EMULSIFIERS IN FOOD TECHNOLOGY

Edited by

Robert J. Whitehurst

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Emulsifiers in Food Technology

Edited by

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Emulsifiers in Food Technology

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Preface

Although beeswax was recorded by the Greek physician Galen in the second century as having emulsifying properties, it was probably the invention of margarine by the French chemist Hippolyte Mège-Mouriès in 1869 that led to the use of emulsifiers in industry. Lecithins (derived from eggs) were initially used in this application but the development of mono- and diglycerides in the 1930s led to an acceleration of their application. During the twentieth century, the rapid expansion of the food processing industry and the technological demands for quality stabilisation, shelf life and new textures further drove the development and utilisation of emulsifiers.

Emulsifiers have the ability to interact at the interface between two phases. Frequently these are immiscible liquids, but they can also be gas/liquid mixtures. It is their surface activity that gives emulsifiers the ability to stabilise mixtures of oil and water, which would otherwise separate.

Emulsifiers are molecules which consist of hydrophilic/lipophobic and lipophilic/hydrophobic parts. They are categorised primarily by their hydrophilic/lipophilic balance (HLB), the theory of which is explained further in Appendix 1.

More than just stabilisers of simple oil/water mixtures, food emulsifiers are now employed for crystal modification and for starch and protein complexing. Applications include modifying the rheology of chocolate, the strengthening of dough, crumb softening and the retardation of staling in bread, stabilisation of protein, fat and water emulsions in processed meat products, and the rheological modification of sorbet, ice cream and other dairy products.

This volume introduces emulsifiers to those previously unfamiliar with their functions and provides a state-of-the-art account of their chemistry, manufacture, application and legal status for experienced food technologists. Although gums and proteins may be regarded as having emulsifying properties, this book concentrates on molecules which demonstrate a surface active effect.

Lecithins, being naturally occurring, are discussed first. There follows a chapter on mono- and diglycerides, which in themselves form the basis of the emulsifiers considered in some of the later chapters. There is comprehensive coverage of emulsifiers based on alternative 'backbones'. Finally, appendices cross-reference emulsifier types with applications, give E-numbers, synonyms and references to analytical standards and methods, and provide an explanation of HLB.

The contributors to this book were chosen carefully for their practical approach to the subject, and for their enthusiasm. My thanks go to them and to my colleagues who provided me with their help and support.

R. J. Whitehurst

Emulsifiers in Food Technology
Edited by Robert J. Whitehurst

1 Lecithins

Hanns-Georg Bueschelberger

Lecithins are among the most widely used emulsifiers in the food industry. However, although used in a vast variety of applications, it is difficult to find systematic data about the emulsification and application properties of lecithin. For the user of lecithin, this information should be of specific interest, as lecithin is not a uniform, standard material but a natural mixture of a series of surface-active components that are contributing to the overall emulsifying performance.

In addition, there is a wide variety of materials that, according to legislation, are called 'lecithin' but vary significantly in their composition and thereby functionality. And the term 'lecithin' might have a substantially different meaning within commercial and food legislational areas from that within the chemistry literature (see Section 1.1).

This chapter therefore will provide a comprehensive overview of all aspects of commercial lecithins – their sources, composition and chemistry, analytical and quality considerations, the types and functionalities, as well as key and potential applications.

1.1 Introduction to lecithins and phospholipids

1.1.1 Some history

Lecithin was discovered in 1846 by the French chemist Maurice Gobley. He isolated an orange-coloured substance from egg yolk, which he called lecithin, after the Greek name for egg yolk ('lekithos').

He later isolated the same substance from brain, blood, bladder and other organic materials. An important characteristic of this material was that it contained phosphorus, organically bound to a lipid-type structure.

It took other scientists a number of years to discover that the isolated chemicals were not of a uniform chemical structure but were a group of chemically similar but clearly differentiated components that are now classified as phospholipids or phosphatides. They also found that this class of chemicals is present in all organic tissue, whether of plant, animal or human origin and that the highest concentrations, apart from egg yolk, are found in oil seeds like soy, sunflower and others.

One of the first individual substances isolated from these mixtures was a phospholipid containing choline. Since this was the first and main constituent that could be identified, this material was named lecithin (sometimes also choline lecithin). Later a substance containing ethanolamine was also isolated, which was named *Kephalin* (sometimes also colamin lecithin). This inconsistency in nomenclature is still reflected when looking for information on lecithin. In scientific literature 'lecithin' is often regarded as referring to the individual component containing choline. In commercial terms, 'lecithin' is always related to the mixture of phospholipids (along with some other components).

In this chapter the term 'lecithin' is always used under the commercial aspect (also see Section 1.4), if we talk about individual constituents, we are referring to *phospholipids* or *phosphatides*.

1.1.2 Phospholipids

In commercial lecithins, glycero-phospholipids are of great importance in terms of both quantity and function.

All natural representatives of this group are derived from *sn*-glycero-3-phosphate and therefore have the basic structure as shown in Fig. 1.1.

If both 'X' and 'Y' are fatty acids, we refer to diacyl-glycerophospholipids. If there is only one fatty acid and 'X' or 'Y' is a hydrogen atom, then we refer to mono-acyl-glycerophospholipids, or lyso-phospholipids.

The acyl residues X and Y attached to carbon atoms C1 and C2 may differ considerably (chain length, saturation) depending on the origin (raw material source). Moreover, in natural products 'X' and 'Y' are rarely of the same chemical nature. The fatty acid attached to C2 is usually less saturated than the one attached to C1.

The individual species of glycerophospholipids differ in the nature of the alcohol 'Z', which is esterified with the phosphate (exception: phosphatidic acid, where 'Z' is a hydrogen atom). It may take the form of an amino alcohol (e.g. choline, ethanolamine), a polyvalent alcohol (e.g. inositol, glycerol) or a hydroxyamino acid (e.g. serine).

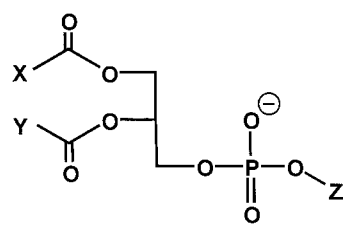

Fig. 1.1 *sn*-glycero-3-phosphate.

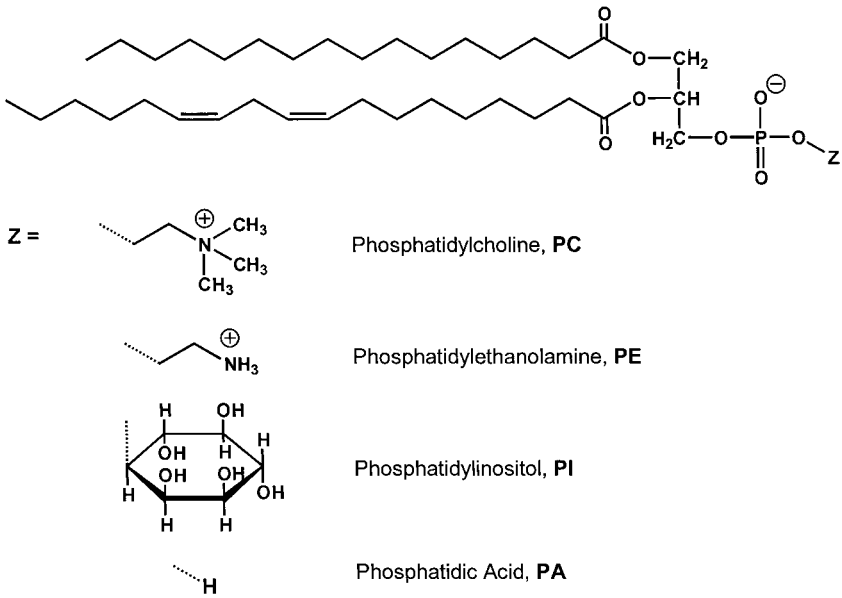

Fig. 1.2 1,2-Diacyl-*sn*-glycero-3-phospholipids, nomenclature according to substituent 'Z'.

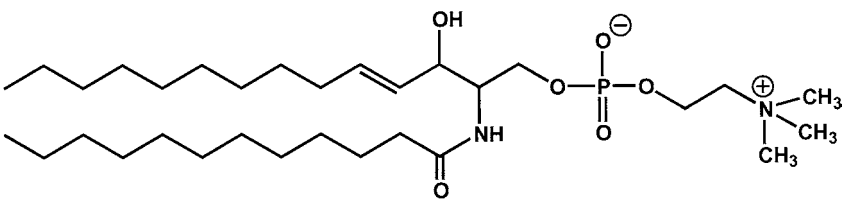

Fig. 1.3 Sphingomyelin.

Figure 1.2 shows the principal groups of diacyl-phospholipids that can be distinguished by the nature of 'Z'.

As further sub-groups of phospholipids, besides glycero-phospholipids, sphingosine-phospholipids and glycolipids also need to be mentioned. One of the best known representatives of sphingosine-phospholipids is sphingomyelin that occurs exclusively in animal organisms. It consists of one molecule each of ceramide, phosphoric acid and choline (ceramide phosphocholine), see Fig. 1.3.

Glycolipids occur mainly in plants and micro-organisms, although small quantities are also found in animals, particularly in the brain.

1,2-Diacyl-*sn*-glycerol is linked to the carbohydrate unit via 3-hydroxy group by means of α- or β-glycosidic bond. The most common representatives of this

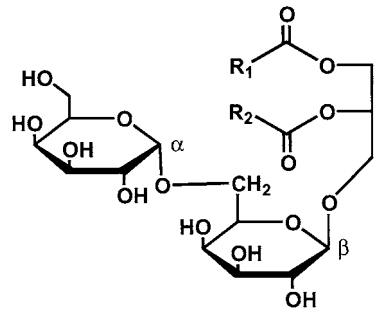

Fig. 1.4 Digalactosyl-diglyceride.

group are monogalactosyl- and digalactosyl-diglycerides (MDGD, DGDG), see Fig. 1.4.

For further details regarding these sub-groups refer to [1,2]. In the scope of commercial lecithins they play only a minor role.

1.1.3 Occurrence of phospholipids

All living organisms – plants, animals or micro-organisms – are made up of tiny functional units, called cells. These cells are surrounded by an external membrane, but numerous membrane structures also exist within the cell. The principal structure-forming substances in these highly functional units (i.e. cells) are the phospholipids. Phospholipids are therefore present in all living organisms and can be obtained from a wide variety of raw materials in the natural world.

Essentially, however, the only raw materials suitable for commercial use are oilseeds and egg yolk. Plant raw materials have a low phospholipid content, which (as a percentage of dry matter) does not exceed 2.5%. Raw materials of animal origin, by contrast, have much higher phospholipid content. In dried whole milk, for example, it is around 2% and in dried egg yolk around 17%.

The phospholipid composition and fatty acid profile generally gives us a clear indication of the origin of the product. Tables 1.1 and 1.2 provide an overview of the phospholipid composition and fatty acid profiles of various vegetable and animal lecithins.

1.2 Production of lecithins

The processes for producing lecithin on an industrial scale may display considerable differences, depending on the raw material in question.

Vegetable lecithins are manufactured exclusively as by-products of the vegetable oil refining process. For animal lecithins extraction processes have been developed and are applied commercially.

Table 1.1 Average composition of plant and animal oil-free phospholipid extracts

	Percentage of total phospholipids					
Phospholipid	Soya	Rapeseed	Sunflower	Corn	Egg yolk	Milk
Phosphatidylcholine	24	25	25	30	74	27
Phosphatidylethanolamine	22	22	11	3	19	36
Phosphatidylinositol	15	15	19	16	1	
Phosphatidic acid	7		3	9		
Sphingomyelin					2	29
Lyso-phospholipids	3	5		5	3	
Other phospholpids	5	19			1	8

Table 1.2 Average fatty acid profiles in plant and animal lecithin extracts

	Percentage within total fatty acids				
Fatty acid	Soya	Rapeseed	Sunflower	Corn	Egg yolk
16:0 Palmitic acid	21	18	15	23	30
18:0 Stearic acid	4	1	3	1	16
18:1 Oleic acid	12	21	13	26	29
18:2 Linoleic acid	57	48	69	48	14
18:3 Linolenic acid	6	7		1	1
20:4 Arachidonic acid					5
20:6 Docosahexaoenic acid					3

1.2.1 Vegetable lecithins

To stabilise vegetable oils against sedimentation and also to enable further refining steps, phospho- and glycolipids must be removed. During the so-called *degumming* process the crude oil is heated to about 70°C, mixed with 2% water and subjected to thorough stirring for about half an hour to one hour. This addition of water to the oil hydrates the polar lipids in the oil, making them insoluble. The resulting lecithin sludge is then separated by centrifugation.

This wet sludge is made up of water, phospholipids and glycolipids, some triglycerides, carbohydrates, traces of sterols, free fatty acids and carotenoids. The crude vegetable lecithin is then obtained by careful drying.

Dozens of modified degumming processes are described in the literature [3], but their objective is to minimise the residual phosphorus content in the oil and hence the phospholipid content that causes problems during further refining. The conditions during the degumming process, such as the quality and origin of the oilseeds, have a considerable influence on the composition and quality of the crude lecithin. Figure 1.5 shows the example for lecithin isolation as part of the oil refining process from soybeans.

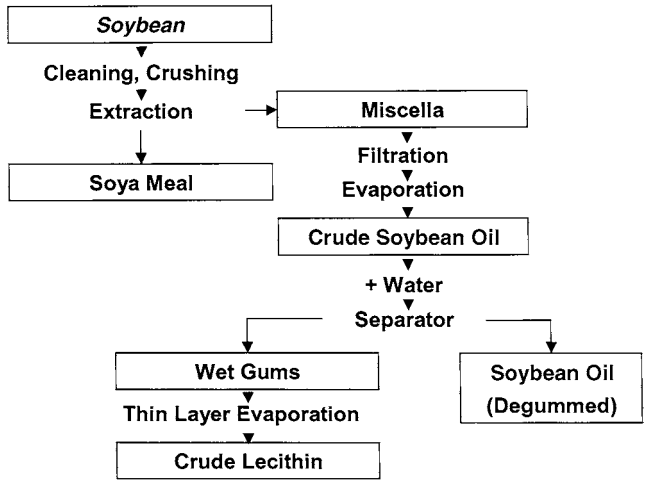

Fig. 1.5 Gaining crude lecithin from soybeans.

1.2.2 Animal lecithins

Unlike the production of vegetable lecithins, there is no comparable industrial process for the production of animal oils. Various methods are therefore used for producing lecithins of animal origin.

Egg lecithin, the most important product in this category, is usually produced by combined extraction with ethanol and acetone. Due to these different processes, egg lecithins are more expensive in their production and are therefore not competitive with plant lecithins in technological driven applications of the food industry. They, however, play a key role, for example, in infant nutrition under physiological aspects (they can deliver high amounts of arachidonic and docosahexaenoic acid) and in highly purified and isolated versions as emulsifiers in pharmaceutical emulsion systems.

1.3 Further processing of lecithins

Crude plant lecithins derived from the above mentioned processes are not yet suitable for use in food applications. One of the first steps for further refining of the lecithins is the microbiological standardisation of the crude material by means of a hydrogen peroxide treatment. Depending on the parameters of such a treatment, a bleaching effect can also be achieved in order to get a pale colour. It has to be mentioned, however, that from a legislational point of view bleaching for foodgrade lecithins is only allowed in certain countries, e.g. the United States, whereas in Europe it is explicitly excluded.

1.3.1 Standardisation

As already mentioned, the composition of lecithins may vary considerably depending on the raw material source. Even when discussing about soy lecithin exclusively, the soy variety, the geographic region, weather, storage and processing conditions have a significant influence on the various quality aspects of lecithins (see also Section 1.4).

As various constituents of lecithins (phospholipids) contribute in a different way to the functionality in the final application (see Section 1.6.1.1), it is reasonable to standardise the final lecithin products by blending different crude qualities in order to guarantee a consistent composition, and thereby its functionality. Also the total phospholipid contents may vary significantly and need to be adjusted (also see Section 1.4.2).

1.3.2 Modifications of lecithins

So far we have only discussed about fluid lecithins as primarily derived from the degumming process and standardised towards a consistent composition. There are, however, a series of technologies and methods that can be applied to such 'standard' grade products.

These various ways of processing lecithin result in a wide range of individual products with fundamental differences in their composition, and hence their functionality.

The aim of these processes is to adapt lecithin for specific application requirements by giving it technical or physiological properties that the natural substance does not possess.

All these potential products are commercially termed 'lecithin'. It is apparent that the end-user of these products needs to know and understand the particular differences and characteristics of the product in order to choose the particular quality that can best suit the requirements of his/her application.

1.3.2.1 Enzymatic modification

Enzymes can be used to modify phospholipids in a wide variety of ways. There are various known hydrolytic enzyme systems that can change the structure of phospholipids. Being all esterhydrolases, they differ in their point of attack on the phospholipid molecule (see Fig. 1.6).

The phospholipases A_1, A_2, C and D can be easily distinguished. It is typical for hydrolytic enzymes that their catalytic influence can be used for *hydrolysis* or for transesterification.

Hydrolysis of lecithin with phospholipase A_2 is of great commercial significance. Originally the enzyme was obtained from the pancreas of pigs, but now are qualities produced from micro-organisms are also used.

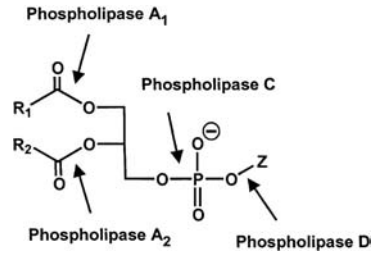

Fig. 1.6 Point attack of various types of phospholipases.

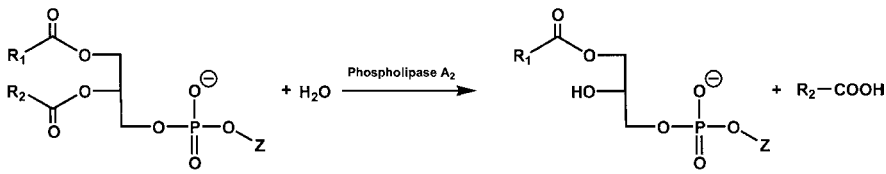

Fig. 1.7 Reaction of phospholipase A_2 in the formation of 1-monoacyl-*sn*-glycero-3-phospholipids.

Phospholipase A_2 splits the fatty acid in the second position, forming lysophospholipids and free fatty acids (see Fig. 1.7).

Phospholipase A_1, by contrast, splits the fatty acid in the first position. After hydrolysis, however, a fatty acid may also migrate from the C2 to the C1 position. Partially hydrolysed lecithin products possess improved emulsifying properties, as seen from Fig. 1.8. The higher the degree of hydrolysis, the smaller the droplets that are generated in a comparative emulsification process.

One method which is of growing interest is enzymatic hydrolysis with phospholipase D. This reaction increases the phosphatidic acid (PA) content in the lecithin. The resulting products have improved emulsifying properties and can effectively mask the bitter taste of various substances.

1.3.2.2 Chemical modifications

Phospholipid molecules can be chemically modified in several ways, but only a few of these processes are used for commercial purposes. This is partly due to the fact that apart from acetylated products, chemically modified lecithins, for legal reasons, can currently only be used in non-food applications. This will be briefly discussed in this chapter.

Hydroxylation. Hydroxylation is a very effective process for improving emulsifying properties of lecithins for o/w systems. Thanks to the catalytic effect of small amounts of organic acids of low molecular weight (e.g. lactic acid),

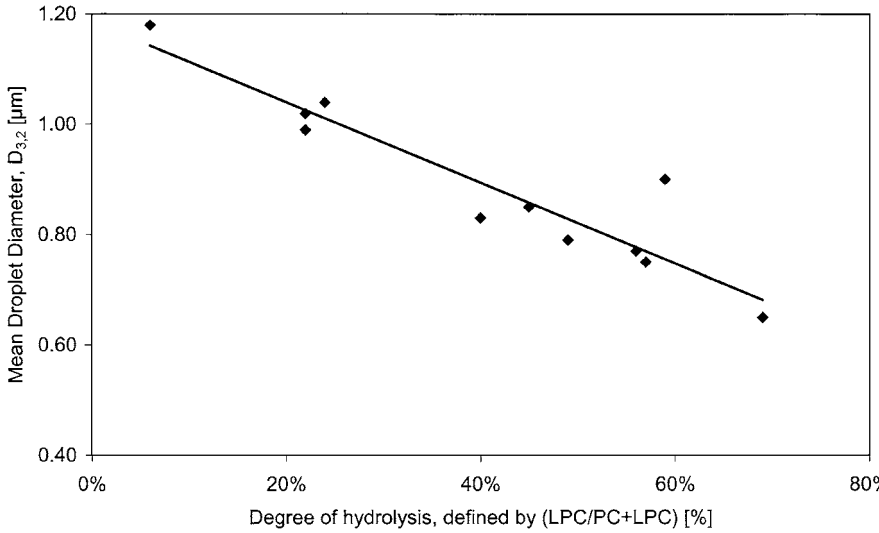

Fig. 1.8 Emulsification capacity of hydrolysed lecithins as a function of degree of hydrolysis.

hydrogen peroxide reacts with the double bonds of unsaturated phospholipid fatty acids and forms very hydrophilic dihydroxy fatty acid derivatives.

Acetylation. Another method of improving the hydrophilic properties of lecithins is acetylation. In a reaction with small amounts of acetic anhydride, the free amino group of the phosphatidylethanolamine (PE) is acetylated. Acetylated lecithin mixtures are excellent o/w emulsifiers and also exhibit good thermal stability. This is due to the fact that there is no longer a primary amino group available for Maillard reactions with the carbohydrate constituents of the lecithin (see Fig. 1.9).

Hydrogenation. All natural lecithin (phospholipid) mixtures contain some amount of unsaturated fatty acids. This makes the products susceptible to oxidative processes, which ultimately leads to undesirable taste and odour (rancidity). A catalytic hydrogenation process can be used to transform the unsaturated fatty acids into saturated fatty acids. Only the use of palladium and platinum catalysers permits acceptable conversion rates. As a side-effect of the hydrogenation, most of the natural pigments are destroyed, turning the resulting products into white, free-flowing powders.

The derived products possess excellent resistance to oxidation and have very good emulsifying properties. Their main application areas are in the cosmetic industry.

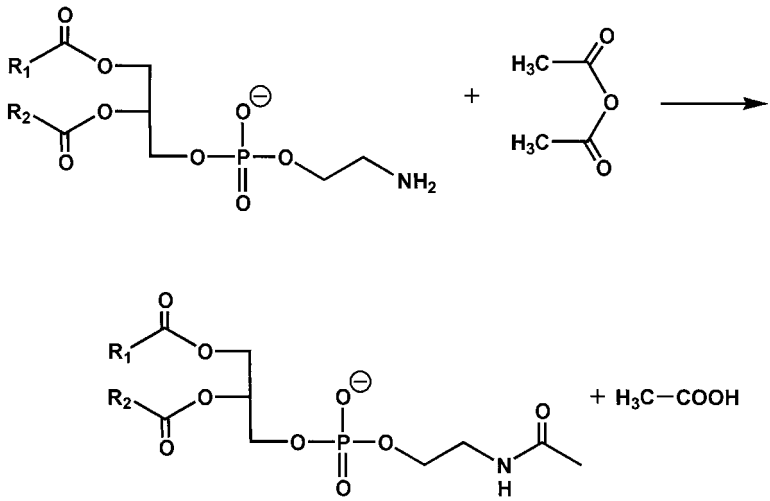

Fig. 1.9 Acetylation of phosphatidylethanolamine with acetic anhydride.

Table 1.3 Average composition of crude (fluid) and de-oiled lecithins from soya (%)

	Crude lecithin	De-oiled lecithin
Phospholipids		
Phosphatidylcholine (PC)	9–17	20–23
Phosphatidylethanolamine (PE)	8–15	16–21
Phosphatidylinositol (PL)	8–11	12–18
Phosphatidic acid (PA)	3–10	7–11
Other phospholipids	5–10	8–13
Total phospholipids	~56	~86
Glycolipids	~6	~10
Neutral lipids		
Triglycerides	35–40	2
Free fatty acids	2	0.25
Sterols	1–2	0.25
Total neutral lipids	38–44	2.5

1.3.3 Solvent extraction

1.3.3.1 De-oiling with acetone

Fluid lecithins contain about 30–40% neutral lipids, mainly triglycerides.

To improve the processing characteristics of these highly viscous materials and to improve dispersability properties, the Industry makes use of the fact that polar lipids (phospholipids and glycolipids) are almost insoluble in acetone whereas neutral lipids dissolve in it. Acetone extraction leads to powdered or granulated products that contain 2–3% residual neutral lipids (see Table 1.3).

To improve their flow properties, products can also be combined with flow agents such as tricalciumphosphate or silicon dioxide. Similar to standard fluid lecithins, enzymatically modified lecithins may also be used as raw materials for de-oiling. The resulting products display a significant improvement in emulsifying capacity and in dispersability in water. The key result of the de-oiling process is that the phospholipids, as the components that provide functionality, have now been concentrated and purified. This results in significantly lower dosage requirements and higher functionality. Moreover, de-oiled products have a more neutral taste than the corresponding liquid products.

1.3.3.2 Fractionation with alcohol

The production of lecithin fractions largely makes use of ethanol or ethanol–water mixtures. The fractionation process takes advantage of the differences in solubility of the phospholipids in ethanol.

Phosphatidylcholine (PC) in particular is readily soluble, whereas phosphatidylinositol and phosphatidic acid are virtually insoluble. Phosphatidylethanolamine, such as the neutral lipids, is found in both fractions, which are of growing economic interest because of their different technological properties: the alcohol-soluble fraction has improved emulsification capabilities in oil-in-water emulsions, whereas the insoluble fraction provides superior water-in-oil emulsion.

The fractionation method with alcohol, in principle, can be used on lecithins of natural composition, on modified lecithins and on de-oiled lecithins. Due to the processing costs involved, for the food industry only the first version is of interest, the other varieties find application in the pharmaceutical, cosmetic and dietetic industry. For these industries further chromatographic purification processes exist, to derive purified (98%) phosphatidylcholine concentrates. Table 1.4 shows the phosphatidylcholine concentrations of various lecithin fractions after fractionation of a liquid and a de-oiled soy lecithin.

1.3.4 Compounding

A further technological option to derive lecithins that are tailored to their final application is the possibility of compounding. In theory, this opens the door to an unlimited range of potential products. Only the most common technologies shall be mentioned here.

Table 1.4 Result of ethanol fractionation of different lecithins

	Starting material	Ethanol soluble fraction	Ethanol insoluble fraction
Fluid lecithin	15	33	12
De-oiled lecithin	24	52	12

1.3.4.1 Fluid compounds

Compounding of fluid lecithins with neutral oils (triglycerides) is typically used for the adjustment of the viscosity of the liquid lecithin. For a standard fluid lecithin, the viscosity is typically around 5–10 Pa·s at 25°C. In certain applications (e.g. in instantising processes) lecithins are sprayed onto the instant products in order to improve the re-constitution behaviour. By mixing lecithin with carrier oil, its viscosity and thereby spraying properties can be adjusted.

Compounding with co-emulsifiers is, for example, used in chocolate industry (see Section 1.6.1.1).

1.3.4.2 Integrated powder compounds

Fluid lecithins can be sprayed on carrier systems. These carriers can be 'neutral' (e.g. flours), in which case the fluid lecithin is converted into a powder structure, which basically influences handling properties. The carrier systems however, can also have a functional (synergistic) effect in the final application. Compounds of lecithins used with lactose or whey powder for baking applications first deliver the functionality of the lecithin, and also significantly improve browning properties.

The spraying of fluid lecithin onto a powder carrier is typically limited to 30–45% of lecithin, due to the final products becoming sticky and lumpy with higher amounts of free surface fat. Higher concentrations of lecithin can be achieved through a spray-drying process. In this case initially a liquid emulsion from lecithin and e.g. whey concentrate is prepared and subsequently spray dried. Through this process the lecithin is encapsulated in the powder structure and is not merely located at the surface of a carrier system. Lecithin concentrations of 50% and above are achievable with this technology.

1.4 Quality aspects of lecithins

Lecithins as food additives are legally regulated in the European Union under directives 95/2/EG (applications) and 96/77/EG (quality requirements) under the number E 322.

In the Unites States lecithins are generally recognised as safe (GRAS), the minimum quality requirements are laid down in the directive 182.4000 FDA.

The main definition of E 322 is given as under:

> Lecithins are mixtures or fractions of phospholipids that are obtained from animal or vegetable foodstuffs by physical processes.
>
> They also include hydrolysed substances, which are obtained by the use of harmless and suitable enzymes. The finished product is not allowed to show any residual enzyme activity.

Lecithin may be bleached in aqueous medium by hydrogen peroxide, but this may not chemically affect the phospholipids.

