ACS Division of Chemical Health and Safety, Washington, 1982 to date (4 issues/yr)
- Chemiarbeit* *Chemiearbeit, Schutzen und Helfen*, Dusseldorf, Berufsgenossenschaft der Chemische Industrie, 1949–1962 (supplement to *Chemische Industrie*)
- Chem. Hazards Ind.* *Chemical Hazards in Industry*, Royal Society of Chemistry Information Group, Cambridge, 1984 to date (monthly abstracts)
- CISHC Chem. Safety Summ.*, *Chemical Safety Summaries*, London, Chemical Industry Safety and Health Council of the Chemical Industries Association, 1974 to 1986 (terminated)
- CHETAH 1990* *The ASTM Chemical Thermodynamic and Energy Release Evaluation Programme*, Version 4.4, 2nd Edn (ASTM Data Series Publication 51A), Davies C. A. *et al.*, Philadelphia, ASTM, Appendix V. Upgrades continue to be issued (1998)
- Cloyd, 1965 *Handling Hazardous Materials*, Technical Survey No. SP-5032, Cloyd, D. R., Murphy, W. J., Washington, NASA, 1965
- Coates, 1960 *Organometallic Compounds*, Coates, G. E., London, Methuen, 1960
- Coates, 1967, 1968 *Organometallic Compounds*, Coates, G. E., Green, M. L. H., Wade, K., London, Methuen, Vol. 1, 1967, Vol. 2, 1968
- Compendium 1985, 1987* *Compendium of Safety Data Sheets, for Research and Industrial Chemicals*, Keith, L. H., Walters, D. B., Deerfield Beach/Weinheim, VCH, vols. 1–3 of 867 sheets 1985, vols 4–6 of 723 sheets, 1987
- Dangerous Loads*, 1972 *Dangerous Loads*, Leicester, Institution of Fire Engineers, 1972
- Dangerous Substances*, 1972 *Dangerous Substances: Guidance on Fires and Spillages* (Section 1, 'Inflammable liquids'), London, HMSO, 1972
- Davies, 1961 *Organic Peroxides*, Davies, A. G., London, Butterworths, 1961
- Davis, 1943 *Chemistry of Powder and Explosives*, Davis, T. L., New York, Wiley, 1943

- DOC 5, 1982 *Dictionary of Organic Compounds*, Buckingham, J., (Ed.), London, Chapman & Hall, 5th edn. in 5 vols. + indices, 1982, annual supplementary vols. to date
- Dunlop, 1953 *The Furans*, ACS 119, Dunlop, A. P., Peters, F. N., New York, Reinhold, 1953
- Ellern, 1968 *Military and Civilian Pyrotechnics*, Ellern, H., New York, Chemical Publishing Co., 1968
- Emeléus, 1960 *Modern Aspects of Inorganic Chemistry*, Emeléus, H. J., Anderson, J. S., London, Rutledge and Kegan Paul, 1960
- Ephraim, 1939 *Inorganic Chemistry*, Ephraim, F., (3rd Engl. edn., Thorne, P. C. L., Ward, A. M.), London, Gurney & Jackson, 1939
- Federoff, 1960 *Encyclopaedia of Explosives and Related Compounds*, Federoff, B. T. (Ed.), Dover (NJ), Piccatinny Arsenal, Vol. 1, 1960; Vol. 10, 1984 (from USNTIS)
- Fieser, 1967–1986 *Reagents for Organic Synthesis*, Fieser, L. F. and Fieser, M., New York, Wiley, Vol. 1, 1967, The series continues after the death of the originator.
- Freifelder, 1971 *Practical Catalytic Hydrogenation*, Freifelder, M., New York, Wiley-Interscience, 1971
- Gallais, 1957 *Chimie Minérale Théorique et Expérimentale (Chimie Électronique)*, Gallais, F., Paris, Masson, 1957
- Gaylord, 1956 *Reductions with Complex Metal Hydrides*, Gaylord, N. G., New York, Interscience, 1956
- Gibson, 1969 *Handbook of Selected Properties of Air-and Water-Reactive Materials*, Gibson, H., Crane (In.), US Naval Ammunition Depot, 1969
- Goehring, 1957 *Ergebnisse und Probleme der Chemie der Schwefelstickstoff-verbinding*, *Scientia Chemica*, Vol. 9, Goehring, M., Berlin, Akademie Verlag, 1957
- Grignard, 1935–54 *Traité de Chimie Organique*, Grignard, V. and various volume Eds., Paris, Masson, Vol. 1, 1935, Vol. 23, 1954