Appearance	Lecithins: High viscous or semi-liquid or powder products of brown colour. Hydrolysed lecithins: High viscous or pasty fluids of light brown to brown colour.
Content	Lecithins: Not less than 60% acetone insoluble substances. Hydrolysed lecithins: Not less than 56% acetone insoluble substances.
Volatile substances	Less than 2%, determined after 1 h drying at 105°C.
Toluene insoluble substances	Less than 0.3%.
Acid value	Lecithins: Less than 35 mg potassium hydroxide per gram. Hydrolysed lecithins: Less than 45 mg potassium hydroxide per gram.
Peroxide value	10 or less, expressed in mequ/kg

The most important quality measures, their meaning and implications shall be briefly described. The respective methods have been agreed by the American Oil Chemists' Society (AOCS) and the Deutsche Gesellschaft für Fettwissenschaft e.V. (DGF).

1.4.1 Acetone insoluble matter (AI)

The wetting and emulsifying effect of lecithin is due to the content of polar lipids and, in particular, the quantity of phospholipids. Since polar lipids are insoluble in acetone, the acetone-insoluble matter serves as a standard for the valuable constituents of lecithin. To determine acetone insolubles, the oil phase is removed quantitatively by kneading the lecithin with acetone and measuring the residue gravimetrically.

The abbreviation 'AI' can also be referred to as Active Ingredients.

1.4.2 Toluene insoluble (TI)

For reasons of purity, taste and action, lecithin must be free from impurities. Measurement of the toluene-insoluble matter includes residues originating from the extraction process (seed particles), turbidities resulting from processing and compounds that have become insoluble during storage. The abbreviation 'TI' can also be referred to as Total Impurities.

In the United States, hexane is being used rather than toluene, therefore the hexane insoluble value is also a reference for the purity of a lecithin. Both methods, in general, deliver identical values when applied to the same material.

1.4.3 Acid value (AV)

If the oilseeds being used as primary source are improperly stored, some of the lipids may degrade (hydrolysis) and free fatty acids make their way into the crude lecithin where they are not required. On the other hand, finished lecithins must have a certain acid value to prevent separation of the constituents and this may be achieved by deliberately adding pure fatty acids. The acid value, therefore, serves as a standard for the age or storage qualities of lecithin, depending on whether the raw materials or the finished products are being analysed.

1.4.4 Peroxide value (PV)

Together with organoleptic testing, the peroxide value provides a criterion for assessing the freshness of lecithins and the absence of deterioration. The first stage in the autoxidation process of lipids is the formation of hydroperoxides as a result of the uptake of oxygen at the double bonds of the unsaturated fatty acids. To comply with the purity requirements for E 322 lecithins, the peroxide value of lecithins used in the manufacture of foods must not exceed 5.

1.4.5 Water content (H_2O)

Being amphiphilic substances, phospholipids and therefore lecithins always contain small amounts of water. Since microbial growth is dependent on water, the content in lecithins is restricted to maximum 2%.

Today the quality of lecithins is additionally determined and described by a series of further analytical measures, such as viscosity, colour, taste, phospholipid and fatty acid profiles, heavy metal, pesticide and solvent residues, microbiology and microbial toxins, etc.

1.5 Physico-chemical aspects of lecithins

1.5.1 Solubility in organic solvents

The solubility of the various components of lecithin in organic solvents is derived primarily from their polar headgroups and depending on the fatty acid composition. The solubility of phosphatidylcholine in ethanol, for example, decreases as the length of the acyl-chains increases. Whilst phospholipids usually do not dissolve in acetone (see Section 1.3.3.1), phospholipids with acyl chains less than C:10 are soluble in acetone. Nevertheless, complete separation of individual phospholipids on the basis of their different solubility in certain solvents is not possible, as each effects the solubility of the other. In certain organic solvents the solutions formed are not molecular dispersions but molecular aggregates are formed. Table 1.5 gives a qualitative overview of solubility in selected solvents.

Table 1.5 Solubility of certain phospholipids in selected organic solvents

Phospholipid	Hexane	Ethanol	Acetone
Phosphatidylcholine	+	+	−
Phosphatiidylethanolamine	+	+/−	−
Phosphatidylinositol	+	−	−
Lyso-phospholipids	+/−	+	−

Table 1.6 Average melting points of selected phospholipids

Phospholipid	Average melting point (°C)
Phosphatidylcholine	230
Phosphatidylethanolamine	196
Phospahtidylinositol	136
Phosphatidic acid	71
Lyso-phosphatidylcholine	240

1.5.2 Behaviour in water

Lecithins/phospholipids are substances that 'dissolve' in water with the formation of a number of highly ordered liquid crystal mesophases. By analogy to its thermal behaviour, this phenomenon is known as lyotropic polymorphism. The formation and structure of these phases are linked to concentration and temperature and are also induced by pH shifts.

Structures such as inverse micelles (globular and tubular), single and multilamellar systems, single- and multilayer liposomes as well as the typical micelles are known. A considerable research has been done in recent years [4,5], mainly on model phospholipids, as phospholipid mixtures/lecithins are even more complex in their behaviour.

1.5.3 Melting points

The melting point, as widely used for the characterisation of organic substances, can only be applied to a limited extent to phospholipids. Typically, the melting behaviour is superseded by chemical degradation processes. In general, the melting behaviour of phospholipids can be better determined by the structure of the polar headgroups than by the length and saturation level of the acyl chains. Average melting points for selected phospholipids can be seen from Table 1.6.

1.5.4 Surface activity

As with all amphiphilic substances, lecithins/phospholipids show surface activity, which is the key origin of their application as emulsifiers. Due to their

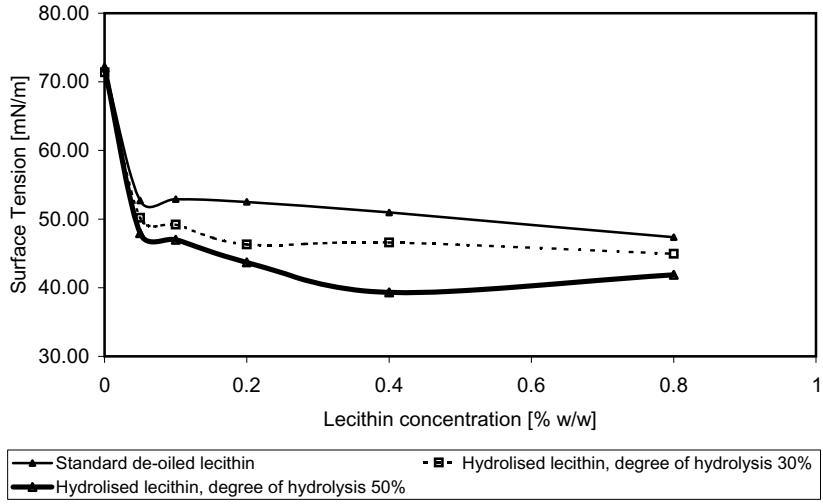

Fig. 1.10 Reduction of water surface tension by different types of lecithins.

chemical structure they always try to align on hydrophilic/lipophilic interfaces, with the fatty acid chains orientated towards the lipophilic phase and the polar headgroups orientated to the hydrophilic phase. Surface activity can be quantified by measuring surface- or interface tensions. Figure 1.10 shows the reduction of water surface tension through different types of lecithins as a function of concentration. It is apparent that hydrolysed lecithins show a much higher surface activity than regular lecithins/phospholipids. This is typical (e.g. well known from mono- and di-glycerides) as through the hydrolysis the phospholipids become more hydrophilic by loosing one lipophilic fatty acid, and the polar headgroup gains more weight in the molecular structure.

Another aspect of surface activity that plays a crucial role in the formation of emulsions are kinetic effects. In an emulsification process new surface area is generated through the comminution of, for example, oil droplets. These newly formed oil droplets can only be made permanent and stabilised against subsequent coalescence by the adsorption of the emulsifier molecules at the interface. The faster this adsorption takes place the higher the efficiency of this effect. Figure 1.11 shows these kinetic effects. Compared here are the interfacial tensions at a newly formed water/oil interface as a function of time. Again the difference between regular and hydrolysed phospholipids becomes obvious, not only with regard to the equilibrium surface tension being reached, but also with regard to the time to reach a certain reduction.

1.5.5 Lecithins and the HLB system

A question that is often asked when dealing with lecithins is related to their allocation within the HLB system. Table 1.7 shows the performance of typical

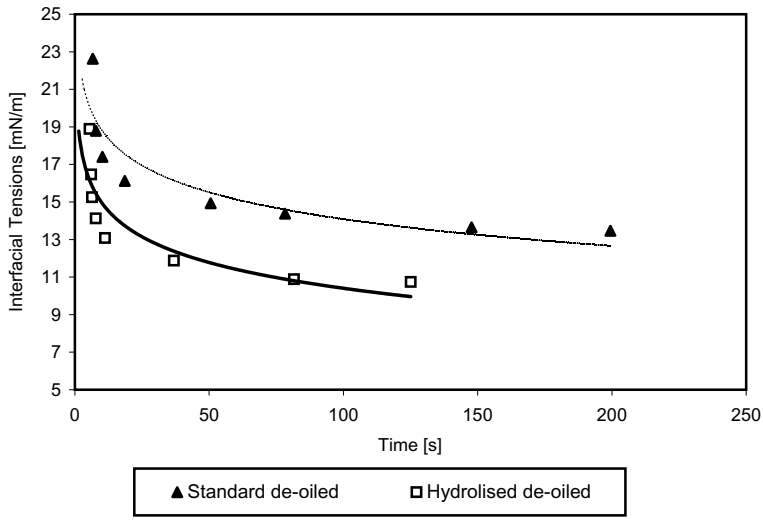

Fig. 1.11 Dynamic interface tension, mygliol/water system, 2% lecithin.

Table 1.7 HLB values related to field of application and solubility behaviour in water

Properties in water	HLB-value
Non-dispersible	0–2
Poor dispersibility	2–6
Milky dispersion	6–10
Stable milky dispersion	8–12
Transparent, clear dispersion	12–15
Clear, colloidal solution	15–20
Field of application	
Anti-foaming agent	1–3
Water-in-oil emulsifier	3–6
Wetting agent	7–9
Oil-in-water emulsifier	8–18
Detergent	13–15
Solubiliser	15–18

emulsifiers as a function or their HLB values. Also shown is their solubility/dispersability in water.

The basic HLB equation is valid for non-ionic molecules. Dispersing behaviour, as a method for classification purposes, was also found to be helpful and relevant for other types of emulsifiers. However, this methodology fails when trying to apply it to lecithins. They are rarely rated higher than an HLB value of 9 (this would be for hydrolysed acetylated lecithins). Standard qualities are

typically classified between HLB values of 2–7. This would imply that lecithins are actually not capable of forming oil-in-water emulsions.

However, a standard fluid lecithin (HLB 2 according to the dispersability) can form such emulsion (also see Section 1.6.4).

1.6 Applications of lecithins in the food industry

From this general introduction to lecithins it is apparent that we are discussing complex systems of surface-active components which through processes like modification, fractionation, de-oiling, compounding etc. and combinations thereof, can be further tailored to their final application.

Considering the large variety of disperse systems in the food industry, it also becomes clear that the 'right' lecithin needs to be chosen to guarantee optimal performance (see Table 1.8).

1.6.1 Lecithin in chocolate, coatings and confectioneries

1.6.1.1 Chocolate

One of the most traditional applications for lecithins is chocolate. Chocolates are very complicated rheological products due to their disperse systems consisting of sugar, cocoa particles, milk ingredients and cocoa butter. The rheology plays a key role not only under processing conditions (e.g. pressure drop in piping systems, layer formation in coating applications), but primarily under organoleptic aspects when experiencing the sensation of a high quality chocolate tenderly melting on your tongue.

During the complex manufacturing process of chocolates one major effect is the grinding of the sugars. The finer the sugar crystals become, the more the viscosity is increased through increased internal friction forces between the crystals. At a certain point the chocolate mass, even above the melting point of the fat phase, would become solid. Of course, this problem could be overcome by adding additional cocoa butter to the mixture and thus 'diluting' the system.

Table 1.8 Classification of disperse systems

Continuous phase	Disperse phase	Type
Liquid	Liquid	Emulsion
Liquid	Solid	Suspension
Liquid	Gas	Foam
Gas	Liquid	Aerosol
Gas	Solid	Aerosol

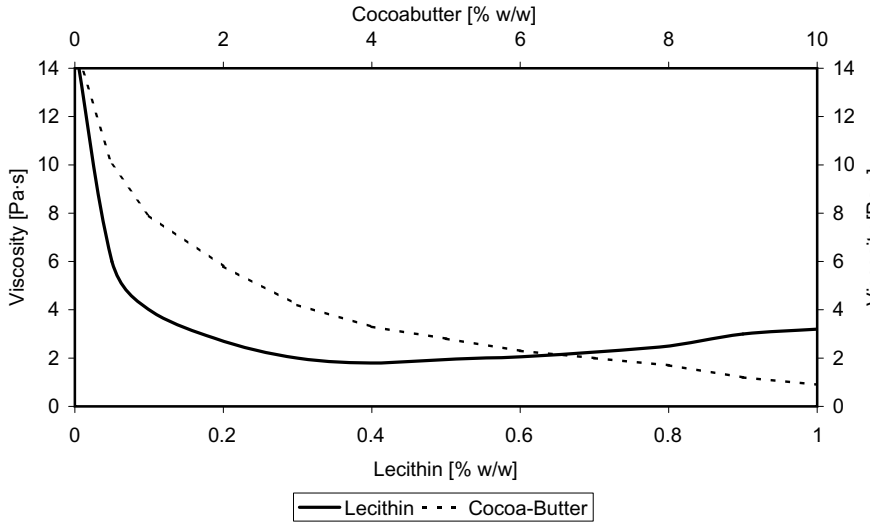

Fig. 1.12 Viscosity reduction in chocolate by (a) lecithin and (b) cocoa butter.

Fortunately, with cocoa butter being the most expensive material, there is a much more elegant and cheaper way to solve the problem. Adding only very little quantities of lecithin, the viscous behaviour can easily be adjusted. Figure 1.12 shows the comparison in viscosity reduction when either adding lecithin or cocoa butter to a chocolate mass.

This effect can be easily explained: the phospholipids align on the surface of the sugar crystals, thus making them 'lipophilic' at their outside (due to the hydrophilic headgroup adsorbing at the hydrophilic surface and the lipophilic fatty acid chains being oriented to the fat phase). These kinds of molecular layers act as lubricant and thereby reduce internal friction and thus viscosity. A very interesting phenomenon can also be seen from the figure. When adding too much lecithin (more than typically 0.3–0.4%) an inverse effect can be seen (viscosity increase). How can this be explained?

Here the phase behaviour of phospholipids and their tendency of forming lamellar structures are the explanations. When sugar crystals are sufficiently covered by phospholipids and lecithin is added in excess, then the additional phospholipids do not simply dissolve in the fat phase but align to other phospholipids again to form lamellas. So a second layer is built on the 'coated' crystals. However, now with the fatty acid chains aligning to each other and thereby making the outside of the entire structure more hydrophilic, The result is an increase in viscosity.

These general observations for 'lecithin' become interestingly differentiated when looking at individual phospholipids.

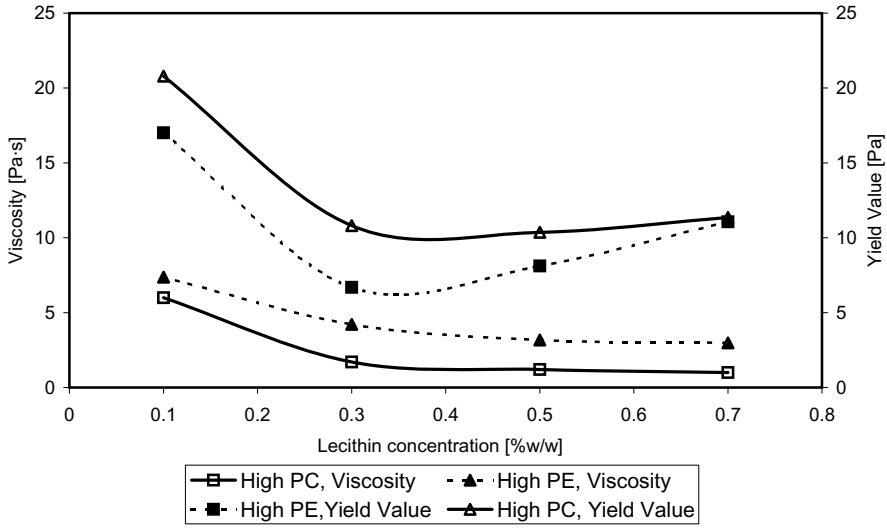

Fig. 1.13 Different effect of phosphatidylcholine and phosphatidylethanolamine on viscosity and yield value of chocolate.

Phosphatidylcholine is a phospholipid primarily responsible for reducing the viscosity having, however, less effect on yield values; by contrast, phosphatidylethanolamine (PE) is not so efficient in viscosity reduction but reduces yield value better than PC (see Fig. 1.13).

These opposing functionalities explain the variation in viscosity and yield value of identical chocolate compositions when conventional unstandardised lecithins are used, due to the phospholipid pattern potentially being significantly different.

By using lecithin grades with a standardised phospholipid pattern, it is possible to achieve a consistent adjustment of the flow characteristics of chocolate compositions. This in turn makes it easier to standardise production conditions.

By choosing a fractionated lecithin with an increased level of phosphatidylcholine, particularly the yield value can be affected in a controlled way. The yield value plays a predominant role in coating processes where a defined thickness and homogeneity of the coating is required.

By combining selected vegetable lecithins with co-emulsifiers, it is possible to achieve synergistic effects in the rheological properties of chocolate compositions. The co-emulsifier can have a stronger and more specific effect on the yield value than lecithin. But the combination with lecithin is necessary to achieve low viscosity. Hence, maximum reduction of both viscosity and the yield value can be ensured by choosing the optimum ratio for mixing lecithin and the co-emulsifier (see Fig. 1.14).

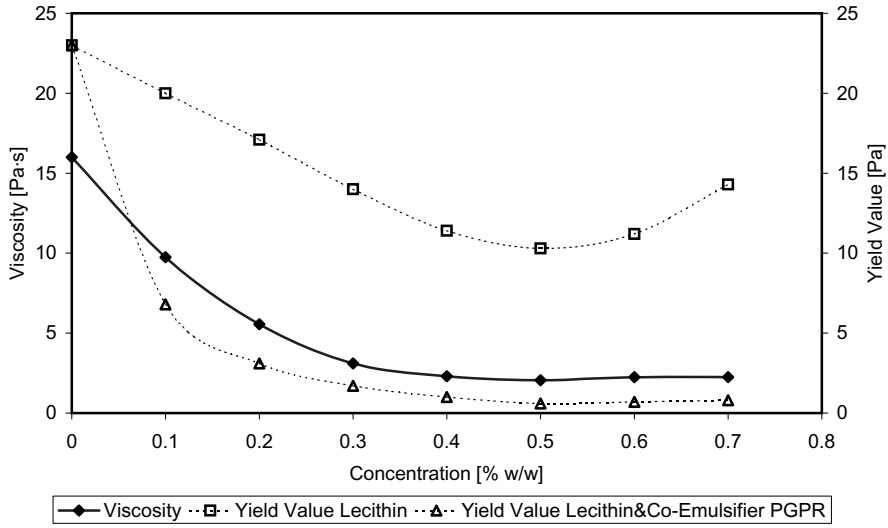

Fig. 1.14 Different effect of lecithin and lecithin/co-emulsifier mixture on yield value of chocolate.

Table 1.9 Qualitative comparison of different lecithin qualities and their effect on yield value and viscosity

Lecithin type	Yield value	Viscosity
Standard lecithin	⇩ ⇩	⇩ ⇩
Standard lecithin with guaranteed PC/PE ratio	⇩ ⇩	⇩ ⇩
Combination of selected standard lecithin and PGPR	⇩ ⇩ ⇩ ⇩	⇩ ⇩
PC-enriched lecithin fraction	⇩	⇩ ⇩ ⇩

Table 1.9 gives a summary on typical lecithin products for chocolate applications and their qualitative effects on viscosity and yield value.

The point at which the lecithin is added during the production process is very important. If added too early it may impair the flavour, since lecithin is hydrophilic and binds the water in the chocolate mass, impeding extraction of the unwanted, steam-volatile flavour components. Also, if allowed to take effect for too long, some of the lecithin may penetrate into the cocoa particles and be lost as functional ingredient acting on the surface of the particles. On the other hand, if the lecithin is added too late, the mixing time is not long enough to ensure a homogeneous distribution of the lecithin in the chocolate and thus results in the reduction of flow properties. It is typically recommended that the lecithin be added towards the end of the conching process with the remaining conching time being at least 60 minutes.

1.6.1.2 Coatings

Rather than using real chocolate for coating purposes, very often coating compounds are used. These coating compounds may be prepared from cocoa butter or cocoa butter substitutes. Generally, such compounds have one thing in common which is a much lower dry-matter content than real chocolate, thereby having lower viscosity effects and therefore they usually do not require lecithin at all.

In the particular case of ice cream coatings, however, we may be confronted with a different problem, i.e. moisture. Coating materials are usually poured over conveyor belts with the ice cream products transported underneath, or the products are dipped into a bath of coating material. The (excess) coating mass is typically re-circulated during the process. Coming into contact with moisture from the ice cream, the coating mass, over time, takes up reasonable quantities of water. This has significant effects on the viscosity of the material, and thereby on the quality of the final coating on the ice cream; for example, uneven thickness of the layer, resulting in excessive use of material, unpleasant appearance of the surface, cracking of the coating or formation of the so-called pinholes with subsequent 'ice-bleeding'.

Figures 1.15 and 1.16 show the effect of moisture on cocoa butter based ice cream coatings and how the problems can be avoided through the use of lecithins. Due to the affinity of phospholipids to water, they absorb moisture and maintain a viscous behaviour. In this particular application again PC-enriched lecithins give superior results than normal lecithins.

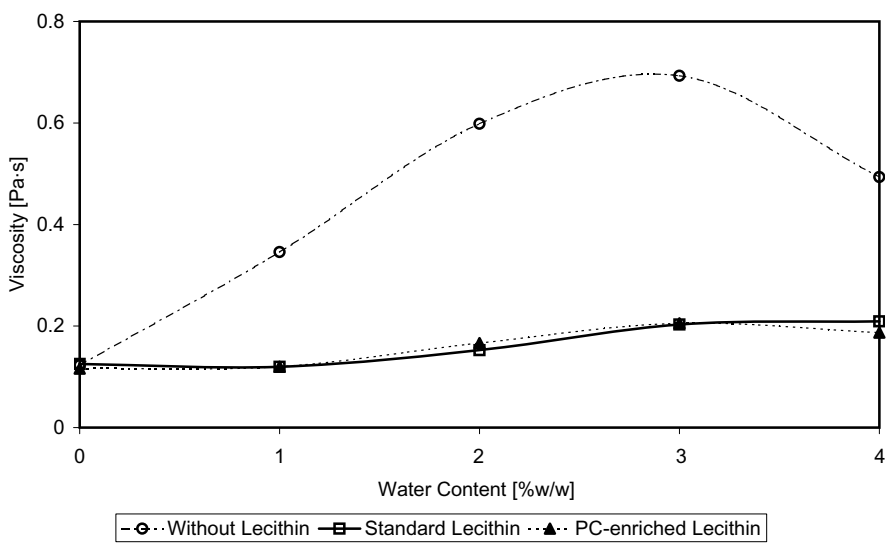

Fig. 1.15 Viscosity of chocolate coating depending on water content; 0.6% w/w lecithin.

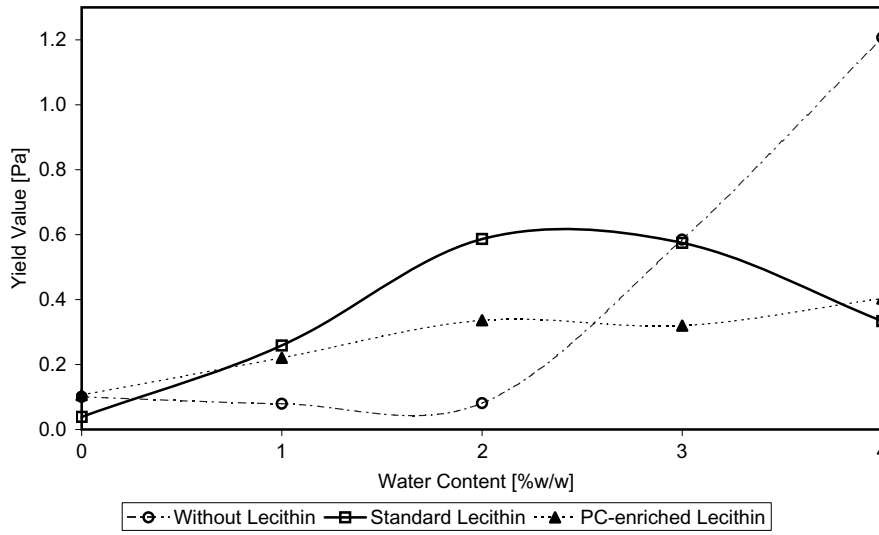

Fig. 1.16 Yield value of chocolate coating depending on water content; 0.6% w/w lecithin.

1.6.1.3 Chocolate products with fat-based fillings

In confectionery industry a wide variety of products sometimes have a creme filling. These fillings are very often chocolate based or contain nuts, almonds or other ingredients that contribute to certain fat levels in the mass.

A characteristic of these products is the problem of the so-called 'fat bloom'. Within the filling, a certain amount of the fat has a comparably low melting point (to provide the filling its creaminess) and is actually liquid at ambient temperatures. As this part is liquid, it is 'mobile' and therefore starts to migrate. This migration also takes place into the surrounding chocolate coating of the praline and then on to the surface, where the effect can then be identified as 'rime'. The process slowly takes place during shelf life. The longer the intended shelf life, the higher the risk for the final consumer to find products that show this defect. Higher temperatures (specifically in warmer countries) accelerate the effects. A method to prevent migration is to add a material to the filling that is able to bind/absorb the liquid part of the fats and thus to 'immobilise' it. It could be shown that a de-oiled lecithin can deliver this functionality. Added to the filling at 0.3–0.6%, it can significantly reduce the problem. It is important to note that a regular fluid lecithin will not show such functionality. In fact, it will even worsen the problem as it brings additional (soybean) oil into the formulation.

It is only through the de-oiling step, that the lecithin provides high affinity to oils in the formula and starts to bind them.

1.6.1.4 Soft and hard caramels, chewing gums

As in the case of chocolate products, caramels, toffees, chewing gums etc. are complex multi-component mixtures. In the primary stages of production the functionality of an emulsifier is particularly aimed to guarantee a homogeneous distribution of the various ingredients and to improve machinability. In the case of fat or milk-based caramels the fat phase needs to be emulsified. In this case hydrolysed lecithins show their optimal properties. Additionally, lecithins provide functionality in the finished products during shelf life. Sugars, for example, start to re-crystallise. If crystal growth exceeds a certain size, the texture of the product becomes brittle. Hydrolysed lecithins are known to control such re-crystallisation processes, keeping crystal growth limited.

For the same reason, very often glucose or dextrose syrups are used instead of crystalline sugar. These, however, add significant quantities of water to the formulation that needs to be stabilised in the final product. Again, due to their emulsifying properties, lecithins deliver this functionality.

A further aspect is a kind of release effect that can be attributed to lecithin: with soft candies, for example, the perception of the consumer is to have a nice chew, however, without the candy sticking to his/her teeth.

The example of chewing gum illustrates the importance of the moisture retention capacities and thus the influence on freshness and shelf life.

Traditionally, lecithin is used as a dispersing aid in the manufacture of gum base. In the final chewing gum process the remaining components such as flavours, sugar syrups etc. are added. The addition of minor quantities of de-oiled lecithins does have a significant influence on moisture retention and the texture of the finished product (see Figs. 1.17 and 1.18)

1.6.2 Lecithins in the baking industry

A second traditional area of application for lecithin is the baking industry.

The technological effect of lecithin differs according to the kind of product. In yeast-leavened wheat doughs, lecithin improves the extensibility of the gluten. This leads to better dough processing, an improved fermentation stability, and ensures a higher volume and a more uniform texture.

In cake, pastry and biscuits lecithin brings about an improved distribution of the basic substances. This essentially yields a homogeneous fat distribution, better paste processing properties and uniform browning. Using lecithin in wafer masses results in a homogeneous distribution of the ingredients, in a good release effect of the wafers from the irons, in an improved texture of the wafer sheets, and in a more even browning.

Looking at the different categories and related functionalities, it becomes clear why the baking industry uses the widest range of lecithin products. Irrespective of whether it is fluid lecithins or de-oiled/compounded varieties, regular

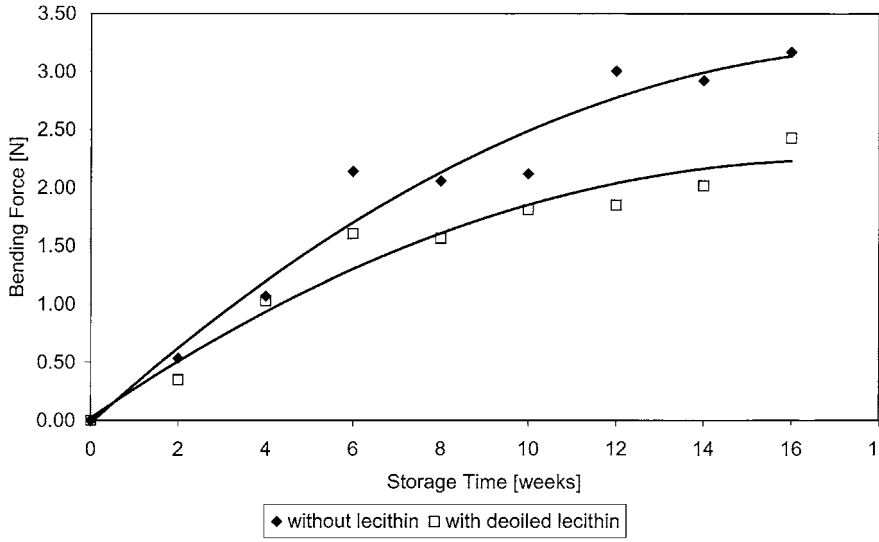

Fig. 1.17 Texture analysis of chewing gum over shelf life.

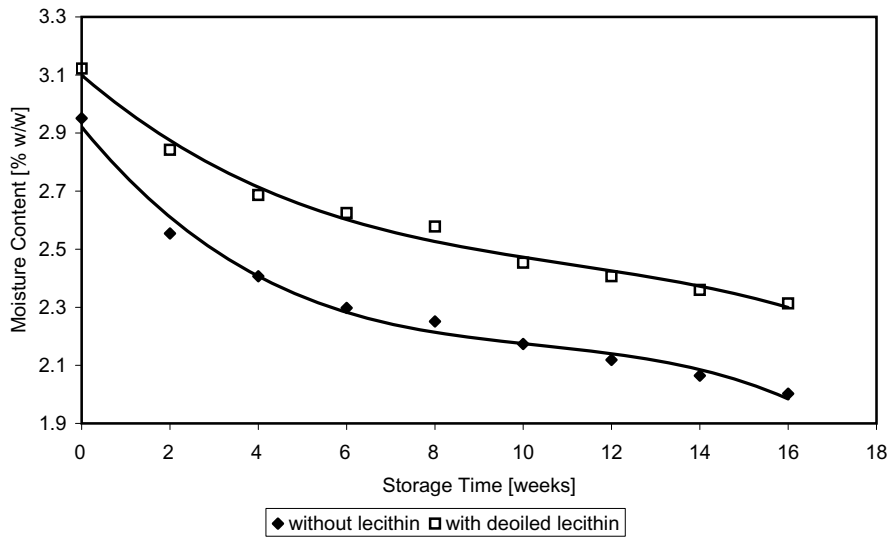

Fig. 1.18 Moisture content of chewing gum over shelf life.

or hydrolysed qualities, application-driven selection of the right product is the key to the final success and thus to the product quality.

1.6.2.1 Yeast-leavened bread and the role of phospholipids

Several models have been proposed to explain the role of (phospho)lipid/protein interactions in bread making. Basically they all have in common the formation of complexes between either proteins and starches or of the various protein fractions of flours, with phospholipids being the link between different components.

Hess and Mahl have proposed that protein is bound to starch granules via a phospholipid layer. Grosskreuz postulated that phospholipids form bi-molecular layers in gluten, with the protein chains bound to the lecithin through salt-type linkages between acidic groups of phospholipids and basic groups of proteins. Hosney proposed a gliadin–phospholipid–glutenin complex (as expressed in [6,7]).

The macroscopic result of these potential models is the same in each case: the elasticity of the dough and therefore the machinability, homogeneity and stress resistance are significantly improved. This again results in an increased gas holding capacity and an optimised baking profile (see Fig. 1.19).

Another particular effect of hydrolysed lecithins in shelf life improvement is the anti-staling effects. One explanation of staling is a change in the helical structure of α-amylose. In the original helix, water is complexed. During the retrogradation process, the helix transforms into another conformation

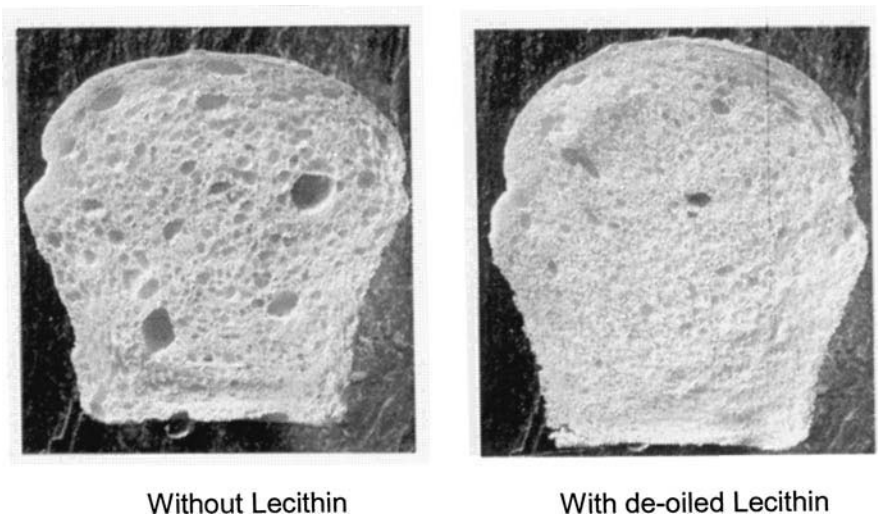

Fig. 1.19 Support of volume development and homogeneous pore structure through lecithin.

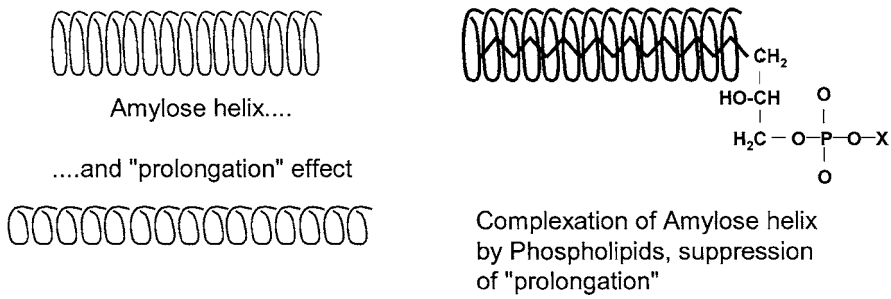

Fig. 1.20 Inclusion complex between amylose and phospholipids.

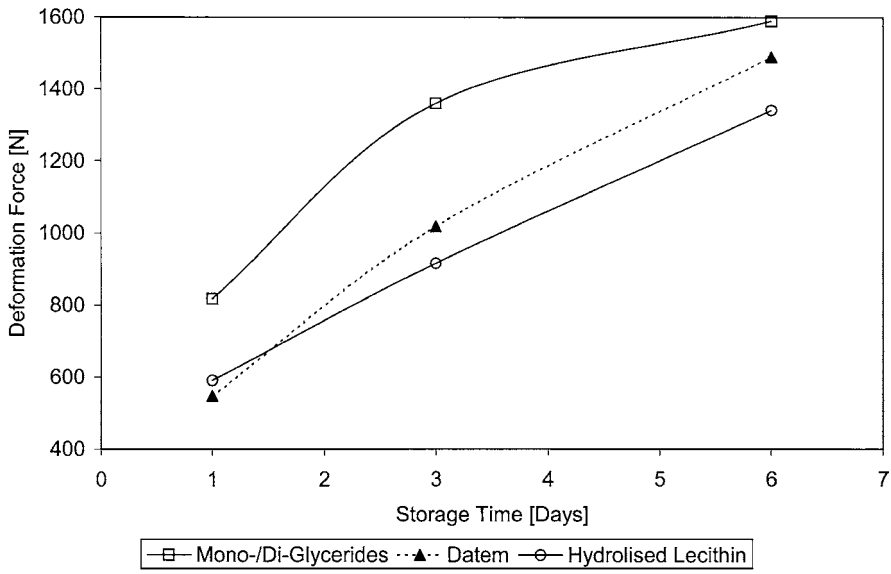

Fig. 1.21 Texture analysis of bread freshness over storage time.

(prolongation effect), at the same time losing the water complexation capability. This results in a loss of moisture and therefore freshness. By avoiding the helical change this effect can be suppressed. Hydrolysed phospholipids have the ability to form inclusion complexes with the αamylose helix as shown in Fig. 1.20. Thus, the retrogradation is hindered, water complexation is maintained, and thereby freshness extended. Figure 1.21 shows these effects as a result of a texture analysis.

1.6.2.2 Frozen doughs

In the continuously growing convenience food market, frozen doughs have become a major sector. Bread, rolls and buns lose their freshness very rapidly. The consumer prefers baked goods fresh from the oven, but with conventional methods this cannot always be fully achieved.

Today the baking industry has the means to interrupt the fermentation process by deep-freezing technologies, thus offering semifinished products that are then finally prepared just in time for consumption. In practice, this means that yeast doughs are frozen after shaping. The freezing process, however, bears one risk: through the ice crystal formation the sensitive gluten network of the dough, as well as the cell membranes of the yeast cells, may be physically damaged by the sharp crystal structure. The consequences are large deficiencies in the final fermentation stability of the dough (once it is thawed again) and in the volume yield of the baked goods. It is evident that the extent of damage depends on the size of the ice crystals. In other words, the smaller the ice crystals, the less the damage. Two main aspects affect crystal size: freezing velocity and storage conditions. The higher the freezing velocity, the smaller the crystals. Modern freezing technology usually provides the necessary requirements; however, storage conditions are a more critical element as temperature fluctuations can lead to re-crystallisation/crystal growth effects.

Using hydrolysed lecithins solves these problems and minimises the associated risks. The emulsifying function effects a homogeneous and fine distribution of the water in the dough. The reduced surface tension also results in small crystals and limits re-crystallisation effects. Therefore, the gluten network and the yeast cells are optimally protected.

Figure 1.22 shows the dough elasticity after varying days of storage, and the effect of hydrolysed lecithin.

1.6.2.3 Other baked goods

The basic effects of lecithins in other baking applications have already been mentioned in the introduction to this section. There is, however, one additional aspect here that should be mentioned, which to a certain extent can be extended to other applications as well. This aspect is related to the question of how do fluid lecithins compare to de-oiled qualities in terms of efficiency?

Theoretically, if the dosage of a lecithin is based on a comparative AI (Acetone Insoluble, Active Ingredients), the effects would be expected to be the same. So, for example, 1% of fluid lecithin (with an AI of 60%) should have the same functionality as 0.6% of a de-oiled variety (with close to 100% AI).

Some interesting effects can be observed from the manufacture of wafers. When operating with fluid lecithins then these are usually added together with some oil, which may be a part of the formula, and when using de-oiled lecithin it is normally just mixed with all the other dry ingredients. While comparing these two methods, we in fact see the same functionality when adding the same

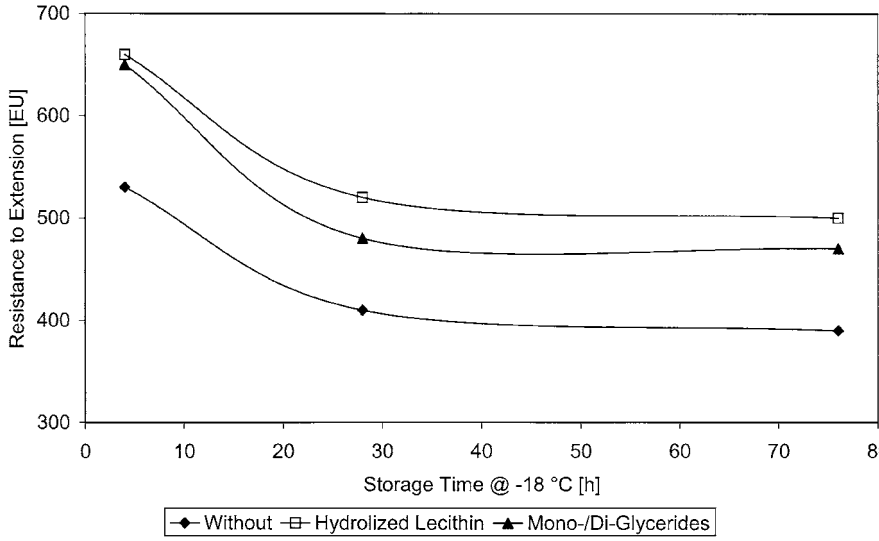

Fig. 1.22 Extensability of frozen dough after different times of storage.

amount of AI. Another possible way of adding de-oiled lecithin to the formula is to prepare a pre-dispersion of some of the water in the recipie with the de-oiled product and then incorporate it into the mixture. When following this approach the dosage of AI can be reduced by approx. 50% compared to the other two options, still achieving the same functionality. This implies that phospholipids generate a higher functionality when in an aqueous environment. We will come back to these effects when discussing emulsion systems in Section 1.6.4.

For the food industry this effect is important from the cost point of view. Due to the extended process, the 'cost of AI' for a de-oiled lecithin is significantly higher than for a fluid lecithin. The above effects, however, guarantee that 'costs of functionality' in the final product can be maintained on a comparable level. Thus, the additional advantages of de-oiled lecithins such as easier handling, neutral taste and less colour impact, do pay off.

1.6.3 Instant technology

Instant products are another important segment of convenience foods. Typical instant products include: whole milk powder, skim milk powder, infant formulations, coffee whitener, protein drinks, cocoa and chocolate drinks, soups, sauces etc. When adding these products to a liquid (water, milk) the expectation of consumers is an immediate reconstitution and the formation of a homogeneous, non-sedimenting drink. Although this sounds easy the processes that take place

during such a reconstitution are indeed complex. These processes can be divided into four basic steps that happen either sequentially and/or simultaneously:

Wetting:	penetration of the liquid into the powder
Sinking:	of the powder particles into the liquid
Dispersion:	of individual, primary powder particles
Dissolving:	of the soluble components

However, because of their surface properties, powder products very often have poor 'instant' reconstitution characteristics. Two main problems can cause insufficient reconstitution performance: The first problem occurs when the surface of the powder is rich in hydrate-forming components (e.g. protein powder). As a result of the formation of hydrates, a gel-like layer is built on the surface and this prevents water from penetrating fast enough into the particle structure. This causes the powder to float on the surface and form lumps.

The second problem occurs when the surface of the powder is rich in hydrophobic components. This can happen in products with a large amount of free surface fat (e.g. whole milk powder or cocoa powder). The hydrophobic surface rejects the penetration of water and the powder again floats to the surface.

By optimising the instantising process, the instant characteristics can significantly be improved. Processes for obtaining this effect can be divided into two basic groups:

Agglomeration. Creation of a coarse particle structure with porous properties, The porous structure supports the penetration of liquids by capillary forces.

Lecithination. Coating the product surface with a surface-active substance. Depending on whether the primary product shows hydrophilic (protein powders) or hydrophobic (whole milk powder) properties, the phospholipids will influence these properties in the corresponding direction. Depending on the orientation of phospholipid molecules at the surface, a hydrophilic surface will become more hydrophobic (with the fatty acid chains being oriented to the 'outside') and *vice versa*.

Both these processes encourage instant performance and are typically combined.

1.6.3.1 Lecithination process

The 'art' of lecithination is mainly the aspect of how to get the phospholipids onto the surface of the powder. In general, we can differentiate between what could be called an 'in-line process' and a kind of 'post-process' lecithination.

A typical in-line process is the production of whole milk powder. It starts with a highly concentrated liquid milk that by means of spray drying is initially transformed into very fine powder. At the exit of the spray tower, this powder

is then transferred to fluid bed systems. In these fluid beds, three processes take place: by means of hot air, residual moisture is removed from the powder. By applying lecithin to the powders, an agglomeration and the lecithination takes place. The lecithin is sprayed as a very fine mist from the top of the fluid bed onto the powder. Thus, individual singular powder particles are coated with lecithin and at the same time start to agglomerate due to adhesive forces generated by the phospholipids, and in certain cases, the carrying liquid.

This carrying liquid in the easiest case, is simply the soybean oil contributed by a fluid lecithin. However, it can also be any kind of oil or fat (such as butter fat) in which a de-oiled lecithin has been dissolved. It can also be water with de-oiled lecithin dispersed in it, in some cases together with agglomeration aids, e.g. lactose.

Spray drying technology is applied to a wide variety of other liquid starting materials. If such products are emulsified systems (such as re-combined milk), then the lecithin might be added in the initial liquid stage, where it will also provide emulsifying properties.

The key to success is to identify the optimal way of lecithination, depending on the processing technology and conditions, product formulation and final quality requirements.

When we want to prepare an 'instantised' product from material that is already a powder or powder blend we discuss 'post-process' lecithination. Again the optimal technology is the use of fluid beds for agglomeration and lecithination purposes and carrying liquids for the lecithin are the same as before. In this case, fluid beds are not needed in the process, because agglomeration is not necessary, some other options exist: The lecithin is sprayed from the top into a closed blending system, ideally with fast moving agitators. Even de-oiled lecithins may be used within the blend, in this case however, a high shear mixing with choppers is necessary, as the phospholipids have to be applied to the primary particle surface by pure mechanical energy. Such dry lecithination processes, therefore, only have limited efficiency. Another example of lecithination by pure mechanical energy is the production of defatted cocoa powder as a basis for instant cocoa drinks. The cocoa powder is derived from the filter cakes as residuals from the cocoa butter production. These filter cakes are crushed and then finely milled to powder. Typically, fluid lecithins are sprayed onto the crush prior to entering the mill. The mechanical energy within the mill is sufficient to coat the powder particles with the lecithin and therefore provide instant characteristics in the final formulation.

1.6.3.2 Choice of 'the right' lecithin

Instantisation is another application which, in terms of success and efficiency, is strongly driven by the type of lecithin chosen. Differences resulting from different grades of lecithins might not be obvious immediately after processing, but may have a significant effect over shelf life.

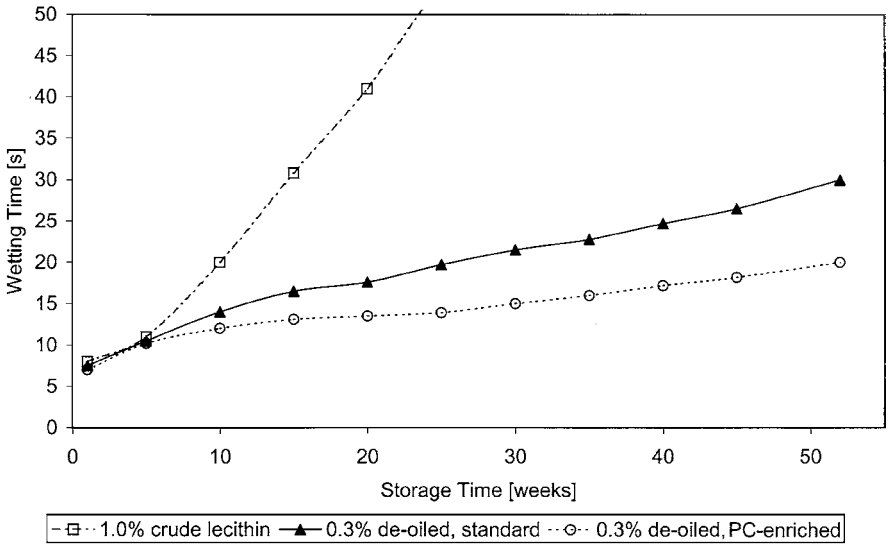

Fig. 1.23 Development of wetting times over shelf life depending on the type of lecithin.

In Fig. 1.23, three different types of lecithins have been used for a whole milk powder: a standard fluid lecithin, a standard de-oiled lecithin and a de-oiled lecithin which through fractionation technology has been enriched in phosphatidylcholine.

The two de-oiled varieties were dissolved in butter fat in order to make them sprayable. Concentrations refer to the addition of the lecithin: based on AI these are 0.6% for the standard fluid quality and 0.3% for the de-oiled versions. The result of the lecithination, expressed as wetting time (being measured by a standardised method) is initially the same. Over shelf life, however, significant changes take place. Whereas the fluid lecithin loses its functionality quite rapidly, the de-oiled varieties show a better performance, with the PC-enriched version being again superior to the standard de-oiled one.

This behaviour can be explained by migration and re-organisation effects. In the case of fluid lecithin the accompanying soybean oil, at ambient temperatures, is liquid and thus over shelf life can migrate into the particle structure. So the local phospholipid concentration on the surface declines. As only phospholipids at the surface contribute to the instant effects, the decrease in efficiency becomes evident. In the case of butter fat such effects are limited as butter fat at ambient temperatures is basically solid and migration processes are at least reduced.

In this case diffusion and re-orientation processes can also take place. It becomes obvious that phosphatidylcholine maintains its orientation at the surface

to a larger extent than other phospholipids. Thus, PC-enriched lecithins maintain their instant effects over a longer time.

1.6.4 Emulsions

In simple terms, emulsions are stable mixtures of two immiscible liquids. The 'art' of emulsification is to form very fine droplets of one of the liquids in the other phase and to keep these droplets stable, i.e. prevent sedimentation and coalescence.

The other key aspect of emulsion preparation is the determination of whether oil droplets are formed in a water phase (o/w) or whether water droplets are formed in an oil phase (w/o). The fact that the type of emulsion is not determined by the ratio of the two phases can easily be seen in the example of 80% oil (or fat) and 20% water.

Both emulsion types are possible! If we have 80% oil emulsified *into* water (oil-in-water emulsion) we have the example of mayonnaise, and if 20% of water is emulsified *into* oil (water-in-oil emulsion) we have the example of a margarine product.

Besides processing conditions, the type of emulsion formed crucially depends on the type of emulsifier chosen.

In this context, the versatility of lecithin again becomes evident. If lecithin is considered as a simple emulsifier, then we can expect the predominant formation of one single type of emulsion from it (o/w or w/o). However, depending on the *type* of lecithin chosen, oil-in-water (o/w) emulsions as well as water-in-oil (w/o) emulsions can be prepared. This is another example of how important the selection of the 'right' lecithin variety is for the success of the final application.

The fractionation of lecithins, in particular, leads to products that predominantly form either the one or the other type of emulsion. This implies that different phospholipids do have different emulsifying properties and that the phospholipid pattern of a lecithin determines the emulsion type that is formed.

One explanation of this phenomenon could be based on the principle of 'mean packing shapes' of lipids and its consequences on three-dimensional orientation of molecules [8].

This theory considers that molecules have a kind of individual 'geometric' shape that determines how they orientate themselves to each other. This shape might not exclusively be generated by the molecular structure itself, but also by interactive forces between molecules.

Several possible geometries are shown together with a correlation to different types of (phospho-)lipids (Fig. 1.24).

It is evident that this shape will have an influence on the curvature of an interface (and thus on the type of droplet formed) when molecules start to aggregate and arrange themselves there. How this might look like is shown in Fig. 1.25.

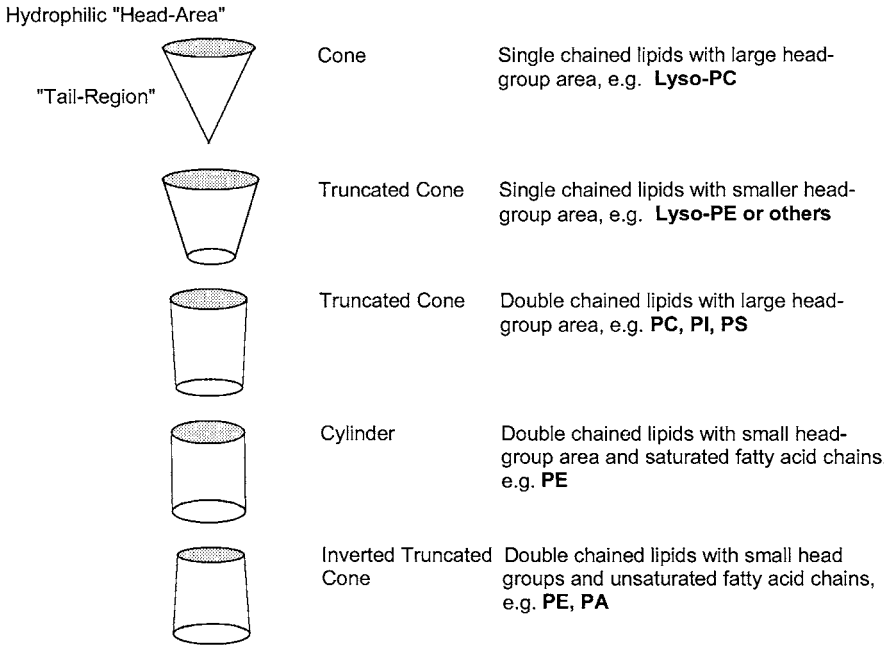

Fig. 1.24 Different 'geometries' of emulsifiers, examples for phospholipids.

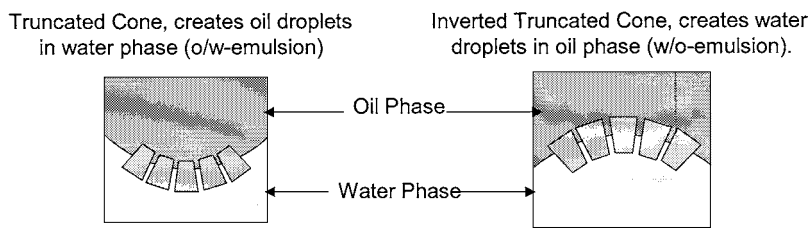

Fig. 1.25 Interface curvatures determined by 'geometry' of emulsifier.

1.6.4.1 Oil-in-water emulsions

This type of emulsion is the most common one in the food industry. Whether dressings, sauces, mayonnaises, marinades, recombined milk products, they are all o/w emulsions. Even products like sausages and, in particular, liver pates can be considered as oil-in-water emulsions.

It is interesting to note that, as these applications do not belong to the 'traditional' lecithin areas, they have only recently found their way into such products. At the same time food emulsions are typically complex multi-component, multi-ingredient products that not only get their final quality from the single ingredient

Table 1.10 Results of comparative emulsification trials with different types of lecithins

Lecithin type	Lecithin in oil phase $D_{4,3}$ (μm)	Lecithin in water phase $D_{4,3}$ (μm)
Standard fluid	1.93	–
Standard de-oiled	2.06	1.54
Hydrolysed fluid	1.75	1.15
Hydrolysed de-oiled	1.63	1.17
Fraction fluid, 33% PC	1.70	1.08
Fraction de-oiled, 98% PC	1.65	1.36

but from a lot of interactions of the various other components. Therefore, this section will only deal with some general aspects of lecithin in o/w emulsions rather than going into details for particular finished products.

Considering what has been mentioned earlier we would expect that hydrolysed lecithins as well as PC-enriched lecithins should deliver superior o-w emulsion capacity than standard lecithins. In standardised comparative emulsification trials [9], this could be proven (see Table 1.10, first two columns).

In these trials a 5% oil-in-water emulsion was prepared. The result is shown as the mean diameter $D_{4,3}$ (μm) of the volume distribution of the oil droplets formed. In order to exclude concentration effects a high concentration was chosen i.e. 2% acetone insoluble w/w, calculated on the *oil phase*!

The most interesting results, however, were found when dispersing the lecithins in the water phase rather than dissolving them in the oil phase. The same concentration was chosen 2% acetone insoluble w/w *on the water phase*. Whilst the different performance as such was confirmed, all lecithins, in general, performed superior when compared to dissolving in oil. It is important to note that this is *not* related to the lecithin concentration when calculated on the *emulsion basis* (0.1% when dissolved in oil, 1.9% when dispersed in water). The *primary* emulsion quality is always related to the emulsifier concentration in the individual phase it is dissolved/dispersed in. This, however, is *different* when talking about *long-term emulsion stability*.

These last trials, in particular, have confirmed the results that were mentioned in Section 1.6.2.3. Evidently phospholipids in an aqueous/polar environment show higher surface activity than in a non-polar medium.

Another important aspect that needs to be mentioned when using lecithins is their comparison against mono-di-glycerides, which are traditionally more commonly used. Typically, mono-di's are saturated in terms of their fatty acid chains. At ambient temperature they are in a crystalline stage. In order to develop their functionality they need to be heated above their melting point, their phase transition temperature is typically around 60°C. As plant lecithins are mainly unsaturated (see Section 1.1.3), they do not show such behaviour and therefore deliver their functionality at ambient or even cold temperature conditions (these

comparative trials were performed at 20°C). This can be of major influence for processes in the food industry. Even though such processes very often involve a heat treatment (e.g. for pasteurisation purposes), the unit operations of 'homogenisation' and 'heat treatment' are usually separated. Having an emulsifier that acts at ambient temperatures, the homogenisation step can deliver a high quality emulsion prior to any heat treatment.