- Guide for Safety*, 1972  
*Guide for Safety in the Chemical Laboratory*, MCA, New York, Van Nostrand Reinhold, 2nd edn., 1972
- Harmon, 1974  
*A Review of Violent Monomer Polymerisation*, Harmon, M., King, J., Rept. AD-017443, Springfield (Va.), NTIS, 1974
- Haz. Chem. Data*, 1975  
*Hazardous Chemical Data*, NFPA 49, Boston, National Fire Protection Association, 1975
- HCS 1980  
*Handling Chemicals Safely*, Dutch Assoc. of Safety Experts, Dutch Chemical Industry Assoc., Dutch Safety Inst., 1980 (Engl. transl. of 2nd Dutch edn.)
- Houben-Weyl, 1953 to date  
*Methoden der Organischen Chemie*, Müller, E. (Ed.), Stuttgart, Georg Thieme, 4th edn., published unsequentially from 1953.
- Inorg. Synth.*, 1939–86  
*Inorganic Syntheses*, various Eds., Maidenhead, McGraw-Hill, Vol. 1, 1939, Vol. 24, 1986
- Jahresber. 1960 to date  
*Jahresberichte*, Berufsgenossenschaft der Chemischen Industrie, Heidelberg, annually since 1960
- JANAF, 1971  
*JANAF Thermochemical Tables*, Stull, D. R., Prophet, H., National Bureau of Standards, 2nd edn., 1971
- Karrer, 1950  
*Organic Chemistry*, Karrer, P., London, Elsevier, 1950
- Janz, 1976  
*Eutectic Data, Table 2 (Safety Hazards, etc.)* Janz, G. J., Allen, C. B., Molten Salts Data Center, ERDA Rept. TID 27163-21, 1976; subsequently publ. in *J. Haz. Mat.*, 1980–81, **4** (1), 145–176
- Kharasch and Reinmuth, 1954  
*Grignard Reactions of Non-Metallic Substances*, Kharasch, M. S. and Reinmuth, O., London, Constable, 1954
- King, 1990  
*Safety in the Process Industries*, King, R., London, Butterworth-Heinemann, 1990
- Kirk-Othmer, 1963–71  
*Encyclopaedia of Chemical Technology*, (3rd edn., 1978–83) Kirk, R. E., Othmer, D. F., London, Wiley-Interscience, Vol. 1, 1963, Vol. 22, 1970, Suppl. Vol. 1971. (4th edn., from 1991 ) 1993;