1.6.4.2 Water-in-oil emulsions

The well-known area of w-o emulsions in the food industry is the field of *margarines* and *spreads*, the 'yellow fat' products. These products may vary widely in the their fat contents and therefore are classified accordingly: 'margarine' (minimum 80% fat), 'high fat spreads' (62–80%), 'reduced fat spreads' (40–62%), 'low fat spreads' (below 20%).

PC-depleted lecithins have the functionality to stabilise these water-in-oil emulsions because of their predominant content in phosphatidylethanolamine and phosphatidic acid (see Figs 1.24 and 1.25). However, in most yellow fat applications lecithins are not used as the sole emulsifier but as the co-emulsifier, with primarily mono-/di-glycerides and partly (whey-) proteins.

In order to understand the complex interactions, it is required to have a closer look at the processes that take place in the manufacture (and also use) of margarines and spreads. A margarine (with 20% of water) can initially be prepared without an emulsifier at all! The low water content can be emulsified by a simple mechanical treatment into the fat phase and can be kept emulsified because this treatment is maintained until the fat phase has crystallised again. Thus, the water droplets formed are physically locked/immobilised in a solid fat matrix, so there is no chance for any coalescence. Only the achievable droplet size depends on the emulsifier (the lower the surface tension, the smaller the droplets at the same input of mechanical energy).

Mono-/di-glycerides and lecithins, however, are added for a various number of reasons: First of all mono-di's support the formation of the right type of emulsion (w-o) which becomes increasingly important with increasing water contents. Also the (typically saturated) mono-di's act as crystallisation support/initiation for the high melting fats in the cooling stage and, therefore, also determine the final texture. With this cooling step the mono-di's, however, 'lose' their functionality since they are crystallising as well. But still new water droplets are formed due to the mechanical energy input in the combinators (scraped surface coolers). This newly formed interfacial surface has to be covered and stabilised by 'mobile' emulsifiers. The function is taken over by the phospholipids (which do not show crystallisation/phase transition phenomena).

Once the product is packed and stored in cooled conditions, the system can be considered as relatively stable due to the 'immobilisation' effects. The stability of the emulsion is later challenged again, when exposed to elevated temperatures.

This can be just at ambient temperatures (when the product is kept outside the refrigerator) and part of the fats start to melt. Again, the lecithins take the primary role of stabilising the emulsion.

It is more challenging when the margarine/spread is used for frying purposes. In this case, the thermal stress is significant and a coalescence/breakage of the emulsion bears a high risk. If the individual water droplets are not kept separated but start to form bigger clusters and recombine, they may explosively evaporate resulting in a severe spattering of the fat phase. Here lecithins play their key role in yellow fat applications. The capability of phospholipids to form very stable interfacial films, particularly with proteins, makes them unique in this respect. Together with whey proteins the phospholipids stabilise the individual water droplets under these extreme conditions and thus help to avoid spattering effects.

It seems like a paradox, that specifically PC-enriched lecithins and hydrolysed lecithins give the best effect. Especially, those types of lecithins that are particular oil-in-water emulsifiers show the highest functionality. But it is the predominant capability of phosphatidylcholine and lyso-phospholipids to form protein-phospholipid complexes as interfacial membranes. Figure 1.26 compares the spatter patterns of a margarine that was produced without lecithins, with a standard fluid lecithin and a fractionated fluid lecithin, respectively.

As long as water contents are low and fat contents high, the type of emulsion is mainly determined by process conditions and by the mono-di's, the use of 'o/w' lecithins is therefore not a contradiction. With higher water contents (reduced fat spreads, low fat spreads) a lecithin has to be chosen that supports the formation of the right type of emulsion, process functionality being the same as for margarines and high fat spreads. With higher water content however, the risk of a phase inversion increases especially during the cooling stage. The lecithins that are now taking over the emulsifying function must not be biased towards

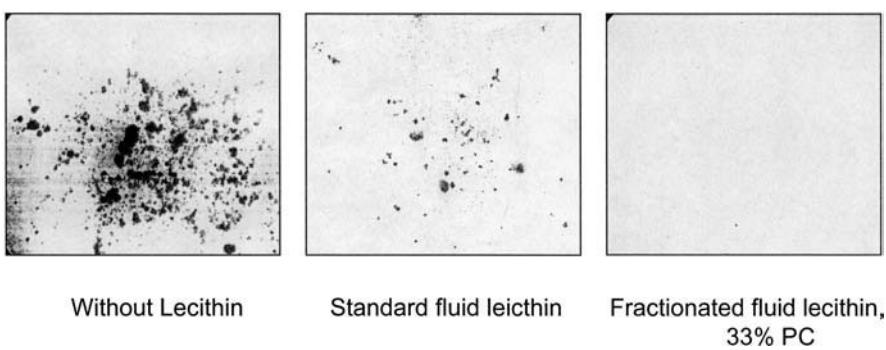

Fig. 1.26 Frying images of margarine with different types of lecithins.

the o/w emulsion type, otherwise the well dispersed internal water phase, may invert. It is in these reduced and low fat spreads that *PC-depleted* lecithins are successfully used. As such spreads are generally not used for frying purposes, the effect of complex formation with proteins is not of importance and the primary emulsification capacity is the focus.

Further examples of the use of lecithins and additional functionality in yellow fat products are as follow:

Cream margarines are whipped products, for example, for the preparation of sponge mixtures and butter creams. In this case, lecithin helps to stabilise the light, spongy texture. In *puff pastry margarines* lecithin provides for greater extensibility so that an unbroken fat film remains even when the pastry is rolled out into thin layers. This film is necessary for puff pastries to acquire their typical structure.

Release agents are preparations that prevent bakery products and confectionery from sticking to the tins and moulds during production. Here the use of lecithin helps to maintain a homogeneous film of release agent at the surface and improves the releasing properties.

1.6.5 Other applications

The key applications mentioned above cover the various functionalities that lecithins can deliver in disperse systems. It is evident that these effects can be transferred to other products as well. Lecithins can play their role in the whole range of food products where any kind of surface-active subtance is required. This chapter has tried to make it clear that it is crucial to select the right lecithin quality in order to have maximum success. The complexity of the composition of lecithins necessitates the consideration of interactions with other components of a food formulation. Very often functionalities in particular products cannot be generalized to the food category, but depend on a number of further contributing factors in the individual formulation. This is one reason why leading lecithin manufacturers offer application support to the food industry and assist them in their product development work.

Acknowledgement

The author would like to thank all past and present colleagues who have contributed to this chapter through their never-ending efforts to unveil the secrets of lecithins, thus making lecithins some of the most successful emulsifiers in the food industry. Despite 75 years of experience, new questions are still arising, which are to awaiting answers.

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2 Mono- and diglycerides

Hans Moonen and Henny Bas

2.1 Introduction

The earliest emulsifier on record was in the form of beeswax, which was used in skin lotion by the second-century Greek physician Galen (in AD 131–203). The first emulsifier used in food applications was egg yolk, to disperse liquid oil into an acidified aqueous phase in, for example, mayonnaise in the early nineteenth century. However, due to the short shelf life of egg yolk-based products, in the 1920s there was a switch to lecithin derived from soybean as a food emulsifier [1].

The first mono- and diglycerides were synthesised in 1853 by the Frenchman Berthelot. The major breakthrough, however, was the application of mono- and diglycerides in the 1930s in the margarine industry on a large scale [2]. High ratio shortenings were introduced, which contained mono- and diglycerides that brought about finer dispersions of fat particles in the dough, giving strengthened cake batters. In 1936, the use of mono- and diglycerides was patented for ice cream applications.

Nowadays, the total world production of emulsifiers is estimated to be in the order of 300,000 metric tons. This includes approximately 20 different types of emulsifier. Mono- and diglycerides and their derivatives account for about 70% of the world production of food emulsifiers and are therefore considered as the most important group of emulsifiers [2]. The major applications are bread, sponge cakes, cakes, margarines, ice cream, chewing gum and chews. Bakery overall is by far the biggest application. Approximately 60% of all monoglycerides are used in bakery – 40% in bread and 20% in sponge cakes and cakes.

Monoglycerides are applied in food technology for several functions (see Table 2.1). These functions are discussed in more detail in Sections 2.3.1 to 2.3.4.

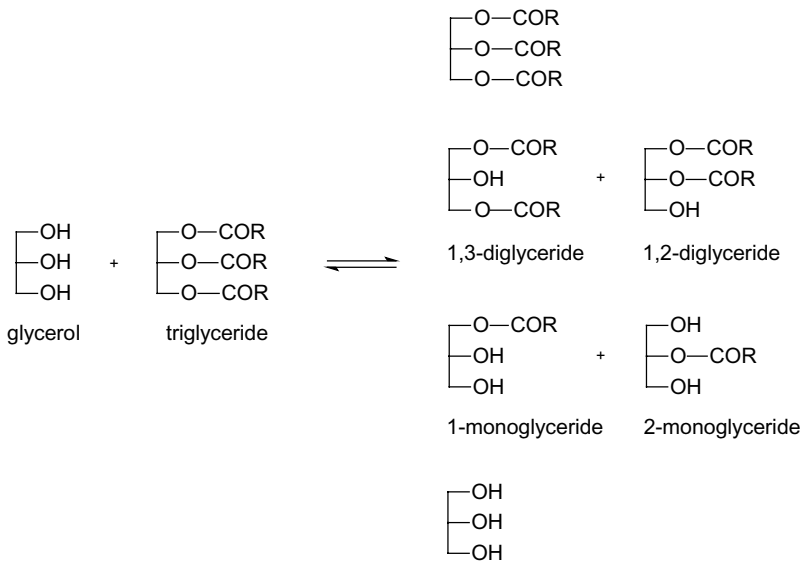
2.2 The products

2.2.1 Production of monoglycerides

Mono- and diglycerides are generally manufactured by interesterification (glycerolysis) of triglycerides with glycerol (Scheme 2.1). Triglyceride reacts with glycerol at high temperature (200–250°C) under alkaline catalysis, yielding a

Table 2.1 Monoglyceride functionality/application

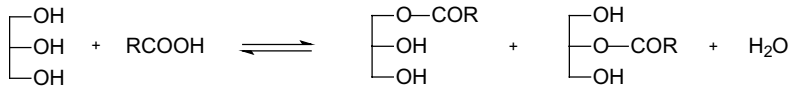
Starch complexation	Bread, sponge cakes, cakes
Aeration	Sponge cakes, cakes, desserts
Emulsification	Margarines, spreads
De-emulsification	Ice cream
Compatible mixing	Chewing gum



Scheme 2.1 Interesterification triglyceride and glycerol.

mixture of mono-, di- and triglycerides and also a small fraction of unreacted glycerol. The proportions of these components are fixed statistically on the basis of the random distribution of fatty acid radicals of the triglycerides among the hydroxyl groups of the glycerol. The content may vary from 10% to 60% monoglycerides depending on the glycerol/fat ratio. Commercial mono- and diglycerides usually contain 45–55% monoglycerides, 38–45% diglycerides, 8–12% triglyceride and 1–7% free glycerol [3].

Mono- and diglycerides are manufactured by the batch process or by the continuous process. In the batch process the reaction time varies form 1 to 4 hours and in the continuous process the time may be less than $\frac{1}{2}$ hour [4, 5]. Mono- and diglycerides may also be prepared via direct esterification of glycerol with a fatty acid as shown in Scheme 2.2. The reaction is carried out at a very high temperature (e.g. 200–250°C) in the presence of an alkaline catalyst, usually sodium hydroxide. The fatty acid should be isolated from the



Scheme 2.2 Esterification of glycerol with a fatty acid.

fat or oil being used, through saponification and subsequent distillation. The water produced by the esterification should be removed. This process is useful when products with high specific fatty acid compositions are required.

2.2.2 Molecular distillation

Monoglycerides may be separated from the di- and triglycerides and glycerol via high-molecular thin film molecular distillation [6]. The concentration by molecular or short-path distillation takes place under high vacuum condition (i.e. down to 10^{-8} mmHg), which allows lower distilling temperatures (ca. 140–170°C) and shorter residence time of the feed liquid. In combination with optimal efficiency in heat and mass transfer, minimal product decomposition and maximum product quality is reached. A typical composition of the distillate contains 95% monoglycerides, 3–4% diglycerides, 0.5–1% free glycerol and 0.5–1% free fatty acids [2].

Monoglycerides produced in this way contain an equilibrium of 1-monoglycerides and 2-monoglycerides. The ratio between the two isomers is dependent on temperature. The rate constant of the equilibrium is low at room temperature and depends on fatty acid composition, crystal form and traces of basic catalyst present. The content of 1-monoglyceride in commercially distilled monoglycerides is usually 90–95% [6].

2.2.3 Chemical and physical properties

The appearance of monoglycerides varies from a pale straw to brown coloured oily liquid to a white or slightly off-white waxy solid. The solid may be in the form of flakes, powders or small beads depending on the finishing equipment used. Monoglycerides are insoluble in water, but can form stable hydrated dispersions. Distilled monoglycerides have a better dispersibility in water than mono- and diglycerides, because the former form liquid crystalline mesomorphic phases, whereas mono- and diglycerides, in most cases, form emulsions due to a relatively high content of triglycerides. The mesomorphic behaviour of distilled monoglycerides is caused by their high purity and well-defined molecular structure. Distilled monoglycerides form ordered bilayers of the fatty acid chains, separated by water layers associated with the polar groups [2].

Monoglycerides are polymorphic, like triglycerides, and can exist in different crystal forms depending on the temperature. They crystallise from melt in the metastable alpha form and transform via beta prime form to the most stable beta crystal form. For some applications the alpha form has some most advantageous effects: such as easier dispersibility, improved aerating properties and increased emulsifying activity. Therefore, it is highly desirable to retard the conversion of the alpha to the beta form. This can be accomplished by incorporating a suitable alpha-stable emulsifier, such as propylene glycol ester, sorbitan ester or lactic acid ester, to stabilise the alpha form of distilled monoglycerides in emulsifier mixtures [7].

2.2.4 HLB value

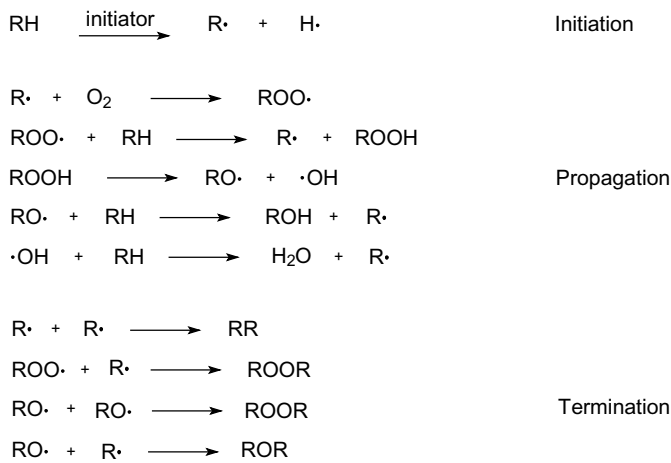
Emulsifiers are often evaluated according to their physicochemical properties. Several methods [8–11] have been developed to classify emulsifiers; the hydrophilic/lipophilic balance concept (HLB) proposed by Griffin [12] is most widely used (see Appendix 1). Monoglycerides possess a lipophilic character and are therefore assigned with a low HLB number (3–6). They dissolve in oil and in, stabilised water-in-oil (w/o) emulsions to form reversed micelles in oil.

2.2.5 Addition of antioxidants

Monoglycerides that incorporate unsaturated fatty acids must be protected against oxidative rancidity. This is an autocatalytic free-radical chain reaction and takes place in three stages via initiation, propagation and termination (Scheme 2.3). During the initiation reaction, unstable fatty acid radicals are formed by initiators, such as light, heat or heavy metals (Cu, Fe). The fatty acid radicals react with atmospheric oxygen to form peroxide radicals, which in turn react again with the fatty acid substrate to produce new radicals and hydroperoxides (propagation). As a final step in the auto-oxidation, radicals react with each other to give compounds such as aldehydes, ketones, alcohols and acids. These are characteristic of the undesirable flavours and odours of oxidative rancidity in unsaturated fatty acid derivatives [13,14].

The radical chain reactions can be terminated by antioxidants, which retard the oxidation of fatty acid derivatives. Antioxidants usually have a phenolic structure and are good free-radical acceptors, which inhibit or interfere with the free-radical mechanism of auto-oxidation. The formed antioxidant free radical is highly stable due to its resonance and will not propagate further oxidation of the oil or fat.

All vegetable oils and fats contain natural antioxidants (i.e. tocopherol). In general, vegetable oils have higher tocopherol content than animal fats and



Scheme 2.3 Oxidation mechanisms.

are therefore often more stable than animal fats with an equivalent degree of unsaturation. Synthetic antioxidants related to tocopherol have been developed [15], such as alkyl gallate, butylated hydroxyanisole (BHA) or butylated hydroxy toluene (BHT).

2.2.6 Legal considerations

Mono- and diglycerides of fatty acids hold a GRAS (generally recognised as safe) status in the United States and within the EU they are generally permitted for use in food products. Mono- and diglycerides have no limitation on the acceptable daily intact (ADI) value; they can be added to foods *quantum satis* [6]. Table 2.2 summarises the EU regulations concerning the use of mono- and diglycerides in foods.

2.2.7 Behaviour of monoglycerides in the presence of water

When distilled monoglycerides are heated to their melting point with water, a gel is formed. The structure of a gel is similar to the lamellar phase, with water layers alternating with lipid bilayers (Fig. 2.1). The exact temperature of gel formation depends on the chain length of the fatty acid and on the purity of the monoglyceride. When a co-emulsifier (ionised amphiphilic molecules) is added, an electric repulsion between charged groups in the opposite bilayers causes an increased swelling, so the water layer thickness may increase [2]. Effective co-emulsifiers are strongly hydrophilic, usually water soluble and may

Table 2.2 EU regulations for mono- and diglycerides

	EU[a]
E-number	E 471
U.S. FDA 21 CRF	184.1505[c]
Mono- and diesters[b]	Min. 70%
Total glycerol[b]	16–33%
Free glycerol[b]	Max. 7%
Polyglycerol[b,d]	Max. 4% + 1%
Sulphated ash[b]	Max 0.5%
Acid value[b]	Max. 6
Water[b]	Max 2%
Arsenic[b]	Max 3 mg/kg
Heavy metals (as Pb)[b]	Max 10 mg/kg
Lead[b]	Max 5 mg/kg
Mercury[b]	Max 1 mg/kg
Cadmium[b]	Max 1 mg/kg

[a] Purity criteria apply to the additive of free sodium, potassium and calcium salts of fatty acids; however, these substances may be present up to a maximum level of 6% (expressed as sodium oleate).
[b] Methodologies as described in EFEMA index (1999).
[c] Generally recognised as safe (GRAS).
[d] Not more than 4% diglycerol and not more than 1% higher polyglycerols, both based on total glycerol content.

be anionic, non-ionic or cationic. The effect of the different co-emulsifiers on the gel phase is quite different. Ionic co-emulsifiers increase the swelling and stability of monoglyceride gels, whereas non-ionic co-emulsifiers do not show this effect. Examples of co-emulsifiers are soaps, polyoxyethylene sorbitan esters and sucrose monoesters [16].

2.2.8 Nutritional value

Emulsifiers give products a consistent texture and prevent oil from water separation. The main applications of mono- and diglycerides in food are typically in fat-based products, such as margarine, spreads and bakery fats (shortenings) and cake mixes. In dairy emulsions, mono- and diglycerides are used in ice cream and recombined milk, in combination with hydrocolloids. All products containing nutrients must be labeled appropriately. Mono- and diglycerides are registered under fat, because of their similarity with triglyceride esters. Distilled monoglycerides are also used in fat-free foodstuffs or products with very low fat content [17]. Typical caloric value for fats and mono- and diglycerides are 900 kcal/100 g.

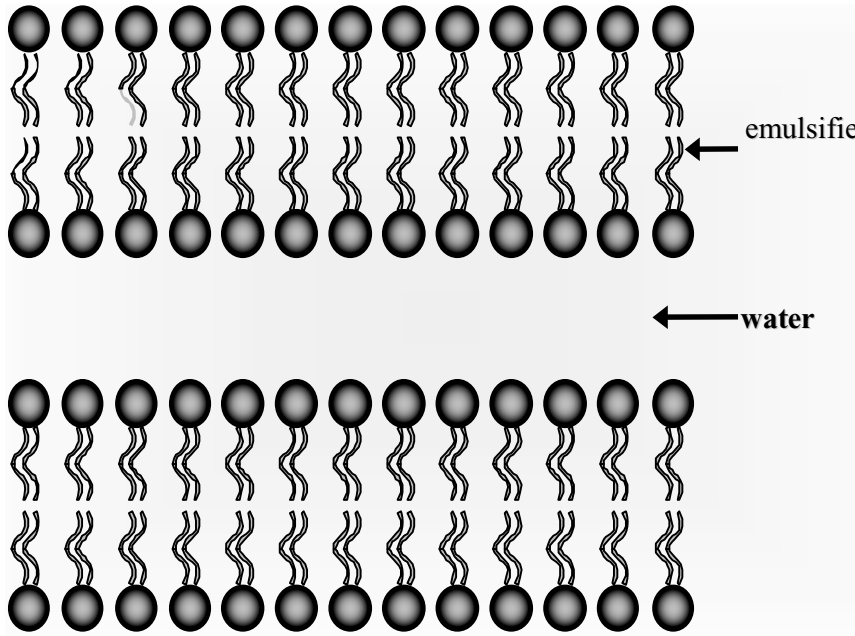


Fig. 2.1 The lamellar phase of lipids.

2.3 Applications

2.3.1 Bread

Bread is by far the biggest application for monoglycerides in food technology. Any functionality of monoglycerides and other emulsifiers in bakery depends on the dispersability properties of the emulsifiers during mixing of the dough. It is evident that if emulsifiers do not disperse during dough kneading or batter mixing, they will hardly show any functionality during the rest of the baking process. The factors that influence dispersability properties during dough mixing are a balance between particle size and hardness or melting point of the monoglyceride. The hardness of the monoglyceride is mainly determined by the hardness of the edible fat from which the monoglyceride has been produced.

Monoglycerides are added to bread doughs for the following reasons: primarily, it is known that monoglycerides increase the fermentation stability of doughs. By fermentation stability we mean that fully fermented doughs are resistant to collapse by mechanical shock during transport in bakeries via trays or belts from the proofing cabinet to the oven.

In the laboratory this can be demonstrated by putting fully fermented doughs on a laboratory shaker and vibrating them vigorously for 1 minute. Alternatively,

Fig. 2.2 Fermentation stability of bread doughs. The doughs on the left-hand side contain 0.2% monoglyceride, the doughs on the right-hand side do not contain any monoglyceride.

the fermented doughpiece in its pan may be subjected to a controlled drop test.

Figure 2.2 demonstrates that the dough at the left-hand side has good fermentation tolerance (dough contains 0.2% on flour of the distilled monoglyceride Myvatex Mighty Soft), and the dough on the right-hand side contains no emulsifier and consequently has very poor fermentation stability.

Besides fermentation stability, complexation of monoglyceride with starch or, more specifically, amylose, is of utmost importance in enhancing the shelf life of bread and cakes. Shelf life in this context mean crumb softness. Freshness of baked goods and the postulated mechanism behind it has been extensively discussed in Zobel and Kulp [18], see Fig. 2.3. In particular, the interaction of monoglycerides with amylose and the enzymatic breakdown of amylopectin by specific amylases are of main importance. In a nutshell, during baking, starch granules will swell and absorb water resulting in the amylose to transfer from an amorphous state into a soluble state and the amylopectin from a crystalline state into a gelatinised state.

During cooling of the freshly baked bread, amylose will retrograde immediately by complex formation with another amylose molecule, or form a complex with a polar lipid thus producing a softer crumb. During storage gelatinised amylopectin will recrystallise again, leading to a harder crumb. However, if

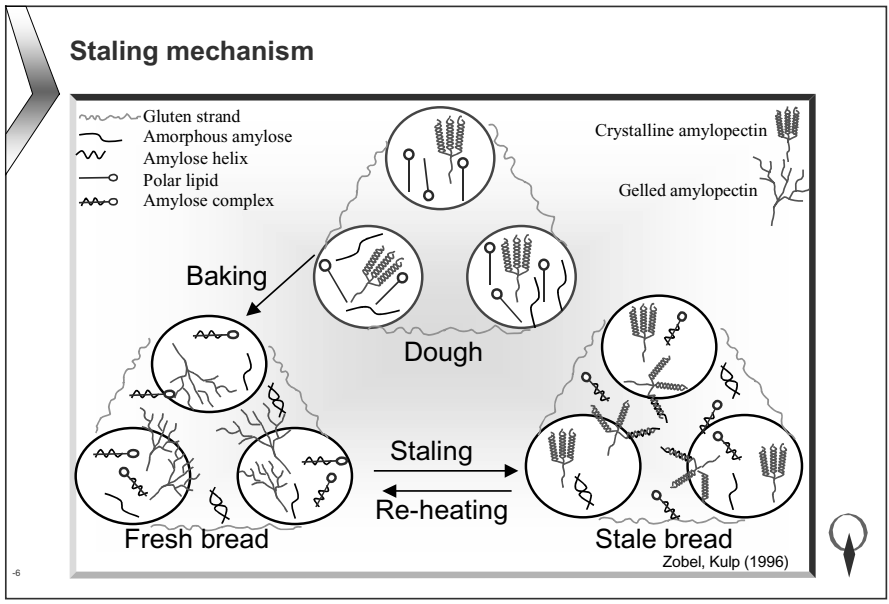


Fig. 2.3 The staling mechanism of baked goods.

specific amylases were added to the dough, amylopectin will be degraded by the enzymes during the baking process and amylopectin will not recrystallise anymore during storage of the bread.

The interaction of monoglycerides with amylose has been extensively studied, see [19] for review. The studies of Lagendijk and Pennings [20] and of Carlson *et al*. [21] are worth mentioning here.

Lagendijk and Pennings proved that complex formation between amylose and monoglycerides is preferred over complex formation between amylopectin and monoglycerides. They also studied the effect of different fatty acid chain lengths on complex formations and found C16 most active, followed by C18.

Carlson *et al*. studied the conformation of the amylose-monoglyceride complex with Raman spectroscopy, and concluded that the fatty acid chain of the monoglyceride is surrounded by three turns of the amylose α-helix. The polar head is outside the hydrophobic core of the α-helix.

Clearly, ingredients that have to be functional during bread baking have to disperse in an active form during dough mixing. In bread baking industry this is still done mainly by the addition of hydrates. To produce hydrates, emulsifiers are melted in heated water. When the temperature reaches 80°C a so-called mesophase (liquid-crystalline phase) forms, built up of double layers of monoglyceride molecules with highly mobile fatty acid chains, which are separated by layers of water. Upon cooling, the fatty acid chains will be structured again

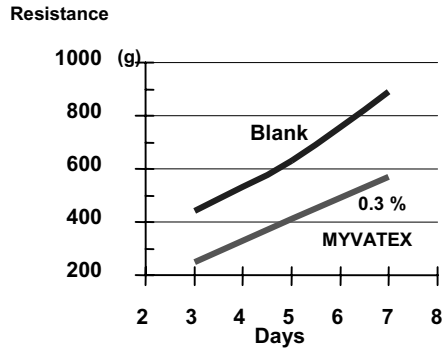


Fig. 2.4 The effect of the addition of distilled monoglycerides on tin bread crumb softness (Myvatex Mighty Soft is a distilled monoglyceride from Kerry Bio-Science).

and a gel will be obtained. In the gel, emulsifiers are crystallised in the α form. The gel phase is not stable and without additions of other α-tending emulsifiers or soap, the gel will transform into crystalline platelets of monoglycerides in the β form, enclosing water. The stabilisation process can be enhanced by acidification to pH 3.3. This opaque white paste called coagel is known as hydrate in bakery literature. In this physical state monoglycerides are very effective regarding complexation with amylose, but it involves a rather complicated way of adding the monoglyceride paste to the dough. In general, the monoglyceride has to be scooped manually from the packaging. As an alternative emulsifier producers have developed powdered products that can disperse relatively easily in an active form in the dough because of their fine particle size and product hardness.

The effect of the addition of appropriate monoglycerides on crumb softness can be studied by measuring crumb hardness by a texture analyser during the storage of bread. As shown in Fig. 2.4, the addition of 0.3% of flour weight of a dedicated distilled monoglyceride (Myvatex Mighty Soft) decreased initial crumb hardness after baking, but hardly effected the rate of increase of crumb hardness during storage time.

Figure 2.4 shows that the addition of monoglycerides increases shelf life of the tin bread by approximately two days. With regard to dispersability properties, the molecular composition of the monoglycerides is chosen so that the emulsifier is rigid enough to be stable in a powder form without melting and lumping during storage or transportation, but soft enough to be adequately dispersed during dough mixing.

Interaction of monoglycerides with starch, and in particular amylose, is also important in the production of dry pasta. Addition of hydrated monoglycerides to the pasta dough will result in less cooking loss and decreased stickiness in the finally cooked pasta.

Fig. 2.5 Impact of addition of monoglycerides to retarded doughs. Bread at top: reference with no monoglycerides added. Bread at bottom: addition of 0.2% on flour of fine powdered monoglycerides.

Another interesting application of monoglycerides is the decrease in blisters in bread prepared with retarded doughs. This process has gained increased popularity with artisan bakers because it reduces working at night. According to the French patent 92 07978, the addition of monoglycerides to retarded dough decreases the occurrence of blisters dramatically. This is shown in Fig. 2.5.

The effect of the addition of powdered monoglycerides is evident, as without monoglycerides there is an unacceptable formation of blisters in baked products and with monoglycerides a smooth surface with less blisters is obtained.

2.3.2 Cakes

Monoglycerides are used in cakes for mainly two reasons: aeration of batters and decrease of crumb hardening over time. Similar to the process used for bread, the most critical step in the production of cakes, with respect to emulsifier addition, is the activation of the added emulsifiers, such as monoglycerides, during the beating of the batter.

Monoglycerides can be added in three different ways: application of emulsifiers via gels is still commonly used in the preparation of industrially prepared sponge cakes. Monoglyceride gels used in the production of cakes and flour-based confectionery are made and stabilised as described in Section 2.3.1. The gel phase, being the most active phase for the aeration of cake batters, can be stabilised in different ways, for example by emulsifier concentration, addition

Table 2.3 Typical gel composition

Monoglycerides	25%
Humectants (glycerol, sorbitol, and/or propylene glycol)	20%
Water	53%
Potassium stearate	2%

of other α-tending co-emulsifiers, such as propylene glycol esters of fatty acids (PGMS), and polyglycerol esters of fatty acids (PGE) to retain gel in the α phase, and addition of anionic emulsifiers like soap to give an electric charge to the lipid bi-layer. During preparation of the gel, air should be excluded, because air bubbles promote transformation from α crystalline gel to β crystals. A typical composition of gels is shown in Table 2.3.

Part of the monoglyceride is sometimes replaced by approximately 5% of other α-tending emulsifiers such as PGMS and PGE. The humectant part can have varying compositions depending on required functionality, cost in use and local legislation.

The gels are added approximately 2–2.5% of the total batter weight. For the artisan bakers or in household sponge cake mixes, the application of gels is too cumbersome. More convenient powdered products are required, such as monoglycerides delivered on a carrier in an active α form. In this way, cold-water dispersible emulsifiers are obtained. Here two methods are available: spray drying of emulsifiers on milk or soy proteins, or extrusion of emulsifiers on starches. These powdered products must contain, in addition to monoglycerides, other α-tending emulsifiers such as PGMS and PGE, otherwise no active aerating products are obtained. The typical dosage of the cold-water dispersible products is approximately 3–4% of the total batter weight.

Figure 2.6 shows a comparison of typical aeration of sponge cake batters by cold-water dispersible emulsifier product like Admul Emulsponge 5306 and a complete milk protein product like Hyfoama Sponge 8234. The emulsifier containing products are found more functional than protein-based products with regard to the aeration of sponge cake batters.

A third method of applying monoglycerides in cake baking is by melting the monoglyceride, in many cases together with other α-tending emulsifiers like PGMS and/or PGE in specialty bakery fats, and after votation the emulsified shortenings are produced. The shortenings are mainly applied in industrial cake baking.

2.3.3 Margarines and spreads

Table margarines and low fat spreads are widely used in the food industry. Industrial applications are also known, such as dedicated cake, cream and puff

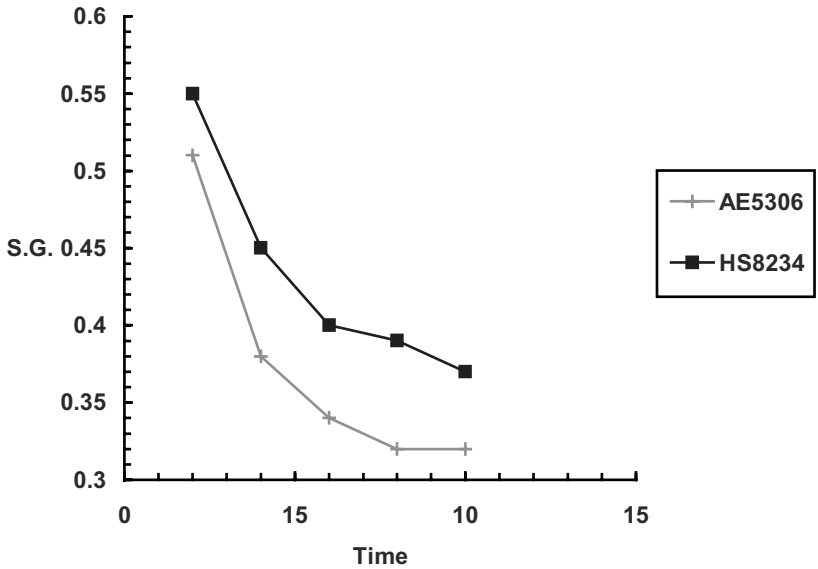


Fig. 2.6 Comparison of aeration of sponge cake batters by cold water dispersible emulsifier (Admul Emulsponge 5306), and milk proteins (Hyfoama Sponge 8234).

pastry margarines. For all these applications different requirements exist which can be facilitated by the appropriate application of emulsifiers.

Typical table margarines are water in oil (w/o) emulsions, with a fat content of 60–80%. The required w/o emulsions are stabilised by fully saturated monoglycerides. The required consistency of the spread is obtained by cooling in a scraped surface heat exchanger called 'votation.' Applied emulsifiers are 0.2–0.5% of distilled monoglycerides or 0.25–0.60% of mono- and diglycerides.

The benefits of the addition of monoglycerides include fine distribution of water droplets in the fat phase, smooth spreading consistency, stable crystalline structure and a pleasant melt-in-the mouth sensation for the consumer.

Low fat spreads are also (w/o) oil emulsions, with a fat content of only 35–45%. The benefits of monoglyceride addition is the same as in table margarines; however, the conditions are much more difficult because the water quantity that needs to be stabilised is three to four times higher than in normal table spreads. The level of monoglyceride used in low fat spreads is equal to table spreads; i.e. 0.2–0.5% of distilled monoglycerides, or 0.4–0.6% monodiglycerides. There is one major difference in this application because unsaturated monoglycerides are used. The reasons for this might be twofold, although different views do exist about the importance of unsaturated monoglycerides in this application.

Table 2.4 Surface tension comparison

	Surface tension (mN/m)
Water	72
Diglyceride (saturated)	56
Diglyceride (unsaturated)	45
Monoglyceride (saturated)	35
Monoglyceride (unsaturated)	30
Milk protein	45

First, unsaturated monoglycerides have a higher surface tension reducing activity than saturated monoglycerides (Table 2.4), so less number of molecules are required to stabilise fine water droplets in the oil phase and second, because it is possible that unsaturated monoglycerides can structure water via the so-called cubic phase [22].

Very low fat spreads, which are o/w emulsions with a fat content of 3%, can only be prepared by the application of α gel technology as described in EP 0558 523 B1. After preparation of the gels, they are transformed into coagels, in which monoglycerides crystallise in a plate-like structure entrapping large quantities of water.

Cake margarines are w/o emulsions containing approximately 80% fat. Saturated monoglycerides (0.2–0.4%) are used to stabilise these emulsions and to obtain a fine water droplet distribution. To achieve other required functionalities in the cake margarine, such as moisture uptake, aeration of the cake batter and fine crumb structure of the cake, other emulsifiers such as unsaturated monoglycerides (0.5%), PGE (0.3–0.5%), and/or PGMS (0.3–0.5%) are required.

Puff pastry margarines contain approximately 80% fat in w/o emulsions. Saturated monoglycerides (0.4–0.8%), or mono- and diglycerides (0.6–1.2%), together with lecithin are used to stabilise the emulsion to achieve a smooth consistency and to initiate a robust fat crystallisation for obtaining a stable crystalline structure.

2.3.4 Ice cream

Ice cream is a complex food system built up from fat globules, air bubbles and ice crystals dispersed in a concentrated solution and/or dispersion of sugars, proteins and salts. Ice cream taste and texture are mainly determined by the presence of two interfaces, namely the air/water and the fat/water interface, and proteins.

Ice cream interfaces are schematically shown in Fig. 2.7. Monoglycerides compete with proteins, in most cases with milk proteins, at the fat/water interface and at the air/water interface.

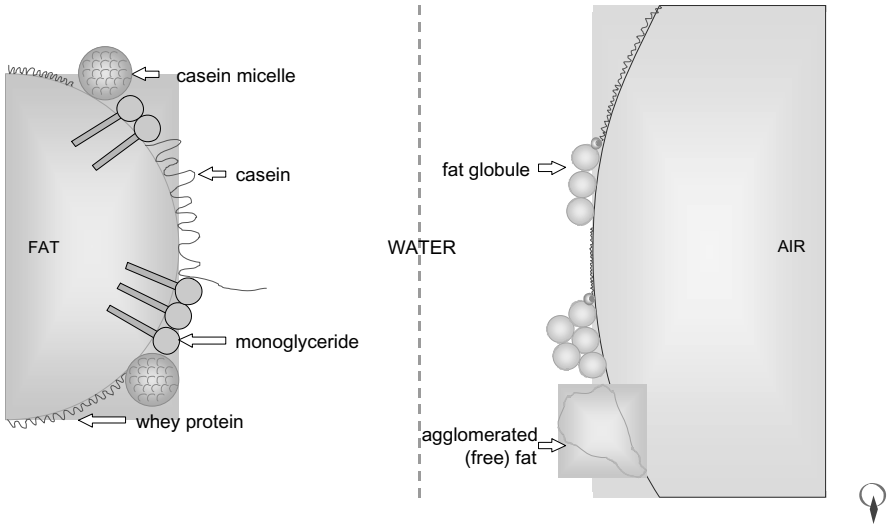


Fig. 2.7 Fat / water and oil / water interfaces in ice cream.

The air/water interface is stabilised by denatured milk proteins, partially destabilised fat and agglomerated fat globules. Monoglycerides are mainly responsible for the partial destabilisation of the fat emulsion.

Denatured milk proteins, casein micelles and monoglycerides stabilise the fat/water interface in the ice cream mix. Proteins are the prime emulsifying agents in most dairy products and also ice cream. Only by applying milk proteins we can obtain very good and stable emulsions. Proteins are surface active and partially cover the fat globules and air bubbles. The usual monoglyceride dosage in ice cream is 0.15%. This is by no means sufficient to cover all fat surfaces. The emulsion stability achieved with only milk protein as surface-active material does not lead to significant de-emulsification/agglomeration during freezing. Low molecular weight surfactants, such as monoglycerides, are needed to control the de-emulsification process.

The first role of monoglycerides is to further reduce the oil/water interfacial tension more than milk protein does alone and in this way the homogenisation process is made more effective. A narrower fat particle size distribution with a well defined total surface area is thus obtained.

The second and most important role of the monoglycerides is to promote the desorption of milk protein from the interface. This results in an interfacial layer with reduced strength or elasticity, a prerequisite for controlled de-emulsification and agglomeration of fat globules during aeration of the ice cream mix in the freezer.

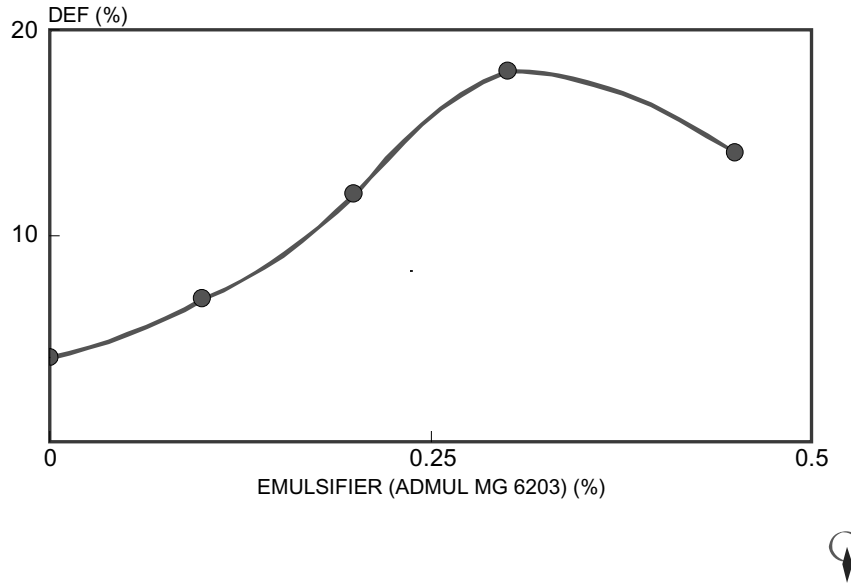


Fig. 2.8 Effect of emulsifier concentration on de-emulsified fat in ice cream (Admul MG 6203 is a 60% monodiglyceride available from Kerry Bio-Science).

The effect of monodiglycerides on the level of de-emulsified fat is shown in Fig. 2.8.

For a standard ice cream (10% fat, 10% non-fat milk solids) approximately 20% of the total fat is de-emulsified. In this case, de-emulsified fat is determined by a polar solvent extraction. The importance of de-emulsified fat on ice cream quality is shown in [23–25].

Laser light scattering methods are now being used to measure fat particle size distribution and fat agglomeration in ice cream mixes and finished ice creams. As shown in Fig. 2.9 the level of de-emulsified fat determines to a great extent the firmness of the ice cream at extrusion, which is measured with a penetrometer.

The level of agglomerated fat (or DEF%) is also directly related to the melting behaviour (Fig. 2.10) and shape retention of the ice cream at ambient temperature. The function of the monoglyceride in ice cream depends to a large extent on the properties of the oil/water interface and thus on the quality and quantity of the added protein.

Partial replacement of milk proteins by whey protein is a common practice in the ice cream industry to achieve cost optimisation. When 50% of milk protein is replaced by whey protein (whilst keeping the total protein constant) the amount of de-emulsified fat decreases significantly. This will result in a softer and wetter

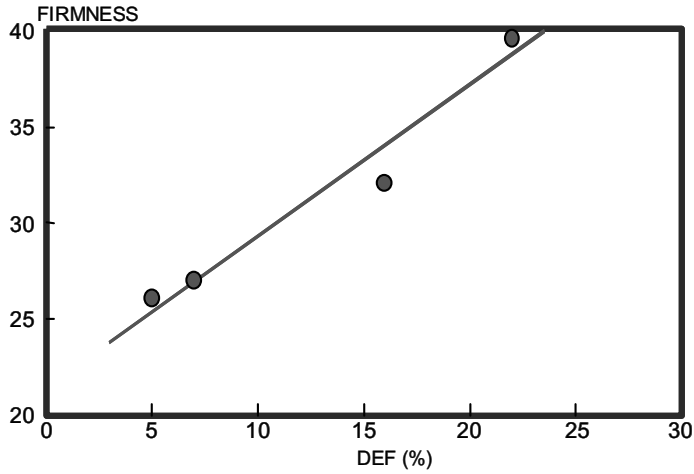


Fig. 2.9 Correlation between level of de-emulsified fat (DEF%) and ice cream firmness at extrusion.

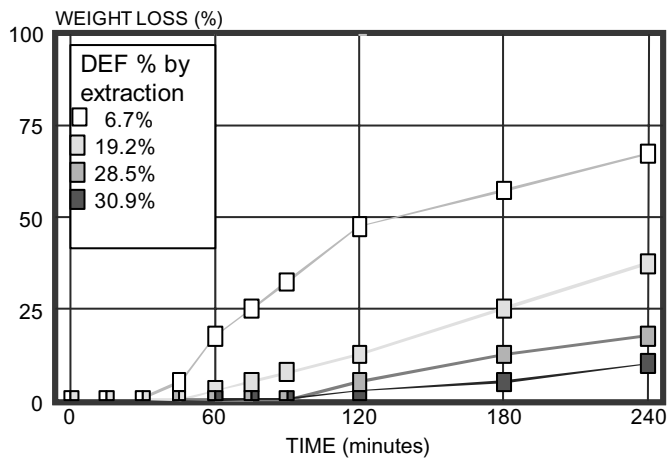


Fig. 2.10 Effect of DEF% (solvent extraction) on melting characteristics (at room temperature) of ice cream.

ice cream at extrusion and relatively fast melting properties of the ice cream (see Fig. 2.11). The reason for this is that whey protein has stronger emulsifying properties than milk protein, and consequently whey protein desorption from the interface by monoglycerides is less effective as compared to milk protein. This increased emulsion stability by whey protein can be counteracted by more effective de-emulsification by either increased monoglyceride concentration or by applying more effective partially unsaturated monoglycerides (see Table 2.4).

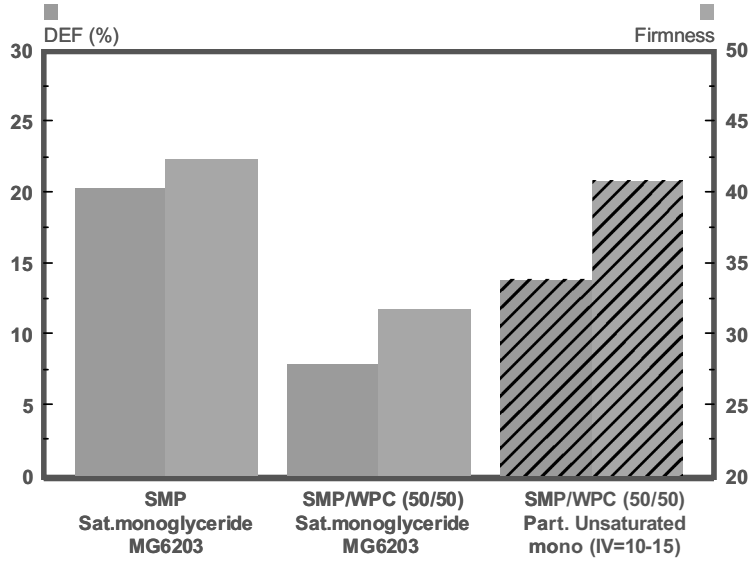


Fig. 2.11 Protein-emulsifier interaction effects on DEF% (extraction) and firmness at extrusion of a 10% fat ice cream (protein/fat = 3.1; overrun = 100%).

Acknowledgements

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3 Acid esters of mono- and diglycerides

Rolf Gaupp and Wolfgang Adams

A general approach to the definition of this group of emulsifiers is that the free hydroxylic groups of mono- and diglycerides of edible fatty acids can be esterified with other short-chain food acids, such as acetic acid, citric acid, lactic acid or tartaric acid, and the result will be the acid esters of mono- and diglycerides.

The possible variations of the above are shown in Table 3.1 and detailed in the following section.

3.1 E472a (ACETEM)

Acid esters of mono- and diglycerides normally consist of a mixture of all the possible products obtained by esterification of acetic acid, mono- and diglycerides. So a mixture of esters formed by the reaction of acetic acid and fatty acids (derived from of edible food fats) with glycerol will result.

Synonyms for ACETEM are:

- Acetic acid esters of mono- and diglycerides
- Acetoglycerides
- Acetylated mono- and diglycerides
- Acetic- and fatty acid esters of glycerol
- Mono- and diglycerides of fatty acids esterified with acetic acid

The chemical structure of ACETEM is shown in Fig. 3.1. The distribution of the ACETEM's principal components depends on the proportion of acetic acid, fatty acids and glycerol, and the reaction conditions used.

3.1.1 Chemical properties of ACETEM

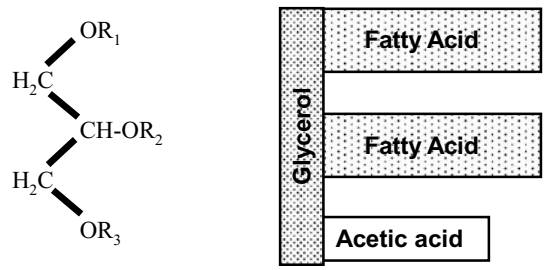
All ACETEM are esters of a polyvalent alcohol. So they show chemical reactions of rearrangement, intra- and intermolecular migration of acylic groups and certain sensitivity towards hydrolysis.

Under thermal stress, ACETEM may dissociate and show migration of acylic groups. The amount of this migration depends on the time and intensity of the thermal stress and also on the degree of acetylation of monoglyceride with acetic acid.

Table 3.1 Overview and labelling of acid esters of mono- and diglycerides

Product	E number	FDA-CFR Number
Acetic acid esters of mono- and diglycerides of fatty acids (ACETEM)	E472a	172.828
Lactic acid esters of mono- and diglycerides of fatty acids (LACTEM)	E472b	172.850
Citric acid esters of mono- and diglycerides of fatty acids (CITREM)	E472c	172.832[a]
Mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids (DATEM)	E472e	184.1101
Tartaric acid esters of mono- and diglycerides of fatty acids (TATEM)	E472d	–
Mixed acetic and tartaric acid esters of mono- and diglycerides of fatty acids (MATEM)	E472f	–

[a] CITREM according the FDA-definition means: A mixture of glycerol monooleate and its citric acid monoester, with a total citric acid content between 14% and 17%.



i.e.: Monoacetylated-diglycerol

At least one of R_1, R_2 or R_3 represents an acetic acid moiety, one represents a fatty acid moiety, and the remainder may represent acetic acid, fatty acid or hydrogen.

Fig. 3.1 Molecular structure of ACETEM.

The thermo-stability of ACETEM, with respect to the level of acetylation, in terms of increased acid value is shown in Fig. 3.2. The more hydrolysed species present in the system, the higher its acid value will be. Another method to prove this behaviour will be the measurement of the content of 1-monoglyceride. Its concentration will decrease with increasing hydrolysis via migration of acylic groups. So a slowly decreasing and low content of 1-monoglyceride will indicate more stability towards the more acetylated ACETEM (see Fig. 3.3) [1].

Surprisingly, an 80% acetylated ACETEM (e.g. Lamegin® EE 80) seems to be totally stable up to temperatures of 120°C. Higher acetylated species show the

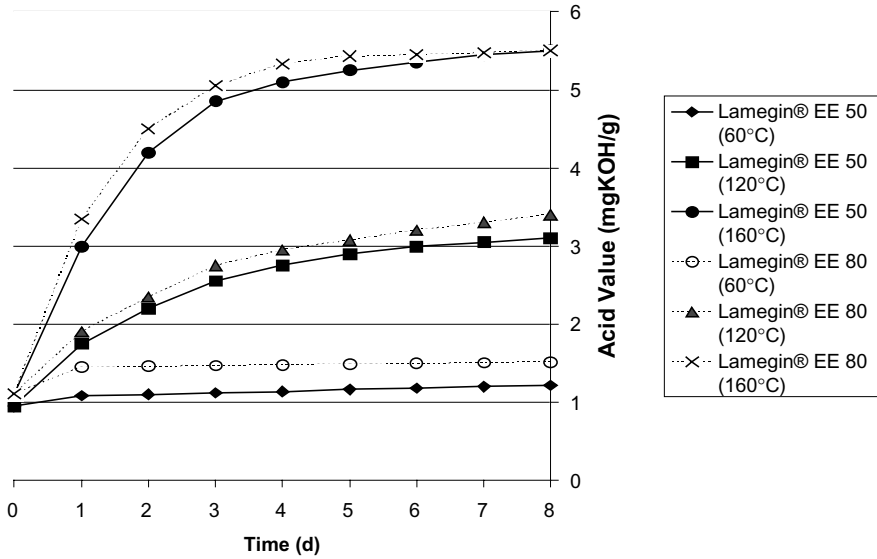


Fig. 3.2 Thermostability of ACETEM over time, with respect to their degree of acetylation, in terms of increased acid value (Lamegin® EE 50 = 50% acetylated monoglyceride, Lamegin® EE 80 = 80% acetylated monoglyceride).

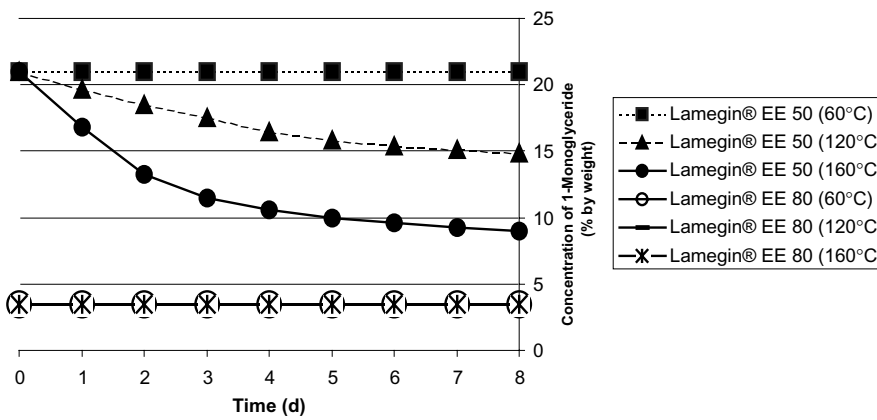


Fig. 3.3 Thermostability of ACETEM over time, with respect to their degree of acetylation, in terms of decreased content of 1-monoglyceride (Lamegin® EE 50 = 50% acetylated monoglyceride, Lamegin® EE 80 = 80% acetylated monoglyceride).

same results. Using acids, alkaline solutions and lipolytic enzymes, it is possible to cleave ACETEM-like triglycerides [2].

Hydrolysis of ACETEM with alkaline solutions will result in the alkaline salts of the released fatty acids, acetic acid and glycerol; and hydrolysis with acids will result in free fatty acids, acetic acid and glycerol. The enzymatic hydrolysis shows some intermediate steps, but the final result will again be free fatty acids, acetic acid and glycerol. All these reactions of hydrolysis are rapid and run completely when the concentration of the substances with hydrolytic activity is high enough [1]. The non-catalysed hydrolysis of ACETEM in aqueous systems depends on temperature and time, and is rather slow [1].

Due to the low sensitivity towards hydrolysis at low and moderate temperatures, ACETEM can be used in aqueous systems, even if they are stored for a certain period.

3.1.2 Manufacturing of ACETEM

ACETEM can be manufactured using the following processes:

- reaction of glycerol with fatty acid and acetic acid
- trans-esterification of partial glycerides with triacetin
- trans-esterification of triglycerides with glycerol and triacetin
- reaction of triglycerides with triacetin
- reaction of mono- and diglycerides of edible fatty acids with acetic acid anhydride

The last three processes are now commercially in use.

The trans-esterification of triglycerides and triacetin, as a balanced reaction, will result in some different triple esterified glycerol species, esterified either with fatty acids or acetic acid. These reactants are sometimes also called 'aceto-fats'. Any surplus triacetin must be removed by distillation. After the reaction of mono- and diglyceride and monoglyceride with acetic acid anhydride, the result will be a mixture of different species with more or less free hydroxylic groups. The ratio of mono-, di- and tri-esterified species depends on:

- the ratio of the reactants: mono-, di-glycerides and acetic acid anhydride
- the reaction's temperature and time
- their purification after the end of the reaction

Besides the desired and isolated species of this reaction (the acetylated monoglycerides), a small amount of non-esterified mono- and diglycerides will always be present. These are obtained either via non-processed reactants or via intramolecular migration of acylic groups from acetylated molecules.

Regarding the *reactants*, which are rather complex mixtures of mono- and diglycerides by themselves, the addition of another acidic moiety results in an increase of the possible resulting components. So isomers of mono-acetylated monoglycerides, di-acetylated monoglycerides, acetylated diglycerides, besides various amounts of mono- and diglycerides and small amounts of free glycerol, triacetin, acetic acid and fatty acids, will be present.

Manufacturing of ACETEM, by trans-esterification of triglycerides is shown in Fig. 3.4. The other method, via acetylation of mono- and diglycerides of fatty acids is shown in Fig. 3.5.

3.1.3 Appearance and physical properties

The appearance of ACETEM is closely linked to their relationship with fats. This fact results in a slightly ambiphilic molecular structure, depending on the degree of acetylation of ACETEM. Taste and odour are determined by the ratio of fatty acid/acetic acid. Almost all ACETEM vary from colourless to ivory coloured and from oily to wax-like, with a consistency determined by the fatty acids and the proportion of acetic acid included in the molecules. This range may vary from liquid to solid and wax-like consistency. The taste will be oily, lard-like or often neutral. Free acetic acid will always indicate some hydrolysis.

In general, ACETEM have a softer consistency and a lower melting point compared to the mono- and diglycerides they are derived from. This indicates the possibility to produce liquid 'aceto-fats' based on saturated fatty acids.

3.1.4 Solubility

All kinds of ACETEM are typically insoluble in strongly polar solvents, such as hot and cold water, or glycerol.

On the other hand, they are dispersible to soluble in all kinds of edible oils and fats and some alcohols, such as ethanol, or iso-propanol.

3.1.5 Phase behaviour

In water, ACETEM do not form mesomorphic phases [1].