- Kirshenbaum, 1956 *Final Report on Fundamental Studies of New Explosive Reactions*, Kirshenbaum, A. D., Philadelphia, Research Institute of Temple University, 1956
- Kit and Evered, 1960 *Rocket Propellant Handbook*, Kit, B., Evered, D. S., London, MacMillan, 1960
- Lab. Hazards Bull.* *Laboratory Hazards Bulletin*, Royal Society of Chemistry Information Group, Cambridge, 1981 to date (monthly abstracts)
- Lawless, 1968 *High Energy Oxidisers*, Lawless, E. W. and Smith, I. C., New York, Marcel Dekker, 1968
- Leleu, Cahiers, 1972–80 *Les Réactions Chimique Dangereuse*, Leleu, J., published serially in *Cahiers de Notes Documentaires*, from 1972 (**68**), 319 to 1980, (**100**), 426
- Loss Prev. Bull.*, 1974 to date *Loss Prevention Bulletin*, Rugby, Institution of Chemical Engineers, 6 issues annually since 1974
- Mackay, 1966 *Hydrogen Compounds of the Metallic Elements*, Mackay, K. M., London, Spon, 1966
- Major Loss Prevention*, 1971 *Major Loss Prevention in the Process Industries, Symposium Series No. 34*, London, Institution of Chemical Engineers, 1971
- Martin, 1971, *Dimethylsulfoxid*, Martin, D., Hauthal, H. G., Berlin, Akademie Verlag, 1971
- Matheson Guide, 1982 *Guide to Safe Handling of Compressed Gases*, Matheson Div. Searle Medical Products, Lyndhurst (NJ), 1982
- MCA Case Histories*, 1950–78 *Case Histories of Accidents in the Chemical Industry*, Washington, MCA, (published monthly, republished as 4 indexed collected volumes 1953–75, discontinued 1978)
- (*MCA SD-Series*) 1947–76 *Safety Data Sheets*, MCA, Washington. The whole series of 101 sheets was withdrawn in 1980, but remains a useful source of collected information on basic industrial chemicals.
- Meidl, 1972 *Hazardous Materials Handbook*, Meidl, J. H., Beverley Hills, Glencoe Press, 1972

- Mellor, 1947–71 *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Mellor, J. W., London, Longmans Green, Vol. 1, repr. 1941, Vol. 16, publ. 1937; and isolated Supplementary vols. up to Vol. 8 Suppl. 3, 1971
- Mellor MIC, 1961 *Mellor's Modern Inorganic Chemistry*, Parkes, G. D. (Revision Ed.), London, Longmans Green, 1961
- Merck, 1976, 1983, 1989, 1996 *The Merck Index*, Chapman and Hall, London., 9th edn. 1976, 10th edn. 1983, 11th edn. 1989, 12<sup>th</sup> edn. 1996
- Merrifield, 1988 *Fire and Explosion Hazards associated with Storage and Handling of Hydrogen Peroxide*, Merrifield, R., Specialist Inspectors Report No. 19, Bootle, HSE. 1988
- Meyer, 1977 *Chemistry of Hazardous Materials*, Meyer, E., Englewood Cliffs (NJ), Prentice-Hall, 1977
- Miller, 1965–66 *Acetylene, its Properties, Manufacture and Uses*, Miller, S. A., London, Academic Press, Vol. 1, 1965, Vol. 2, 1966
- Moissan, 1900 *Le Fluor et ses Composés*, Moissan, H., Paris, Steinheil, 1900
- NFPA 491M, 1975 *Manual of Hazardous Chemical Reactions*, NFPA 491M, Quincy (MA), National Fire Protection Association, 5th edn., 1975 (larger format of same text, 1985)
- Nolan, 1983 *Case Histories of Runaway Reactions*, Nolan, P. F., London, Polytechnic of the South Bank, 1983. A summary of the conclusions on the causes was published in *J. Haz. Materials*, 1987, **14**, 233–239
- Org. Synth.*, 1941 to date *Organic Syntheses*, various Eds., New York, Wiley, Collective Vol. 1, 1944; Coll. Vol. 2, 1944; Coll. Vol. 3, 1955; Coll. Vol. 4, 1962; Coll. Vol. 5, 1973; Coll. Vol. 6, 1987; Coll. Vol. 7, 1990; Coll. Vol. 8, 1993; annual volumes (from 70) thereafter.
- Partington, 1967 *General and Inorganic Chemistry*, Partington, J. R., London, MacMillan, 4th edn., 1967

Pascal, 1956–70	<i>Nouveau Traité de Chimie Minérale</i> , Pascal, P. (Ed.), Paris, Masson, Vol. 1, 1956; Vol. 20.3, 1964; Vol. 15.5, 1970
Pieters, 1957	<i>Safety in the Chemical Laboratory</i> , Pieters, H. A. J., Creighton, J. W., London, Academic Press, 2nd edn., 1957
<i>Plant/Oper. Progress</i>	<i>Plant Operations Progress</i> continues as <i>Process Safety Progress</i> 1993-
<i>Pot. Incid. Rept.</i>	<i>ASESB Potential Incident Report</i> , Washington, Armed Services Explosives Safety Board
<i>Proc. nth Combust. Symp.</i>	<i>Proceedings of Combustion Symposia</i> , various Eds. and Publishers, dated year following the event. 1st Symposium 1928; 19th Symposium, 1982
Renfrew, 1981	<i>Safety in the Chemical Laboratory</i> , Collected reprinted articles from <i>J. Chem. Educ.</i> , Renfrew, M. M. (Ed.), Vol. IV, 1981
Rodd, 1951–62	<i>The Chemistry of Carbon Compounds</i> , Rodd, E. H. (Ed.), London, Elsevier, Vol. 1A, 1951, Vol. 5, 1962; 2nd edn. began in 1979
<i>RSC Data Sheets</i> , 1982 to date	<i>Laboratory Hazard Data Sheet Series</i> , Cambridge, Royal Society of Chemistry, No. 1, 1982; No. 89, 1989, issued monthly, ceased 1993
<i>RSC Safety Data Sheets</i> , 1989	<i>Chemical Safety Data Sheets</i> , Cambridge, Royal Society of Chemistry, 1989 Generally similar to the monthly Laboratory Hazards Safety Data Sheet series, but the information is presented under headings reflecting legislative requirements. Volume 1 deals with some 100 largely organic liquid solvents and reagents, while Volume 2 covers main group metals and their compounds, 122 items in all. Vol. 3; Corrosives and Irritants, 1990. Vol 4; Toxic Chemicals, Pt. I 1990, Pt. II 1991. Vol 5, Flammables, 1989. There is considerable overlap among the volumes
<i>Runaway Reactions</i> , 1981	<i>Runaway Reactions, Unstable Products and Combustible Powders</i> , Symposium Series No. 68 (Chester 1981), Rugby, Institution of Chemical Engineers, 1981

- Rüst, 1948 *Unfälle beim Chemischen Arbeiten*, Rüst, E., Ebert, A., Zurich, Rascher Verlag, 2nd edn., 1948
- Rutledge, 1968 *Acetylenic Compounds*, Rutledge, T. F., New York, Reinhold, 1968
- Schmidt, 1967 *Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems*, SP-3037, Schmidt, H. W., Harper, J. T., Washington, NASA, 1967
- Schumacher, 1960 *Perchlorates, their Properties, Manufacture and uses*, ACS 146, Schumacher, J. C., New York, Reinhold, 1960
- Schumb, 1955 *Hydrogen Peroxide*, ACS 128, Schumb, W. C., Satterfield, C. N., Wentworth, R. L., New York, Reinhold, 1955
- Shriver, 1986 *Manipulation of Air-Sensitive Compounds*, Shriver, D. F. and Drozdov, M. A. (Eds.), New York, Wiley, 2nd edn., 1986
- Sichere Chemiarb.* *Sichere Chemiarbeit*, Heidelberg, Berufsgenossenschaft der Chemischen Industrie, 1963 to date
- Sidgwick, 1950 *The Chemical Elements and their Compounds*, Sidgwick, N. V., Oxford, Oxford University Press, 1950
- Sittig, 1981 *Handbook of Toxic and Hazardous Chemicals*, Sittig, M., Park Ridge (NJ), Noyes Data Corp., 2nd ed., 1985
- Smith, 1965–6 *Open-Chain Nitrogen Compounds*, Smith, P. A. S., New York, Benjamin, Vol. 1, 1965; Vol. 2, 1966
- Sorbe, 1968 *Giftige und Explosive Substanzen*, Sorbe, G., Frankfurt, Umschau Verlag, 1968
- Steere, 1971 *Handbook of Laboratory Safety*, Steere, N. V. (Ed.), Cleveland, Chemical Rubber Publishing Co., 2nd edn., 1971. 3rd edn., Furr, A. K. (Ed.), 1989
- Steere, 1967, '71, '74 *Safety in the Chemical Laboratory*, N. V. Steere (Ed.), Collected reprinted articles from *J. Chem. Educ.*, Vol. I, 1967; Vol. II, 1971; Vol. III, 1974