3.1.6 Surface-active properties

ACETEM are non-ionic substances. During their manufacturing process one or both of the free hydroxyl groups of the mono- and diglycerides, which are responsible for the polar properties in the molecule, are esterified with acetic

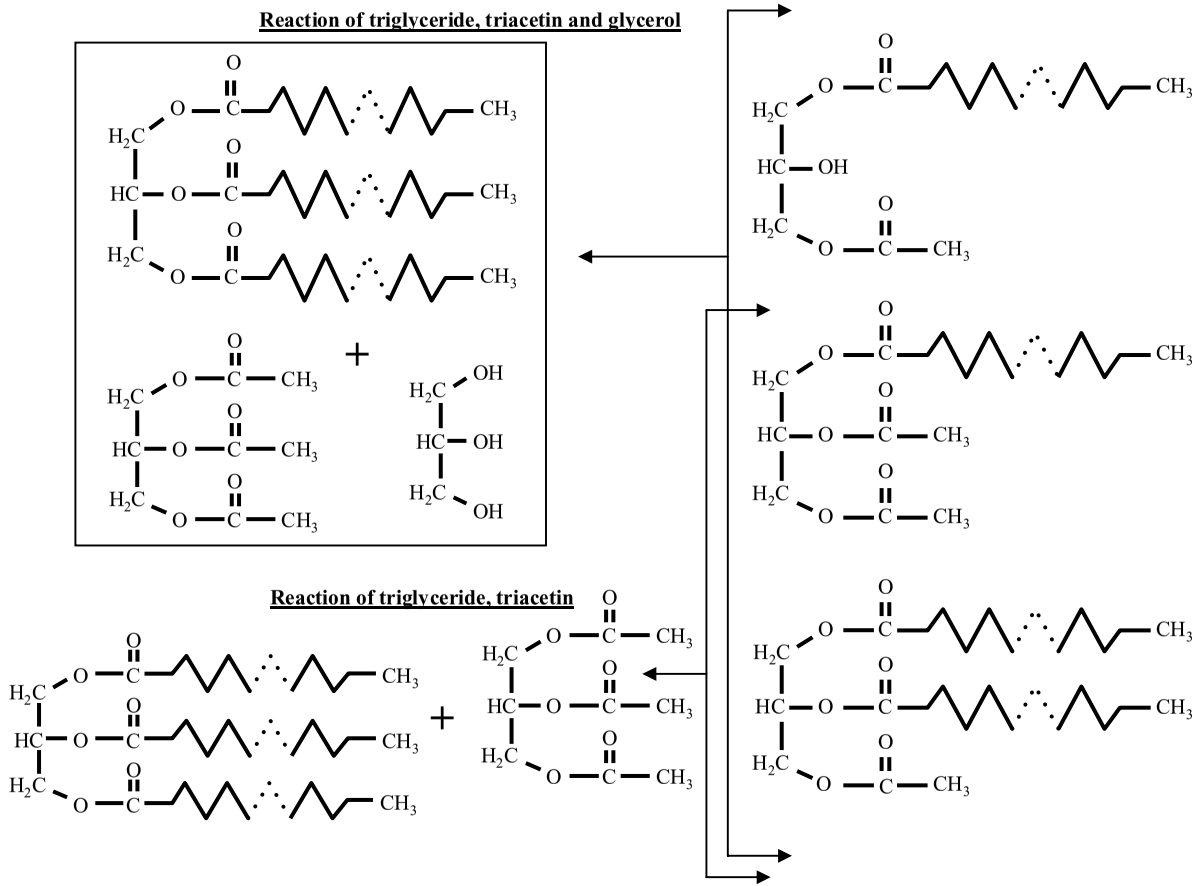


Fig. 3.4 Manufacturing of ACETEM via transesterification of triglycerides.

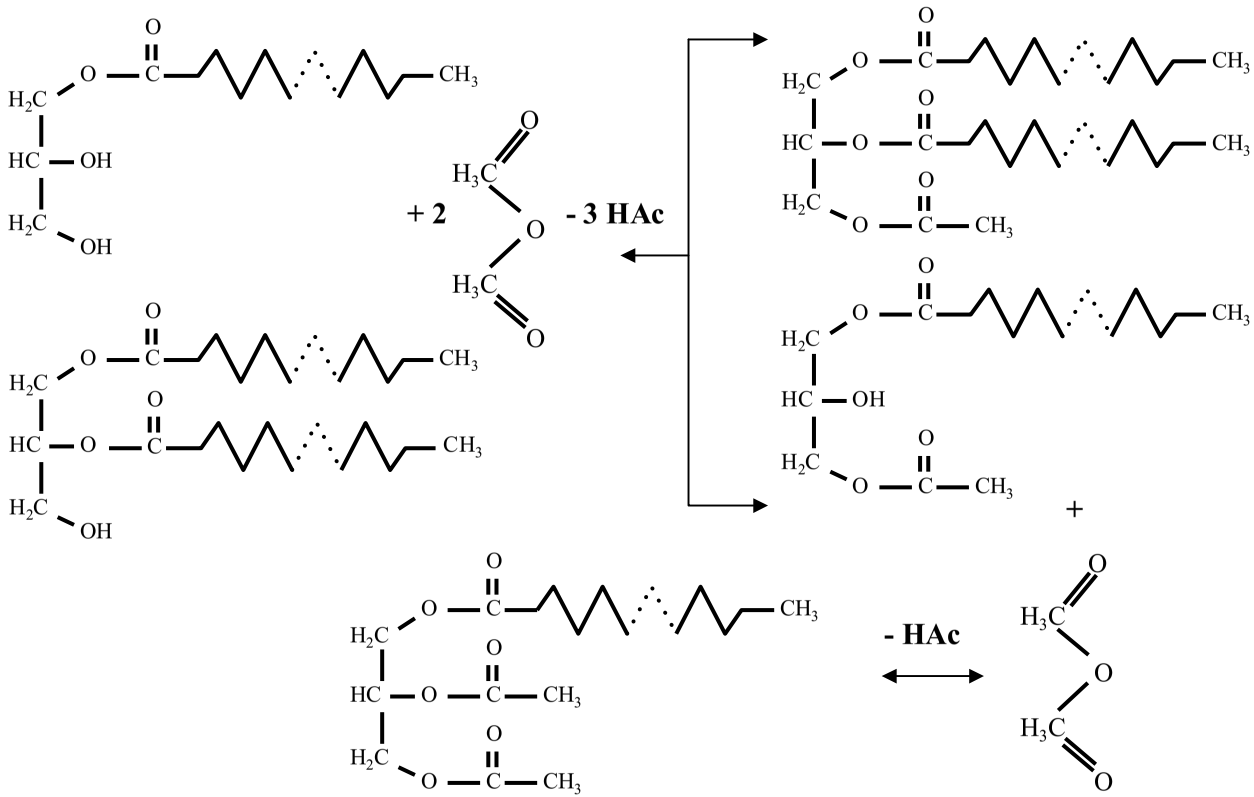


Fig. 3.5 Manufacturing of ACETEM via acetylation of mono- and diglycerides of fatty acids.

acid. This means that the HLB value of ACETEM will definitively be lower compared to the mono- and diglycerides. As a result, a reduced surface tension of the phase barrier in water-in-oil emulsions containing ACETEM will occur, so the use of ACETEM as emulsifiers for this kind of systems will be rather limited.

3.1.7 Special properties of ACETEM

3.1.7.1 Coating properties

Due to the presence of saturated long-chain fatty acid moieties and the short-chain acetic acid moieties within the ACETEM molecules, ACETEM can form plastic, but rather hard and mechanically stress-resistant films. Such films can be used as a stable coating material for foodstuff (i.e. sausages or cheese) to avoid dehydration or for protection against microbiological activity.

3.1.7.2 Lubrication properties

ACETEM, totally esterified with saturated, medium- or short-chain mono- and diglycerides, are liquid under standard conditions. They offer good lubrification qualities and can be used without restriction as lubricants in food processing industry.

3.1.7.3 Stability and anti-dusting applications

As a result of the relative high stability of totally acetylated ACETEM towards hydrolysis and oxidation, they are often used as anti-dusting agents during the mixing of powder form ingredients or used to protect the working staff from being exposed to rather dusty environments.

The stability of liquid ACETEM towards oxidation can also be explained by the stability of the totally saturated fatty acids within these molecules.

3.1.7.4 Stabilisation of polymorphic alpha-fat phases

ACETEM are able to stabilise the alpha-fat crystal form of fats. This alpha-modified fat, contained in topping and shortening products, has a rather good whipping performance. Consequently, ACETEM are often used as synergistic components in the recipes of whipped toppings and shortenings [3, 4].

Specification and analytical parameters of ACETEM are shown in Table 3.2.

3.1.8 Safety

Acetic acid esters of mono- and diglycerides of fatty acids have been evaluated by the Joint FAO/WHO Expert Committee on Food Additives (4) and the Scientific Committee for Food (5).

Table 3.2 Specification of ACETEM and the most important parameters of their analysis

	EU[a] (1)	FAO/WHO (2)	FCC (3)	Recommended method of analysis[b]
Total acetic acid	9–32%	–	–	A23 [5]
Total glycerol	14–31%	–	–	A22 [6]
Free glycerol	max. 2%	–	–	A16 [7]
Free fatty acids and acetic acid (as oleic acid)	max. 3%	–	–	A15 [8]
Sulphated ash	max. 0.5%	–	–	A6 [9]
Acid value	–	–	max. 6	A18 [10]
Reichert–Meissl value	–	–	75–150	A32 [11]
Arsenic	max. 3 mg/kg	max. 3 mg/kg	–	A3 [12]
Heavy metals (as Pb)	max. 10 mg/kg	max. 10 mg/kg	max. 10 mg/kg	A1 [13]
Lead	max. 5 mg/kg	–	–	A2 [14]
Mercury	max. 1 mg/kg	–	–	A5 [15]
Cadmium	max. 1 mg/kg	–	–	A4 [16]

[a] Purity criteria apply to the additive free of sodium, potassium and calcium salts of fatty acids, however these substances may be present up to a max. level of 6% (expressed as sodium oleate).
[b] Do not necessarily reflect the official methods used for the stated specifications.

References:
(1) Commission Directive 98/86/EC of 11 November 1998 amending. Commission Directive 96/77/EC laying down specific purity criteria on food additives other than colours and sweeteners.
(2) *Compendium for Food Additive Specifications*, Volume 1, 1992, p.13. *Combined Specifications from 1st through the 37th Meetings 1956–1990*.
(3) *Food Chemical Codex*, 4th edn, 1996, p. 12.

Evaluation status:

Acceptable daily intake (ADI): not specified.

(4) WHO Food Additive Series No. 5, 1974, page 210–213. Toxicological evaluation of some food additives including anti-caking agents, anti-microbials, anti-oxidants, emulsifiers and thickening agents.
(5) Reports of the Scientific Committee for Food, Seventh Series, 1978.

3.1.9 Typical applications in food

Within the EU acetic acid esters of mono- and diglycerides are generally permitted for use in foodstuff (6):

(6) European Parliament and Council Directive No. 95/2/EC of 20, February 1995, on food additives other than colours and sweeteners.
Directive 98/72/EC of the European Parliament and Council Directive 95/2/EC on food additives other than colours and sweeteners.

Acetic acid esters of mono- and diglycerides have excellent aerating and foam stabilising properties. They are also used as lubricants and release agents. Applications include topping powders, whipped topping concentrates, chewing gum base, coatings cakes.

3.1.10 Non-food applications

Some of the non-food applications of ACETEM include:

- emulsifiers in cosmetic preparations
- plasticising and slipping agent for waxes on paper products
- plasticiser for polyvinyl chloride and other plastics.

3.2 E472b (LACTEM)

Lactic acid esters of mono- and diglycerides of fatty acids are normally obtained by esterification of lactic acid and mono- and diglycerides. So a mixture of esters formed by lactic acid and fatty acids of edible food fats with glycerol will result.

Synonyms for LACTEM are:

- Lactic acid esters of mono- and diglycerides
- Lactoglycerides
- Lactic acid and fatty acid esters of glycerol
- Mono- and diglycerides of fatty acids esterified with lactic acid
- Glycerol-lacto esters of fatty acids
- Lactated mono- and diglycerides
- GLP

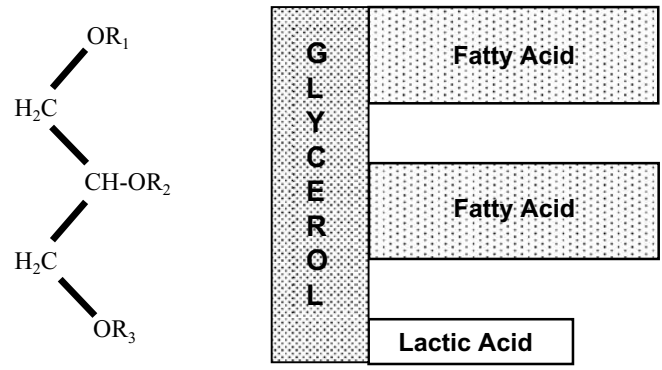
The chemical structure of LACTEM is shown in Fig. 3.6.

The distribution of the principal components depends on the proportion of lactic acid, fatty acids, glycerol and the current conditions of reaction.

3.2.1 Chemical properties of LACTEM

All LACTEM are esters of a polyvalent alcohol, therefore they show reactions of rearrangement, intra- and intermolecular migration of acylic-groups and a certain sensitivity towards hydrolysis.

Under thermal stress, LACTEM may show migration of acylic groups. The amount of this migration depends on the time and intensity of the thermal stress. The thermo-stability of LACTEM, with respect to this degree of lactylation, in terms of increased acid value, is shown in Fig. 3.7. The more the hydrolysed



i.e.: Monolactylated-diglycerol

At least one of R_1, R_2 or R_3 represents a lactic acid moiety, one represents a fatty acid moiety, and the remainder may represent lactic acid, fatty acid or hydrogen.

Fig. 3.6 Molecular structure of LACTEM.

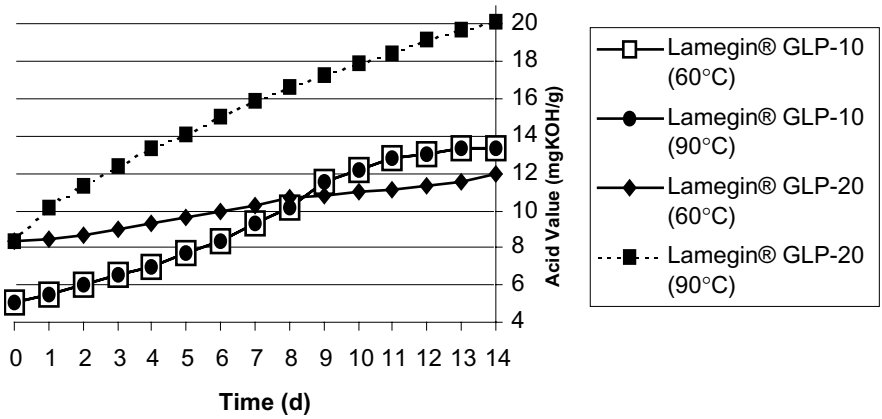


Fig. 3.7 Thermostability of LACTEM over time, with respect to their degree of lactylation, in terms of increased acid value (Lamegin® GLP-10 = 10–12% lactylated monoglyceride, Lamegin® GLP-20 = 18–20% lactylated monoglyceride).

species present, the higher will be the acid value of this system.These experiments have been carried out with two different types of LACTEM. The first one containing 12–14% of lactic acid (Lamegin® GLP-10) and the other one containing 18–20% of lactic acid (Lamegin® GLP-20).

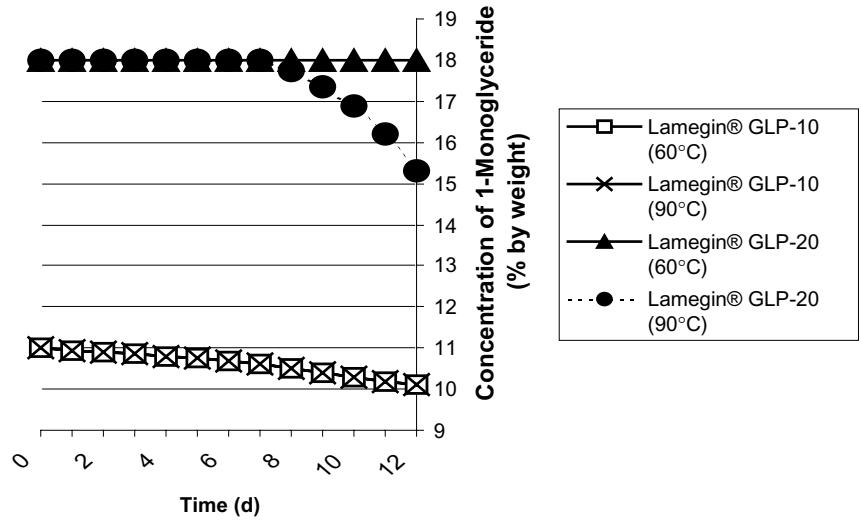


Fig. 3.8 Thermostability of LACTEM over time, with respect to their degree of lactylation, in terms of decreased content of 1-monoglyceride (Lamegin® GLP-10 = 10–12% lactylated monoglyceride, Lamegin® GLP-20 = 18–20% lactylated monoglyceride).

Essentially, the more lactylated LACTEM seems to be more stable during longer storage periods at temperatures around 60°C. This is due to the reduced number of free hydroxyl groups resulting from the higher degree of lactylation.

Another method to prove this is the measurement of the content of 1-monoglyceride. Its concentration will decrease with increasing hydrolysis, via migration of acylic groups. This shows that LACTEM is quite stable at ambient temperatures for a period of about 10 days. Figure 3.7 illustrates this point [1].

Surprisingly, a 20% lactylated LACTEM (e.g. Lamegin® GLP-20) seems to be stable for several days up to temperatures of 90°C.

The changes in different LACTEM caused by heating, as shown in Figs 3.7 and 3.8, give a clear indication that stressing of LACTEM using high temperatures over a longer period of time is not recommended. Apart from the changes in the chemical parameters, a deterioration of the sensory properties will always occur.

LACTEM are hydrolysed similar to triglycerides, using acids, alkaline solutions and lipolytic enzymes. Hydrolysis of LACTEM with acids will result in free fatty acids, lactic acid and glycerol; and hydrolysis with alkaline solutions will result in the alkaline salts of the fatty acids and the lactic acid, as well as glycerol. The enzymatic hydrolysis will results in free fatty acids, lactic acid and glycerol. All these hydrolytic reactions are rapid and complete when the concentration of enzymes, acids and alkaline solutions is high. The non-catalysed

hydrolysis of LACTEM essentially depends on temperature and time, and is rather slow.

LACTEM are very sensitive towards any hydrolytic reaction. The food technologist may pay some attention to this fact during their use in aqueous systems or during a rather long storage time by preventing them from higher temperatures [1].

3.2.2 Manufacturing of LACTEM

LACTEM is manufactured either by the esterification of glycerol with lactic acid and edible fatty acids (Fig. 3.9A), or by lactylation of a mixture of mono- and diglycerides of edible fatty acids (Fig. 3.9B). The resulting number of different positional isomers will be high. Their distribution in LACTEM depends on the molar ratios of the processed raw materials and also on the temperature and time of reaction. The largest number of positional isomers are of mono- and dilactoyl-monoglycerides and also mono- and diglycerides. The by-products will be glycerol, free lactic acid, polymerised lactic acid, esters and free fatty acids.

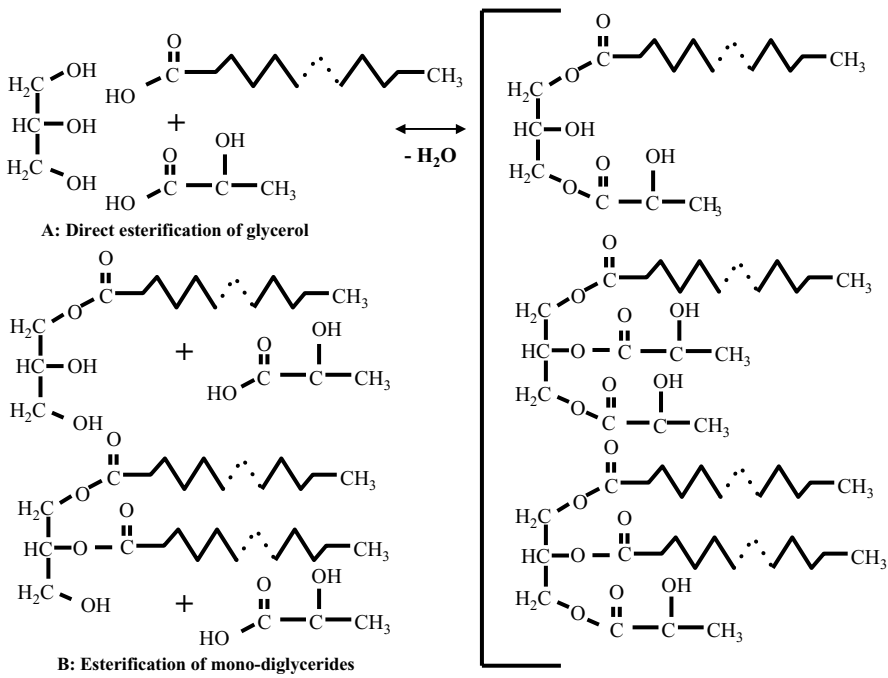


Fig. 3.9 Different ways of the manufacturing of LACTEM.

3.2.3 Appearance and physical properties

In general, the LACTEM have a softer consistency and a lower melting point compared to the monoglycerides they are derived from.

The rheological properties of LACTEM are linked to their very close relationship with fats. Their taste, odour and consistency depend on the structure of the included fatty acid moiety and the amount of esterified lactic acid. The product will be slightly yellow to amber-coloured, and oily to wax-like in consistency. The taste and odour may vary from neutral to bitter.

3.2.4 Solubility

LACTEM are typically not soluble in hot water and 1, 2-propylen-glycol. They are soluble in some hot alcohols (ethanol, iso-propanol or xylol) and fats, such as soybean oil or lard.

3.2.5 Phase behaviour

LACTEM do not show mesomorphic phase behaviour in water [1].

3.2.6 Surface activity

LACTEM are non-ionic substances. During the esterification with lactic acid, the free hydroxyl groups of the mono- and diglycerides will disappear. These groups are responsible for their hydrophilic character. However, as a result of the esterification of lactic acid, hydroxyl groups will now be included into the molecule. When the esterification with lactic acid is complete, their number will remain same, as in the non-esterified mono- and diglyceride, but the total molecular weight of the resulting molecule will be much higher. Therefore, its HLB value will be lower compared to the mono- and diglycerides.

LACTEM are able to reduce the surface tension of any oil–water system and can be classified as water-in-oil emulsifiers. Figure 3.10 illustrates this via the reduction of surface tension in an emulsion of soybean oil/water.

3.2.7 Special properties of LACTEM

LACTEM tend to remain in their alpha-crystal modification and do not show any polymorphous tendency. Additionally they are able to stabilize the alpha-crystal modification of other triglycerides and offer a rather good air inclusion capacity, so that they can be used as synergistic components for whipped toppings [4].

Specification and analytical of parameters of LACTEM are shown in Table 3.3.

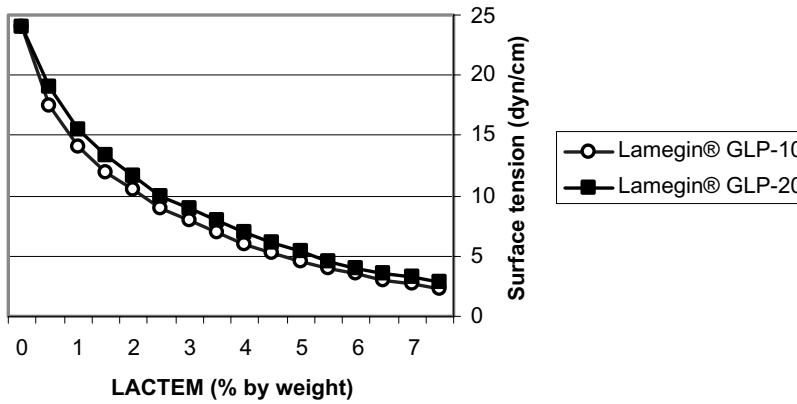


Fig. 3.10 Reduction of surface tension into the system of soybean oil/water, with respect to the concentration of two different LACTEM.

Table 3.3 Specification of LACTEM and the most important parameters of their analysis

	EU[a] (1)	FAO/WHO (2)	FCC (3)	Recommended method of analysis[b]
Total lactic acid	13–45%	–	–	A24 [17]
Total glycerol	13–30%	–	–	A22 [6]
Free glycerol	max. 2%	–	–	A16 [7]
Free fatty acids and lactic acid (as oleic acid)	max. 3%	–	–	A15 [8]
Sulphated ash	max. 0.5%	–	–	A6 [9]
Unsaponifiable matter	–	–	max. 2.0%	A14 [18]
Residue on ignition	–	–	max. 0.1%	A6 [9]
Arsenic	max. 3 mg/kg	max. 3 mg/kg	–	A3 [12]
Heavy metals (as Pb)	max. 10 mg/kg	max. 10 mg/kg	max. 5 mg/kg	A1 [13]
Lead	max. 5 mg/kg	–	max. 5 mg/kg	A2 [14]
Mercury	max. 1 mg/kg	–	–	A5 [15]
Cadmium	max. 1 mg/kg	–	–	A4 [16]

[a] Purity criteria apply to the additive free of sodium, potassium and calcium salts of fatty acids, however these substances may be present up to a max. level of 6% (expressed as sodium oleate).

[b] Do not necessarily reflect the official methods used for the stated specifications.

References:

(1) Commission Directive 98/86/EC of 11 November 1998 amending. Commission Directive 96/77/EC laying down specific purity criteria on food additives other than colours and sweeteners.

(2) *Compendium for Food Additive Specifications*, Volume 1, 1992, p.13. *Combined Specifications from 1st through the 37th Meetings 1956–1990*.

(3) *Food Chemical Codex*, 4th edn, 1996, p. 12.

3.2.8 Safety in use

Lactic acid esters of mono- and diglycerides have been evaluated by the Joint FAO/WHO Expert Committee on Food Additives (4) and the Scientific Committee for Food (5).

Evaluation status:

Acceptable daily intake (ADI): not specified.

(4) WHO Food Additive Series No. 5, 1974, page 231–233. Toxicological evaluation of some food additives including anti-caking agents, antimicrobials, anti-oxidants, emulsifiers and thickening agents.
(5) Reports of the Scientific Committee for Food, Seventh Series 1978.

3.2.9 Typical applications in food

Within the EU, lactic acid esters of mono- and diglycerides are generally permitted for use in foodstuffs (6).

(6) European Parliament and Council Directive No. 95/2/EC of 20 February, 1995, on food additives other than colours and sweeteners.
Directive 98/72/EC of the European Parliament and Council Directive of 15 October, 1998, amending Directive 95/2/EC on food additives other than colours and sweeteners.

Lactic acid esters of mono- and diglycerides are used to improve aeration and foam stability as well as texture and volume. Applications of LACTEM include:

- topping powders
- non-dairy creams
- dairy and recombined creams
- fine baked goods
- shortening
- chocolate compounds

3.3 E472c (CITREM)

Citric acid esters of mono- and diglycerides of fatty acids are obtained by the esterification of citric acid and edible fatty acids, with glycerol.

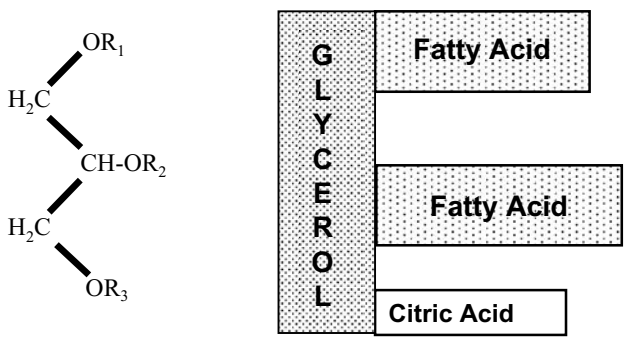
A mixture of different species formed by the esterification of citric acid and fatty acids (deriving from edible food fats) with glycerol will result.

Synonyms for CITREM are:

- Citric acid esters of mono- and diglycerides of edible fatty acids
- Mono- and diglycerides of fatty acids, esterified with citric acid
- Monoglycerol citric acid esters
- Monoglycerol citrates
- Citric acid monoglycerides
- Citric acid monoglycerol esters
- Citric acid esters of glycerides
- Citric acid–fatty acid–glycerides
- Citric- and fatty acid esters of glycerol
- Citroglycerides

All these synonyms are also used for the substances obtained by partial or total neutralisation of esterified CITREM. Here the non-esterified carboxylic groups of the citric acid are neutralised by the use of alkaline solutions, therefore CITREM with a neutral or slightly acid pH-value can be produced. For several applications of CITREM, a neutral pH-value will be very important. The chemical structure of CITREM is shown in Fig. 3.11.