- Stull, 1977 *Fundamentals of Fire and Explosion*, AIChE Monograph Series No. 10, Stull, D. R., New York, American Institute of Chemical Engineers, 1977
- Swern, 1970-52 *Organic Peroxides*, Swern, D. (Ed.), London, Wiley-Interscience, Vol. 1, 1970; Vol. 2, 1971; Vol. 3, 1972
- Ullmann, 1998 *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, 6th edn. 1998 (CD update 1999)
- Urbanski, 1964-84 *Chemistry and Technology of Explosives*, Urbanski, T., London, MacMillan, Vol. 1, 1964; Vol. 2, 1965; Vol. 3, 1967; Oxford, Pergamon, Vol. 4, 1984
- Van Wazer, 1958-61 *Phosphorus and its Compounds*, Van Wazer, J. R., New York, Interscience, Vol. 1, 1958; Vol. 2, 1961
- Vervalin, 1973 *Fire Protection Manual for Hydrocarbon Processing Plants*, Vervalin, C. H. (Ed.), Houston, Gulf Publishing Co., 2nd edn., 1973
- Vogel, 1957 *A Textbook of Practical Organic Chemistry*, Vogel, A. I., London, Longmans Green, 3rd edn., 1957
- von Schwartz, 1918 *Fire and Explosion Risks*, von Schwartz, E., London, Griffin, 1918
- Weast, 1988 *Handbook of Chemistry and Physics*, Weast, R. C. (Ed.), Boca Raton (Fa.), CRC Press, 1988; continued under the editorship of Lide, D. R.
- Whitmore, 1921 *Organic Compounds of Mercury*, Whitmore, F. C., New York, Chemical Catalog Co. Inc., 1921
- Yoshida, 1980 *Handbook of Hazardous Reactions with Chemicals*, Yoshida, T., Tokyo, Tokyo Fire Department, 1980 (copy in British Library, Boston Spa)
- Zabetakis, 1965 *Flammability Characteristics of Combustible Gases and Vapours*, Zabetakis, M. G., Washington, US Bureau of Mines, 1965

## Appendix 2

# Glossary of Abbreviations and Technical Terms

Aerobic	In presence of air
AIT	Autoignition temperature
Alloy	Mixture of 2 or more metals
Amalgam	Alloy of a metal with mercury
Ambient	Usual or surrounding
Anaerobic	In absence of air
Analogue	Compound of the same structural type
AO	Active oxygen content of peroxides
Aprotic	Without labile hydrogen atom(s)
Aqua regia	Mixture of nitric and hydrochloric acids
ARC	Accelerating rate calorimetry
ASTM	American Society for Testing and Materials
Autoxidation	Slow reaction with air
BAM	Bundes Anstalt fur Materialsprufung (similar to ASTM)
Basic	Fundamental, or, alkaline (acting as a base)
BLEVE	Boiling liquid expanding vapour explosion
Blowing agent	Material producing much gas on decomposition
b.p.	Boiling point
BSC	Bench scale calorimeter
Carbonaceous	Containing elemental carbon (as opposed to organic, containing combined carbon)
CHETAH	A computer program to predict energy release hazards
CIT	Critical ignition temperature
Class	Collection of related chemical groups or topics
COI	Critical oxygen index
conc.	concentrated
Congener	Compound with related but not identical structure
COT	Cyclooctatetraene
Critical diameter	Minimum diameter of an explosive charge capable of maintaining detonation
Cryogenic	At a very low (freezing) temperature
CVD	Chemical vapour deposition

Deflagration	Self sustaining internal combustion propagating by means of molecular heat transfer slower than the speed of sound (the explosion mechanism gunpowder and other 'low' explosives)
DH°f	Standard heat of formation
Desiccate	Dry intensively
Detonable	Capable of detonation
Detonation	A self sustaining decomposition reaction propagating faster than the speed of sound by means of a shock wave (the characteristic property of 'high' as opposed to 'low' explosives).
Diglyme	Diethyleneglycol dimethyl ether
Digol	Diethyleneglycol
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EL	Explosive limits (or Flammable limits), vol% in air
Endotherm	Absorption of heat
ESCA	Electron scanning chemical analysis
Exotherm.	Liberation of (reaction) heat
Freeze drying	Drying without heat by vacuum evaporation of frozen solvent
GLC	Gas-liquid chromatography
Glyme	Diethyleneglycol monomethyl ether
Halocarbon	Partially or fully halogenated hydrocarbon
HMPA	Hexamethylphosphoramide
HMSO	Her Majesty's Stationery Office
Homologue	Compound of the same (organic) series
Hypergolic	Ignites on contact
Ignition source	A source of energy which ignites flammables
IMS	Industrial methylated spirit (ethanol)
Induction period	Delay in reaction starting, caused by inhibitors
Inorganic	Not containing combined carbon, of mineral origin
Intermolecular	Between different molecules
Intramolecular	Within the same molecule
IR	Infrared spectroscopy
Initiation	Triggering of explosion or decomposition
LAH	Lithium tetrahydroaluminate
Lanthanide	Of the group of rare-earth metals
LRS	Laser Raman spectroscopy
LPG	Liquefied petroleum gas
MAPP	Methylacetylene/propadiene/propene mixture
Molecular sieve	A zeolite lattice with micropores of specific sizes, useful for molecular separations

m.p.	Melting point
MRH	Maximum reaction heat
NMR	Nuclear magnetic resonance spectroscopy
Nomenclature	System of naming chemicals
Off-spec.	Off-specification (low quality)
Oleum	Sulfur trioxide dissolved in sulfuric acid
Organic	A compound containing combined carbon
Organometallic	Containing carbon to metal bonding
Oxidant	Oxidising agent (electron sink)
PCB	Polychlorinated biphenyl
PTFE	Polytetrafluoroethylene
Propagation	Spread or transmission of decomposition, flame or explosion
Propellant	Energetic composition used in ballistics
PVC	Polyvinyl chloride
Pyrophoric	Igniting on contact with air (or frictional sparking)
Q	Heat of (exothermic) reaction or polymerisation
Quaternary salt	Tetra-substituted ammonium salt etc.
RCHD	Reactive Chemical Hazards Database, which you are using
Redox compound	Compound with reducing and oxidising features
Reducant	Reducing agent (electron source)
Refractory	Heat resisting
REITP2	A computer program to calculate MRH
RSC	Reaction Safety Calorimeter, or Royal Society of Chemistry
Runaway	Reaction out of control
Self-accelerating	Reaction catalysed by its own products
Self-heating	When substance generates heat faster than it is dissipated
Silicones	Organic derivatives of a polysiloxane chain
Slurry	Pourable mixture of solid and liquid
Smelt	Molten sodium sulfide and carbonate from evaporated sulfite liquor
Substance	Not a single chemical species, often of natural origin
Superheated	A liquid at a temperature above its boiling point
Tait24	Temperature of adiabatic storage which gives an induction time to exothermic decomposition of 24 hours
Thermite reaction	Reaction of aluminium powder and iron oxide producing molten iron (and analogous reactions)
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
Thermochemistry	Study of heat effects of chemical reactions
TLC	Thin layer chromatography
TNT	Trinitrotoluene
U	Heat of (exothermic) decomposition



Unit operation	A single operational stage of a chemical process sequence
Unit process	A single chemical reaction stage in a process sequence
USNTIS	US National Technical Information Service
UV	Ultraviolet spectroscopy