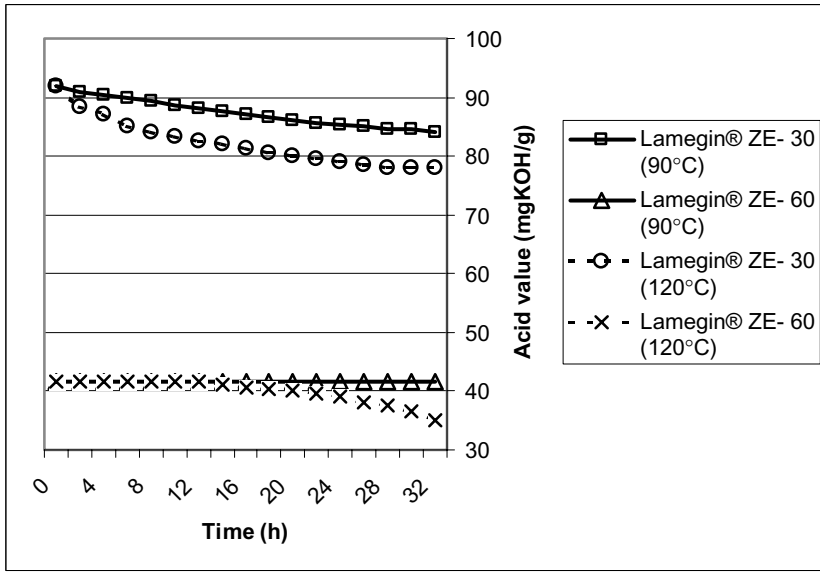
The distribution of the principal components is dependant on the proportion of citric acid, fatty acids, glycerol and the reaction conditions being used. The product can be partially or wholly neutralised resulting in the corresponding sodium or potassium salts.



i.e.:Monocitrylated-diglycerol

At least one of R_1, R_2 or R_3, represents a citric acid moiety. One represents a fatty acid moiety, and the remainder may represent citric acid, fatty acid or hydrogen.

Fig. 3.11 Molecular structure of CITREM.



(LameginZE®-30: non neutralized CITREM, pH-value (10% in water): 3-4; LameginZE®-60: partially neutralized CITREM, pH-value (10% in water): 5-6.)

Fig. 3.12 Thermostability of CITREM, with respect to the decrease of acid value.

3.3.1 Chemical properties of CITREM

The general chemical properties of all CITREM are due to the fact that all these substances are esters of a polyvalent alcohol and hence show reactions of rearrangement, inter- and intramolecular migration of acylic-groups and a certain sensitivity towards hydrolysis. Additionally, free carboxylic groups derived from the citric acid moiety will always present in these molecules showing all the corresponding reactive possibilities.

The thermal stress towards CITREM will result in inter- and intramolecular migration of acylic-groups. Due to the presence of free carboxylic- and hydroxyl groups, further esterification may result depending on the time and intensity of the thermal exposure. The thermal stability of non-neutralised and partially neutralised CITREM is shown in Fig. 3.12. Besides the decrease of the acid value, a drastic coloration caused by the decomposition of citric acid and the formation of polymeric substances will result [1].

During the application of CITREM, repeated thermal stress should be avoided, otherwise organoleptic problems may result in the final product.

Irrespective of whether neutralized or not, all CITREM show a certain sensitivity towards hydrolysis. They may be cleaved using acids, alkaline solutions

and lipolytic enzymes, in the same way as triglycerides. Hydrolysis with acids will result in free fatty acids, citric acid and glycerol; and hydrolysis with alkaline solutions will release their alkaline salts with fatty acids or citric acid, and free glycerol. The final result of the enzymatic hydrolysis will be free fatty acids, citric acid and glycerol [1]. All the above-mentioned reactions of hydrolysis will be faster and complete. The non-catalysed hydrolysis depends on temperature and time, and runs remarkably slower.

The food technologist may also consider the fact that when CITREM products contain water, or show a low pH-value, they can't be stored for longer periods at elevated temperatures.

3.3.2 Manufacturing of CITREM

The product can be manufactured by the esterification of glycerol with citric acid and edible fatty acids, or by the reaction of a mixture of mono- and diglycerides of edible fatty acids with citric acid.

The esterified CITREM may be partially or totally neutralised. In the last case, CITREM will be present as an alkaline salt of citric acid. The final CITREM is the result of a balanced chemical reaction with some polyfunctional reactants. The number of the possible individual species will therefore be rather high due to numerous possible positional isomers. Their distribution into the final CITREM depends on the molecular amounts of the reactants and also on reaction temperature and time. The majority of them will be the positional isomers of monoglycerides esterified with citric acid once or twice. Besides these species, monoglycerides, glycerol and free citric acid will also be present. Partially hydrolysed CITREM will also include the alkaline salts of these substances. The ratio of all these substances will depend on the pH-value of the final CITREM. Figure 3.13 shows all these variations.

3.3.3 Appearance and physical properties

CITREM are ambiphilic molecules because of the characteristic of its raw materials. Mono- and diglycerides are rather lipophilic substances and citric acid is a very hydrophilic component. All physico-chemical properties of CITREM are derived from the following facts.

The organoleptic properties of CITREM are normally comparable with fats. Nevertheless, the citric acid has some other influences. The consistency of CITREM vary from liquid, through waxy and solid. This depends on the fatty acid moiety of the used mono- and diglycerides, irrespective of whether they are saturated or unsaturated. It also depends on the amount of esterified citric acid and their degree of neutralisation.

The higher the amount of esterified citric acid, the more brittle they are. All non-neutralised types will be of lower melting points compared to the partially

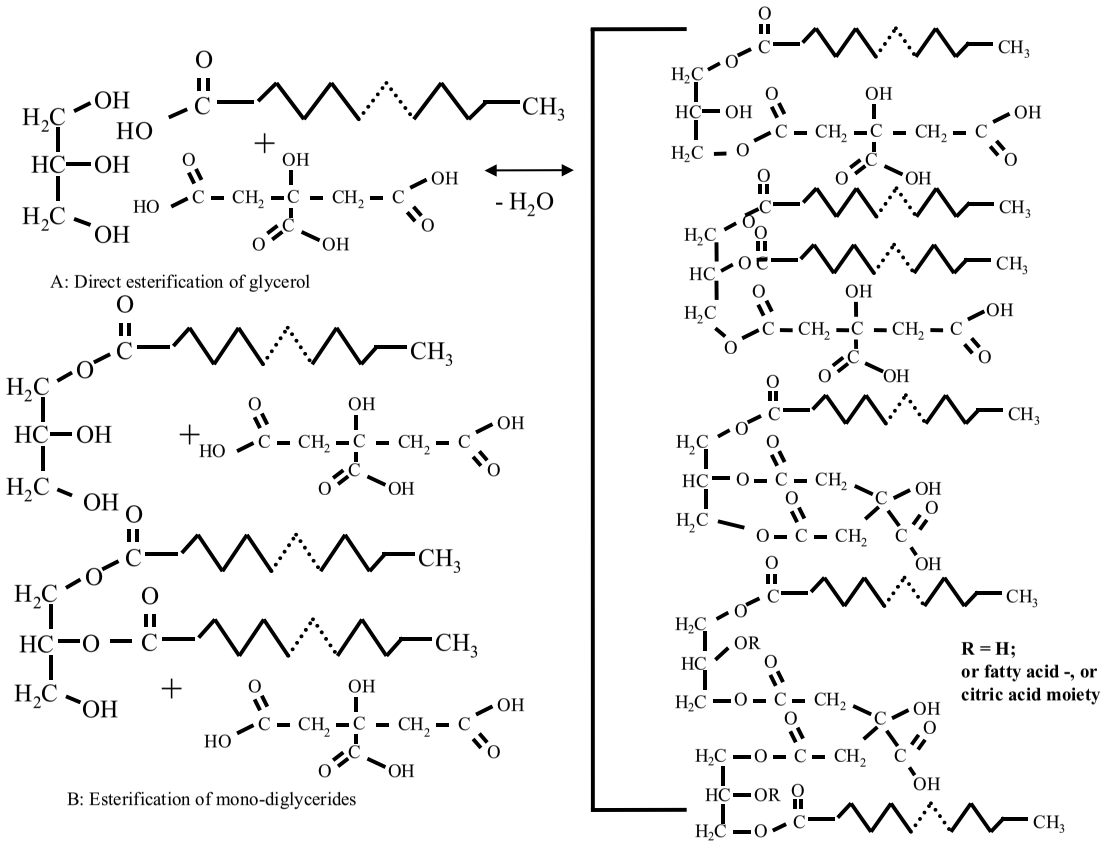


Fig. 3.13 Synthesis of CITREM.

neutralised ones. Colour, odour and taste will also depend on the included fatty acid moieties, the amount of esterified citric acid and the degree of neutralisation. The colours range from white- to ivory-coloured. The odour is neutral to slightly fatty and their taste will also be fatty to slightly sour, for the neutralised types, and fully sour for all the others.

3.3.4 Solubility

CITREM are typically dispersible in hot water, insoluble in cold water and soluble in edible oils and fats.

3.3.5 Phase behaviour

CITREM do not form mesomorphic phases in water [1]. They form stable emulsions above their melting points. In their liquid phase CITREM form a status of high orientation. They show a tendency towards thermotrophic mesomorphism, which is caused by a strong molecular interaction between the participating polar groups [19].

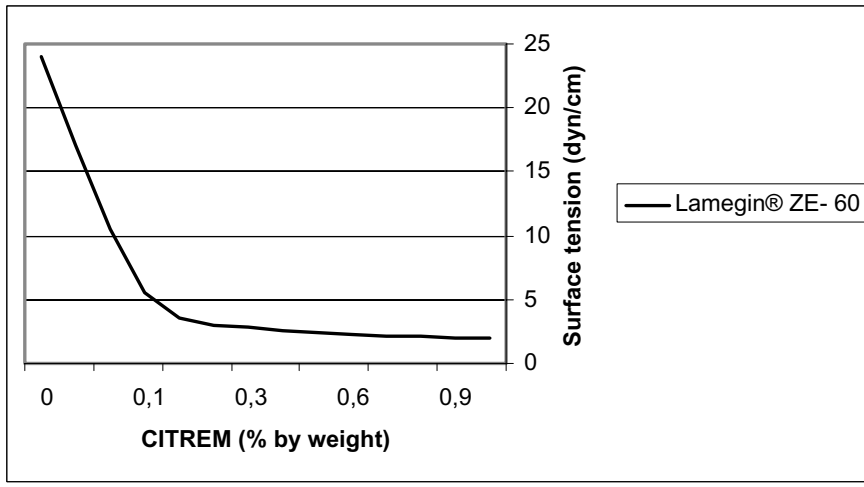
3.3.6 Surface-active properties

CITREM are ionic oil-in-water emulsifiers. Some of the free hydroxylic groups of the mono- and diglycerides disappear after the esterification, but they are partially replaced by the free hydroxylic groups of the citric acid. The hydrophilic part of the whole molecule is therefore formed by hydroxylic groups, deriving from the mono- and diglyceride part, the hydroxylic group of the citric acid and their carboxylic group. During the partial or total neutralisation of the carboxylic group, the hydrophilic part of the molecule will not increase substantially. But by its transformation into the salt, the hydrophilicity of the whole molecule will increase tremendously.

This means CITREM can be adapted to the specific individual applications. The HLB value of CITREM will be much higher compared to the mono- and diglycerides they are derived from. This is shown within the system of soybean oil/water in Fig. 3.14.

3.3.7 Special properties of CITREM

CITREM are able to bind traces of heavy metals as citric acid complexes. Therefore, they are often used as fat-soluble complexation agents within formulations for anti-oxidant blends. There they act as synergistic components and guarantee a much better performance of these kinds of products. The specification of CITREM and the most important parameters of their analysis are shown in Table 3.4.



(LameginZE®-60: partially neutralized CITREM, pH-value (10% in water): 5-6.)

Fig. 3.14 Surface tension into the system soybean oil/water, at 60°C, with respect to the CITREM concentration.

Table 3.4 Specification of CITREM and the most important parameters of their analysis

	EU[a] (1)	FAO/WHO (2)	FCC (3)	Recommended method of analysis[b]
Total citric acid	13–50%	13–50%	–	(2)
Total glycerol	8–33%	8–33%	–	(2)
Free glycerol	max. 2%	max. 4%	–	A16 [7]
Free fatty acids (as oleic acid)	max. 3%	–	–	No official method
Total fatty acids (as oleic acid)	–	37–81%	–	(2)
Sulphated ash	max. 0.5%	max. 0.5% / max. 10%[c]	–	A6 [9]
Arsenic	max. 3 mg/kg	max. 3 mg/kg	–	A3 [12]
Heavy metals (as Pb)	max. 10 mg/kg	max. 10 mg/kg	–	A1 [13]
Lead	max. 5 mg/kg	–	–	A2 [14]
Mercury	max. 1 mg/kg	–	–	A5 [15]
Cadmium	max. 1 mg/kg	–	–	A4 [16]

[a] Purity criteria apply to the additive free of sodium, potassium and calcium salts of fatty acids, however these substances may be present up to a max. level of 6% (expressed as sodium oleate).

[b] Do not necessarily reflect the official methods used for the stated specifications.

[c] Not neutralized products: max. 0.5%;
Partially or wholly neutralized products: max. 10%.

References:

(1) Commission Directive 98/86/EC of 11 November 1998 amending. Commission Directive 96/77/EC laying down specific purity criteria on food additives other than colours and sweeteners.

(2) *Compendium for Food Additive Specifications*, Volume 1, 1992, p.13. *Combined Specifications from 1st through the 37th Meetings 1956–1990.*

(3) No Food Chemical Codex specifications available.

3.3.8 Safety in use

Citric acid esters of mono- and diglycerides have been evaluated by the Joint FAO/WHO Expert Committee on Food Additives (4) and the Scientific Committee for Food (5).

Evaluation status:

Acceptable daily intake (ADI): not specified.

(4) WHO Food Additive Series No. 5, 1974, page 220–221. Toxicological evaluation of some food additives including anti-caking agents, antimicrobials, anti-oxidants, emulsifiers and thickening agents.
(5) Reports of the Scientific Committee for Food, Seventh Series 1978.

3.3.9 Typical applications in food

Within the EU, citric acid esters of mono- and diglycerides are generally permitted for use in foodstuffs (6).

(6) European Parliament and Council Directive No. 95/2/EC of 20 February, 1995, on food additives other than colours and sweeteners.
Directive 98/72/EC of the European Parliament and Council Directive of 15 October, 1998, amending Directive 95/2/EC on food additives other than colours and sweeteners.

Citric acid esters of mono- and diglycerides are widely used within the food industry, e.g. as emulsifiers, stabilisers, anti-spattering agents and as synergistic components with anti-oxidants.

The following should be considered as a list of their major applications:

- In fats for stabilising, but also as synergistic components for antioxidants
- In baking fat emulsions, bakery margarines and shortening for stabilising
- In fondants for improved gloss and smoothness
- In margarine as emulsifiers and anti-spattering agents
- In mayonnaise, salad dressings, sauces etc. as emulsifiers and stabilisers
- In sausages for enhancing the binding effects of meat
- In low-calorie food for fats, shortenings and baking fat emulsions with high water content
- With yeast containing products, soup powders and fat powders, to enhance instantinisation
- As flavour solubilisers
- As an effective non-GMO lecithin substitute in margarine and chocolate

3.3.10 Non-food applications

Some of the non-food applications of CITREM include:

- pharmaceutical preparations and cosmetic creams
- as blending agent in coatings for cellophane food-contact films

3.4 E472e (DATEM)

Please refer to Chapter 4 of this book.

3.5 E472d (TATEM)

Tartaric acid esters of mono- and diglycerides (TATEM) are an existing category of legal food additives within the EU food legislation. In fact, there are no manufacturer for these substances, nor any individual applications, which will need especially such types of emulsifiers.

The conclusion is therefore that their individual use can be well compensated for by the use of other esterified mono- and diglycerides.

3.6 E472f (MATEM)

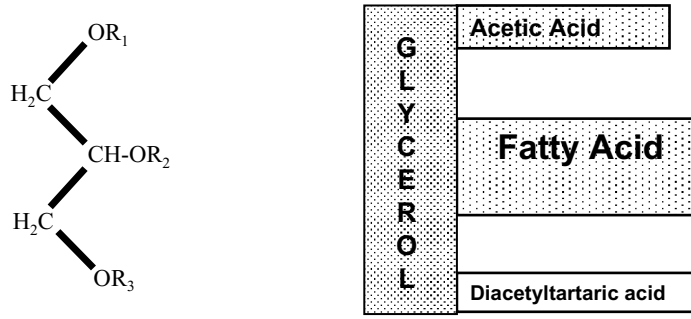
Mixed acetic-, tartaric- and diacetylated tartaric acid esters of mono- and diglycerides of edible fatty acids normally consist of all possible products obtained by esterification of acetic-, tartaric-, diacetylated tartaric acid and edible fatty acids with glycerol.

Synonyms for MATEM are:

- Mono- and diglycerides of fatty acids esterified with acetic- and diacetylated tartaric acid
- Diacetylatedtartaric-, acetic- and fatty acid esters of glycerol, mixed

The chemical structure of MATEM is shown in Fig. 3.15. The products are obtained either by reacting mono- and diglycerides of fatty acids with tartaric acid anhydride in the presence of acetic acid, or by esterification of mono- and diglycerides with tartaric acid and acetic acid in the presence of acetic acid anhydride [20].

Due to an inter- and intramolecular exchange of the acylic group, both methods of manufacturing result in the same essential components. The distribution of the principal components depends on the proportion of the basic raw materials and the reaction conditions used. The products may contain small amounts of



" i.e.:Acetylated-diacetyltartaric acid glycerol"

At least one of R_1, R_2 or R_3 represents a fatty acid moiety.
The remainder is either:
a) a tartaric acid moiety,
b) an acetic acid moiety,
c) a hydrogen,
d) a diacetylated tartaric acid moiety,
e) a monoacetylated tartaric acid moiety.

Fig. 3.15 Molecular structure of MATEM.

free glycerol, free fatty acids, free tartaric-, free diacetylated tartaric acid, acetic acid and free glycerides. The product may also contain mono- and diacetyltartaric esters of mono- and diglycerides of fatty acids.

3.6.1 Appearance

The product varies from sticky liquids to solids and from white to pale yellow in colour.

3.6.2 Solubility

The product is typically dispersible in water and soluble in methanol, ethanol and acetone. The specification of MATEM and the most important parameters of their analysis are shown in Table 3.5.

3.6.3 Safety in use

Mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids have been evaluated by the Joint FAO/WHO Expert Committee on Food Additives (4) and the Scientific Committee for Food (5).

Table 3.5 Specification of MATEM and the most important parameters of their analysis

	EU[a] (1)	FAO/WHO (2)	FCC (3)	Recommended method of analysis[b]
Total tartaric acid	20–40%	10–40%	–	(2)
Total acetic acid	10–20%	8–32%	–	(2)
Total glycerol	12–27%	11–28%	–	(2)
Free glycerol	max. 2%	max. 2.0%	–	A16 [7]
Free fatty acids (as oleic acid)	max. 3%	max. 3%	–	No official method
Sulphated ash	max. 0.5%	max. 0.5%	–	A6 [9]
Arsenic	max. 3 mg/kg	–	–	A3 [12]
Heavy metals (as Pb)	max. 10 mg/kg	–	–	A1 [13]
Lead	max. 5 mg/kg	max. 2 mg/kg	–	A2 [14]
Mercury	max. 1 mg/kg	–	–	A5 [15]
Cadmium	max. 1 mg/kg	–	–	A4 [16]

[a] Purity criteria apply to the additive free of sodium, potassium and calcium salts of fatty acids, however these substances may be present up to a max. level of 6% (expressed as sodium oleate).
[b] Do not necessarily reflect the official methods used for the stated specifications.

References:
(1) Commission Directive 98/86/EC of 11 November 1998 amending. Commission Directive 96/77/EC laying down specific purity criteria on food additives other than colours and sweeteners.
(2) *Compendium for Food Additive Specifications*, FAO Food and Nutrition Paper 52, Addendum 6, 1998, p. 49.
(3) No Food Chemical Codex specifications available.

Evaluation status:

Acceptable daily intake (ADI): 0–50 mg/kg body weight evaluation by JECFA.

Acceptable daily intake (ADI): 0–25 mg/kg body weight (temp.) evaluation by SCF.

(4) WHO Food Additive Series No. 5, 1974, page 222–224. Toxicological evaluation of some food additives including anti-caking agents, antimicrobials, antioxidants, emulsifiers and thickening agents.
(5) Minutes of the 107th Meeting of the Scientific Committee for Food, 1997.

3.6.4 Typical applications in food

Within the EU mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids are generally permitted for use in foodstuffs (6).

(6) European Parliament and Council Directive No. 95/2/EC of 20 February, 1995, on food additives other than colours and sweeteners.

Directive 98/72/EC of the European Parliament and Council Directive of 15 October, 1998, amending Directive 95/2/EC on food additives other than colours and sweeteners.

Mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids are used as dough conditioners for all baked products, particularly yeast-leavened products, white bread and rusks, and in ready mixed flours, particularly for use in the 'all-in' method.

Other applications of MATEM include:

- Beverage whiteners
- Cream analogues
- Chewing gum
- Meat and poultry products
- Emulsified sauces
- Canned coffee or tea
- Carriers or solvents for colours and food anti-oxidants

References

[1] Adams W.F. & Schuster G., *Emulgatoren für Lebensmittel*, Springer, Berlin, 1985, p. 95. *et. seq.*
[2] FAO Nutrition Meetings Report Series No. 53 A; WHO Food Additive Series No. 5, 1974, 210.
[3] Martin, J.B. & Lutton, E.S., *J. Am. Oil Chem. Soc.,* 1972, **49**, 683.
[4] Flack, A. & Korg, N., *Food Trade review,* 1970, **40,** 27.
[5] A23: Total acetic acid, *Food Chemicals Codex IV*, 119.
[6] A22: Total glycerol, *Food Chemicals Codex IV*, 120.
[7] A16: Free glycerol, *FAO Food and Nutrition Paper 5*, Rev. 2, 195.
[8] A15: Free fatty acids, DGF Einheitsmethoden C-III 2 (97).
[9] A6: Sulphated ash/residue on ignition, *FAO Food and Nutrition Paper 5*, Rev. 2, 77.
[10] A18: Acid value, *FAO Food and Nutrition Paper 5*, Rev. 2, 189.
[11] A32: Reichert-Meissl value, Food Chemical Codex IV, 826.
[12] A3: Limit test for arsenic, *FAO Food and Nutrition Paper 5*, Rev. 2, 69.
[13] A1: Limit test for heavy metals, *FAO Food and Nutrition Paper 5*, Rev. 2, 73.
[14] A2: Limit test for lead, *FAO Food and Nutrition Paper 5*, Rev. 2, 76.
[15] A5: Limit test for mercury, *FAO Food and Nutrition Paper 5*, Rev. 2, 77.
[16] A4: Limit test for cadmium, *FAO Food and Nutrition Paper 5*, Rev. 2, 59.
[17] A24: Total lactic acid, *Food Chemicals Codex IV*, 181.
[18] A14: Unsaponificable matter, *Food Chemical Codex IV*, 828.
[19] Larsson, K., Structures of emulsifier water phases, in *Foods*, Monograph No. 32, London Society of Chemical Industry, London, 1968, p. 8.
[20] EFEMA (European Food Emulsifier Manufacturers' Association e.V.) *Index of Food Emulsifiers*, 3rd edn, November 1999.

Emulsifiers in Food Technology
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4 Di-acetyltartaric esters of monoglycerides (DATEM) and associated emulsifiers in bread making

Rolf Gaupp and Wolfgang Adams

4.1 What are DATEM?

EFEMA, the European Food Emulsifier Manufacturers' Association e.V., defines DATEM as 'Mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids'. The e-number for DATEM is E472e.

Synonyms for DATEM are:

- diacetyltartaric acid esters of mono- and diglycerides
- diacetyltartaric and fatty acid esters of glycerol
- mono- and diglycerides of fatty acids esterified with diacetyltartaric acid

4.1.1 Chemical characterisation

DATEM are glycerol derivates esterified with edible fatty acids and mono- and diacetyl tartaric acids. In principle, two different processes exist for the manufacturing of these species.

The first one is the esterification of mono- and diglycerides with tartaric- and acetic acid in the presence of acetic acid anhydride. The other process is the reaction of diacetyl tartaric acid anhydride in the presence of acetic acid with mono- and diglycerides. First, the diacetyl tartaric acid anhydride is manufactured via the reaction of diacetyl tartaric acid with acetic acid anhydride. The acetic acid liberated in this reaction has to be separated by distillation. Then the reaction with monoglycerides is possible. The process of manufacturing of DATEM is schematically shown in Fig. 4.1.

The result of these two ways of synthesis is an inter- or intramolecular migration of acylic-groups leading in both cases to the structure shown in Fig. 4.2. The distribution of the components described into the final DATEM depends on the manufacturing process and the use and concentration of the basic raw materials. This means that the DATEM of each manufacturer offers a slightly different and individual composition of the occurring molecular species. Such products may also contain small amounts of free glycerol, fatty acids, tartaric and acetic acid, and their combinations with glycerol as free glycerides [1]. This complex composition of DATEM was confirmed by Sudraud *et al.* [2]. Figure 4.3 shows the possible variations occurring within this chemical reaction.

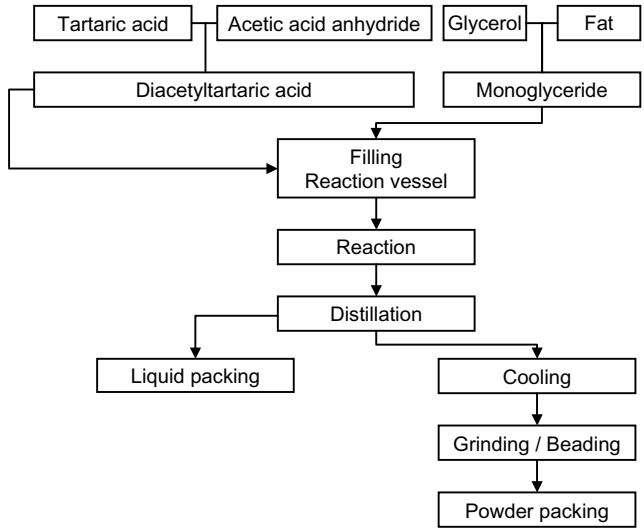
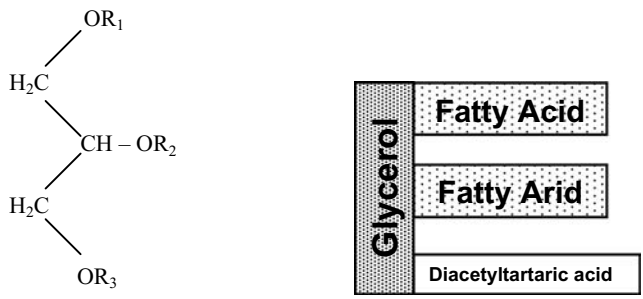
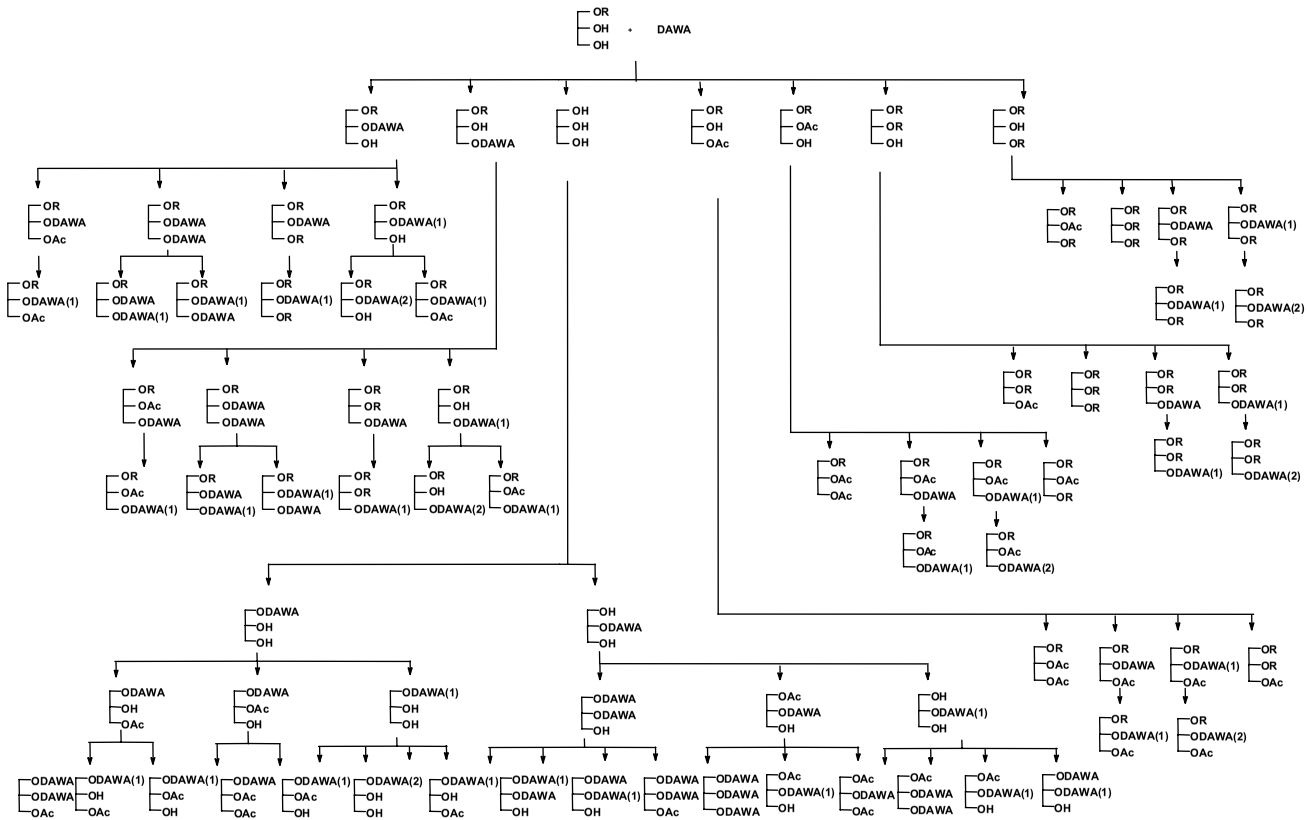


Fig. 4.1 Manufacturing of DATEM.



Where R_1, R_2 and R_3 (or two of them), are a fatty acid moieties. The remainder being either
a) diacetylated tartaric acid moiety,
b) monoacetylated tartaric acid moiety,
c) tartaric acid moiety,
d) acetic acid moiety,
e) hydrogen.

Fig. 4.2 Molecular structure of DATEM.



R = alkyl, DAWA = diacetylated-tartaric-acid, DAWA(1) = monoacetylated-tartaric-acid, DAWA(2) = tartaric-acid

Fig. 4.3 Synthesis of DATEM, possible components.

4.2 General properties of DATEM

All the different types of DATEM are esters of a polyvalent alcohol, so they show reactions of rearrangement, intra- and intermolecular migration of acylic-groups and a certain sensitivity towards hydrolysis. Also the presence of a free carboxyl group within the diacetylated tartaric acid moiety allows all its specific reactions.

4.2.1 Appearance

DATEM come as sticky viscous liquids with a consistency like fats or yellow waxes, or in flake and powder form.

4.2.2 Thermostability

Due to thermal influences, an intra- and intermolecular migration of acylic-groups may occur. The free carboxyl- and hydroxyl groups may also be esterified. Heating DATEM for a maximum period of 7 h up to 180°C may result in further esterification. According to Lauridsen and Cristensen [3], this results in a dramatic decrease in the concentration of free carboxyl groups (i.e. decrease in acid value) in combination with a significant increase in viscosity and molecular weight. In parallel with this, the dielectric constant also decreases. This is an indication of decreasing molecular polarity. This will result in a loss of hydrophobicity and transformation of an oil-in-water emulsifier into a water-in-oil type [4].

One of the most important application effects of DATEM (the stabilisation of increase in volume in yeast-raised baked goods made from wheat) is linked directly to this decrease in acid value. During tempering for at least 4 h between 90 and 120°C, the stabilisation effect decreases by as much as 20% compared to non-tempered material.

It is important to note that this effect will occur before any change in the chemical parameters of the product (acid value and saponification value) can be detected [5].

4.2.3 Hydrolysis

Acids, alkaline solutions and lipolytic enzymes are able to cleave DATEM. Hydrolysis with acids results in free fatty acids, tartaric acid, acetic acid and glycerol. Hydrolysis with alkaline solutions will form the alkali salts of these acids and glycerol. Enzymatic hydrolysis first yields diacetylated tartaric acid, and then, respectively, monoacetylated tartaric acid and the mono- and diglycerides of fatty acids. They are hydrolysed further into glycerol and fatty acids [6].

All these reactions are rapid if the concentration of the substances with hydrolytic activity is high enough. Non-catalysed hydrolysis depends on temperature and time, and is rather slow.

Adams and Schuster demonstrated that DATEM of mono- and diglycerides as well as DATEM of pure monoglycerides show almost the same hydrolytic

behaviour. Both systems are highly sensitive towards hydrolysis, especially when water is present and temperatures are elevated [5].

4.2.4 Storage

During storage there is always a slight hydrolysis in moist air (liberating acetic acid) even at lower temperatures.

4.3 Physical and chemical properties of DATEM

The polarity of DATEM molecules influences almost all of these properties.

4.3.1 Physical properties

The near structural relation to fat influences the rheological and physical properties, nevertheless the diacetylated tartaric acid creates new influences. The consistency varies between liquid and wax-like solid. This depends on the molecule's fatty acid moieties within the mono- and diglyceride part, and on the amount of esterified diacetylated tartaric acid. The melting point of DATEM decreases with an increasing amount of diacetylated tartaric acid, with a corresponding increase in plasticity. DATEM have lower melting points than the mono- and diglycerides they are derived from.

Below their melting points DATEM will become plastic and ground DATEM will agglomerate at temperatures far below their melting point.

The colour of DATEM also depends on the fatty acid moieties. It may vary from brown to yellowish and from ivory to white. Another characteristic is the taste and odour of free acetic acid. It is possible to do a neutralisation of this free acetic acid to get rid of this taste. The resulting alkaline salts taste slightly bitter or have a fat-like taste.

4.3.2 Solubility

The product is dispersible in both hot and cold water, and offers certain solubility in warm fats, oils and in some alcohols, such as methanol or ethanol, and also in acetone.

4.3.3 Mesomorphic phase behaviour

The mesomorphic phase behaviour of DATEM depends heavily on its pH value [7]. Non-neutralised DATEM contain a free carboxylic group. In an aqueous phase, they form a dispersion with a pH value of 2–3. Their swelling ability within this pH range is rather limited and increasing the pH value (partial

neutralisation) to 4–5 enables them to swell totally. DATEM based on saturated fatty acid-monoglycerides form a very temperature-sensitive mesomorphic and lamellar phase, which is stable between 20 and 80°C. The dispersion formed from DATEM with a high surplus of water is very similar to the type formed from saturated monoglycerides. Once swollen with water, DATEM remain in this liquid/crystalline state, even if they are cooled down to the temperature at which lamellar phases are formed normally.

The carbohydrate chains of the fatty acids within the DATEM show only a limited tendency to form any gel structures [5].

4.3.4 Surface-active properties

DATEM are ionic oil-in-water emulsifiers. During the reaction of mono- and diglycerides with diacetylated tartaric acid anhydride, the free hydroxyl groups of the mono- and diglycerides, which are responsible for their hydrophilic properties, are esterified. At the same time, a huge hydrophilic and polar moiety with a free carboxylic group is transferred into the molecule via the esterified diacetylated tartaric acid. Due to the partial esterification of hydroxyl groups of the mono- and diglycerides with diacetylated tartaric acid anhydride, free hydroxyl groups, together with the diacetylated tartaric acid moiety, form the hydrophilic part into the DATEM molecules. DATEM are more hydrophilic compared to the mono- and diglycerides that they are made of. The hydrophilic part within these molecules is therefore bigger and hence they show a higher HLB value. The strong reduction of the surface tension into the soybean oil/water system, even in very low concentrations, reflects these facts [8].

Specification of DATEM and some important parameters of analysis are given in Table 4.1.

4.3.5 Safety

Mono- and diacetyl tartaric acid esters of mono- and diglycerides of edible fatty acids have been evaluated by the Joint FAO/WHO Expert Committee on Food Additives (4) and the Scientific Committee for Food (5).

Evaluation status:

Acceptable daily intake (ADI), actually = 0–50 mg/kg bw evaluation by JECFA
Acceptable daily intake (ADI), actually = 0–25 mg/kg bw (temp.) evaluation by SCF

(4) WHO Food Additive Series No. 5, 1974, page 222–224. Toxicological evaluation of some food additives including anticaking agents, antimicrobials, antioxidants, emulsifiers and thickening agents.
(5) Minutes of the 107th Meeting of the Scientific Committee for Food, 1997.

Table 4.1 Specification of DATEM and important parameters of analysis

	EU[a] (1)	FAO/WHO (2)	FCC (3)	Recommended method of analysis[b]
Total tartaric acid	10–40%	10–40%	17.0–20.0 g/100 g	(2)
Total acetic acid	8–32%	8–32%	14.0–17.0 g/100 g	(2)
Total glycerol	11–28%	11–28%	min. 12%	(2)
Free glycerol	max. 2%	max. 2%	–	A16(i)
Free fatty acids (as oleic acid)	max. 3%	max. 3%	–	no official method
Total fatty acids	–	–	min. 56.0 g/100 g	A21(ii)
Sulphated ash	max. 0.5%	max. 0.5%	–	A6(iii)
Acid value	–	–	62–76 mg KOH/g fat	A18(iv)
Residue on ignition	–	–	max. 0.01%	A6(v)
Saponification value	–	–	380–425 mg KOH/g fat	A19(vi)
Arsenic	max. 3 mg/kg	–	–	A3(vii)
Heavy metals (as Pb)	max. 10 mg/kg	–	max. 10 mg/kg	A1(viii)
Lead	max. 5 mg/kg	max. 2 mg/kg	–	A2(ix)
Mercury	max. 1 mg/kg	–	–	A5(x)
Cadmium	max. 1 mg/kg	–	–	A4(xi)

[a] Purity criteria apply to the additive free of sodium, potassium and calcium salts of fatty acids, however these substances may be present up to a max. level of 6% (expressed as sodium oleate).
[b] do not necessarily reflect the official methods used for the stated specifications.

(i) A16: Free Glycerol, FAO Food and Nutrition Paper 5, Rev. 2, 195.
(ii) A21: Total fatty acids, DGF Einheitsmethoden C-III 2 (97).
(iii) A6: Sulphated ash / Residue on ignition, FAO Food and Nutrition Paper 5, Rev. 2, 77.
(iv) A18: Acid Value, FAO Food and Nutrition Paper 5, Rev. 2, 189.
(v) A6: Sulphated ash / residue on ignition, FAO Food and Nutrition Paper 5, Rev. 2, 53.
(vi) A19: Saponification Value, FAO Food and Nutrition Paper 5, Rev. 2, 203.
(vii) A3: Limit test for Arsenic, FAO Food and Nutrition Paper 5, Rev. 2, 69.
(viii) A1: Limit test for Heavy metals, FAO Food and Nutrition Paper 5, Rev. 2, 73.
(ix) A2: Limit test for Lead, FAO Food and Nutrition Paper 5, Rev. 2, 76.
(x) A5: Limit test for Mercury, FAO Food and Nutrition Paper 5, Rev. 2, 77.
(xi) A4: Limit test for Cadmium, FAO Food and Nutrition Paper 5, Rev. 2, 59.

References:
(1) Commission Directive 98/86/EC of 11 November 1998 amending Commission Directive 96/77/EC laying down specific purity criteria on food additives other than colours and sweeteners.
(2) Compendium for Food Additive Specifications. FAO Food and Nutrition Paper 52, Addendum 6, 1998, page 49–52.
(3) *Food Chemical Codex*, 4th edn, 1996, pp. 119–120.

4.4 Typical applications of DATEM in food

Within the EU, mono- and diacetyl tartaric acid esters of mono- and diglycerides are generally permitted for use in foodstuffs (6). Mono- and diacetyl tartaric acid esters of mono- and diglycerides are used as dough conditioners for all

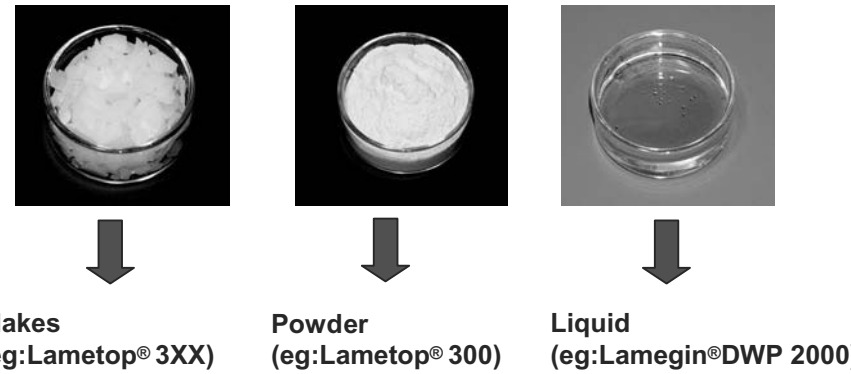


Fig. 4.4 Physical forms of DATEM.

baked products, particularly yeast-leavened products, white bread, rolls rusks, and in flour mixes for convenience food.

Other applications include:

- Beverage whiteners
- Cream analogues
- Chewing gum
- Meat- and poultry products
- Emulsified sauces
- Canned coffee or tea
- Carriers of solvents for colours and food antioxidants

(6) European Parliament and Council Directive No 95/2EC 0f 20th February, 1995 on food additives other than colours and sweeteners. Directive 98/72/EC of the European Parliament and Council Directive of 15 October, 1998, amending Directive 95/2/EC on food additives other than colours and sweeteners.

4.5 DATEM in the baking process

The use of DATEM as food ingredients for baked goods is not limited to their pure action as emulsifiers. They also influence the quality and the properties of baked goods during manufacturing, storage and consumption.

These effects are due to their influence on the distribution of different phases in food, and results in an improvement in consistency, viscosity, texture and the taste of different baked goods.

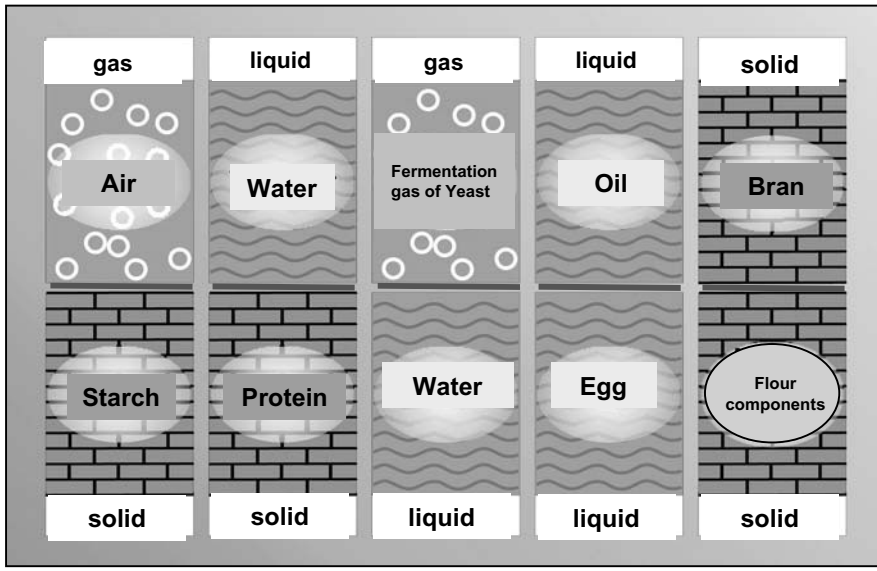


Fig. 4.5 Different phases in dough making.

Here we have to differentiate between surface activity (classic emulsifier action) and any specific action for the special type of food. All the resulting effects correspond directly to the amount of emulsifier being adsorbed at the different surface barriers, their form, thickness, rheology and the interaction of the emulsifier with the different food components. The different possible phases in dough are shown in Fig. 4.5.

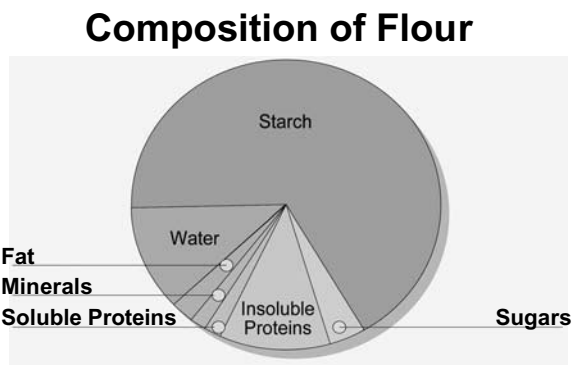
The following sections will concentrate on the action of DATEM within the processing of baked goods based on wheat flour. These baked goods will be called bread, including all the different forms of this 'food type'.

4.5.1 Bread making

The first step of bread making is the preparation of dough. Dough consists of flour, water, yeast, salt and some other ingredients. The main part within this recipe is covered by flour. Therefore, we should first discuss the composition of flour.

4.5.2 Flour

The average composition of flour according to Auermann and Kosmina [9,10] is shown in Fig. 4.6. The main ingredient of flour is starch, therefore, we should have a closer look at starch.



73.5% Carbohydrates	71.0% Starch 2.4% Sugars 0.1% Cellulose
11.0% Proteins	10.0% Gluten proteins 1.0% Water soluble proteins
14.0% Water	
1.0% Fat	
0.5% Minerals	

Fig. 4.6 Average composition of wheat flour [9, 10].

4.5.3 Interaction of DATEM with starch

Starch is one of the major components of grain kernels. In wheat kernels, it makes up to 70% of the dry weight. This depends on the type of wheat and the cultivation conditions, hence the quality of the starch influences both the preparation of flour and the processing of baked goods.

Let us concentrate on the various interactions between starch and DATEM. Starch is present in cereal grains as granules imbedded in a protein matrix. These are solid particles with a high degree of organisation and with defined physical and chemical properties. They are formed within plant cells and organised into molecules of amylose and amylopectin. The chemical structures of amylose and amylopectin are shown in Fig. 4.7.

These are highly polymeric compounds consisting of α-D-glucose monomers. Wheat starch consists of 17–29% of amylose [11]. Amylose is in general an unbranched molecule made of glucose units connected by α-1,4-glucoside linkages, but it normally contains small amounts of branched moieties [12].

It is water-dispersible, forms a deep blue inclusion complex with iodine, and is cleaved by the combined action of α- and β-amylase into maltose and some glucose monomers.

Amylopectin is a branched molecule that consists of polyglucose chains, joined by α-1,4-glucoside linkages and branched with α-1,6-glucoside linkages.

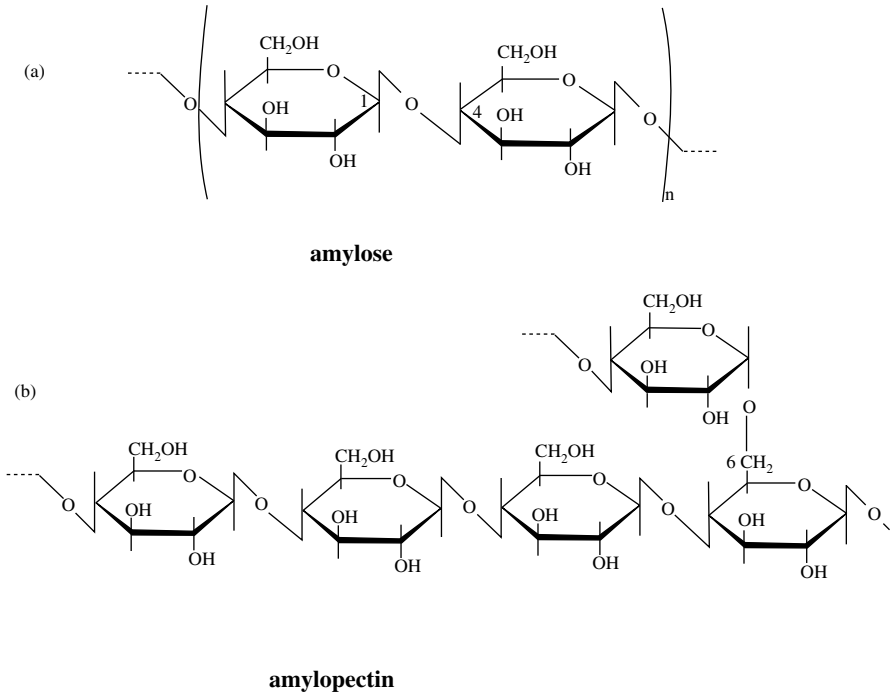


Fig. 4.7 Chemical structure of amylose and amylopectin.

Amylopectin is insoluble in water, but capable of swelling. It reacts with iodine to form a violet to red-violet inclusion complex and is cleaved by the combination of α- and β-amylase, into maltose, isomaltose, and glucose.

The starch granule also contains mineral substances, protein and lipids. The lipids are bound to the highly polymeric carbohydrates and form inclusion compounds with amylose [13].

The structural and the functional properties of starch are influenced via the concentration of linear and branched macromolecules and their degree of polymerisation and association [14]. The most important functional property of starch is its temperature-dependent behaviour in the presence of water. When starch is added to water, the granules absorb some water and swell slightly. This process is reversible at room temperature. The birefringence index and the crystalline state of the granule are unchanged. At 50°C, the internal structure of the wheat starch granule is evidently altered somewhat because the point of gelatinisation shifts to a higher, but more sharply defined temperature [15]. The temperature necessary for gelatinisation depends on the starch type and the properties of the individual granule.

According to Rotsch [16–18] starch is responsible for the principal properties of dough and bread. He based this view on the fact that he was able to

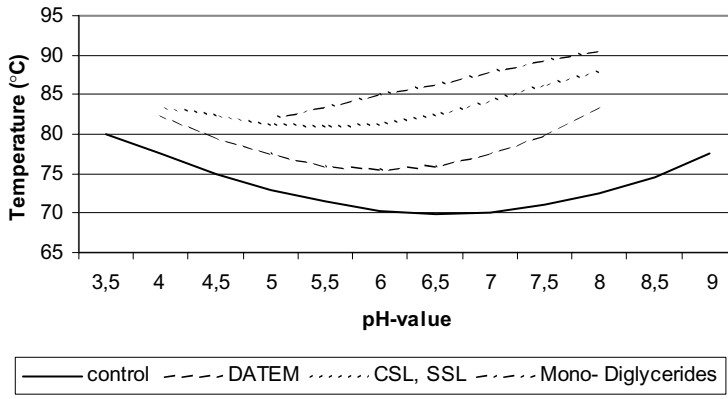


Fig. 4.8 Gelatinisation temperature of wheat-based starch in distilled water depending on pH value.

prepare bread without gluten but not without starch. This was supported by Jongh [19] who pointed out the importance of emulsifiers, in this case mono- and diglycerides, for bread without gluten.

The interaction of emulsifiers with starch is very important and this has been thoroughly investigated and described. Via the molecular structure of starch, an interaction with lipids, and especially emulsifiers, is possible. Here some of the most essential properties for the baking process of starch are influenced.

A certain reduction of water absorption and swelling is observed and an increase of the gelatinisation temperature also occurred [20–25]. Another important observation is the reduction of the retrogradation of starch [26]. The different emulsifiers available nowadays influence the gelatinisation temperatures of different starches in variable ways [25].

DATEM, for example, increase the gelatinisation temperature and viscosity maximum of wheat starch. But all these parameters are influenced via ion concentration as well. This effect is shown in Figs 4.8 and 4.9.

The absorption of water by starch is reduced by these emulsifiers during heating [27], and their efficacy is not influenced by the presence of fat [28–31]. One of the reasons for this alteration of the properties of starch is due to a formation of complexes between starch and/or lipids and emulsifiers. These complexes may exist on the surface of the starch, or as inclusion compounds between starch and emulsifiers. The formation of such complexes depends on the temperature, the concentration of the emulsifier and its physical structure [32].

The kind of molecules suitable to be included into starch depends on geometric parameters. The different capability of emulsifiers to form complexes can be expressed via the Amylose-Complexing-Index (ACI) defined by Krog [32].

The ACI corresponds to the different iodine concentrations found in starch, before and after exposure to emulsifiers. DATEM (e.g. Lamegin® DWP) show ACI values of 49.

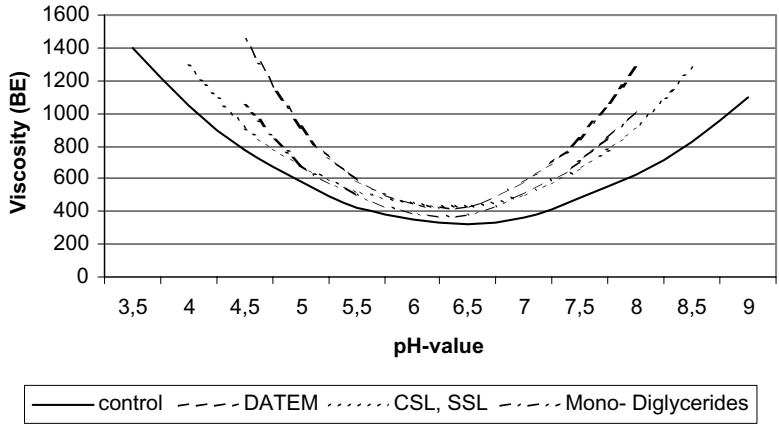


Fig. 4.9 Maximum viscosity of wheat-based starch in distilled water depending on pH-value.

The capability of emulsifiers for starch complexing depends on the chain length of the fatty acid moiety in the molecule. Saturated C16- and C18-chains are preferred for complex forming [31,33].

A possible explanation of the mechanism of complexing within the starch helix is as follows:

The hollow space in starch helix is rather disadvantageous to its energetic potential, but a certain stability results via the inclusion of suitable molecules. The lipophilic interior of the starch helix is best suited to the inclusion of lipophilic fatty acid moieties. The result will be a stable amylose–emulsifier complex. A dramatic increase in stability of such complexes against enzymatic degradation compared with starch seems to prove this idea [27,34,35]. Figure 4.10 shows a model for the amylose–emulsifier complex.

The hydrocarbon chain of the emulsifier seems to be oriented as in the crystalline phase. It is enclosed by three spirals of the starch helix and the polar group of the emulsifier is not included [33,36]. Some authors also insist on the observation that starch, in aqueous phase, is a statistical clue and the helix is formed as soon as molecules with a potential of forming complexes are present [37,38]. Essentially, amylopectin does not form complexes as easily as amylose due to a reduced formation of helices. Any interaction of amylopectin with emulsifiers should occur on the starch surface via hydrogen bridges [39].

4.5.4 Interaction of DATEM with flour proteins

All the results of research concerning interaction of lipids with flour proteins can be extrapolated to emulsifiers. In principle, gluten is the product of the reaction of flour lipids and proteins. Here the polar flour lipids act similar to emulsifiers.

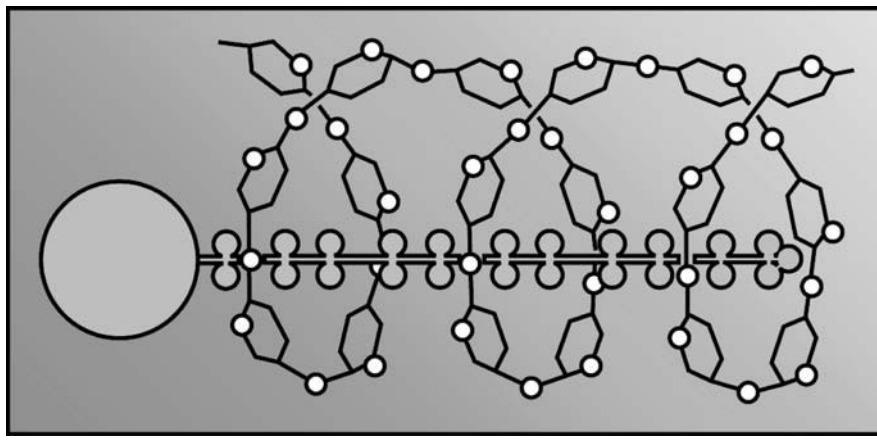


Fig. 4.10 Complex formation between starch and emulsifiers.

Kneading of the dough during the manufacturing of bread results in a transfer of flour lipids into the gluten phase [40]. The better the kneading and mixing of the dough, the more effective the binding of polar lipids to the glutenine fraction [41]. After baking, DATEM can only be extracted from bread with very polar solvents. This reflects a strong interaction with the flour proteins [42]. The reaction of fatty acid esters with proteins at isoelectric point is strong like the reaction with free fatty acids. This means that their carboxylic group is not the active principle, because mainly hydrophobic bonds will result. All occurring interactions become stronger with the higher intake of mechanical energy into the system. Proteins are protected against denaturisation via the interaction with lipids [43]. One possible model is shown in Fig. 4.11.

Ionic emulsifiers, such as DATEM, offer a huge ability towards the formation of hydrogen bridges with amidic groups of the gluten-proteins. Orientating the hydrophobic emulsifier moieties to the non-polar side chains of the proteins (i.e. ethylene chains) these emulsifiers can form an intermolecular matrix via hydrogen bridges as well [44].

The following are some ideas concerning the nature of such lipoprotein structures. According to research results from X-rays, electron- and optical microscopy, there are existing structural relationships between proteins, lipids and starch in wheat flour [45]. These results indicate a lipid double layer covering the protein molecules and an adhering protein layer, which includes starch particles.

Some other trials using electrophoresis experiments prove a certain complex formation between emulsifiers and gluten–protein fractions. These complexes are stabilised by hydrogen bridges and hydrophobic bonds and are shown schematically in Fig. 4.12 [46].

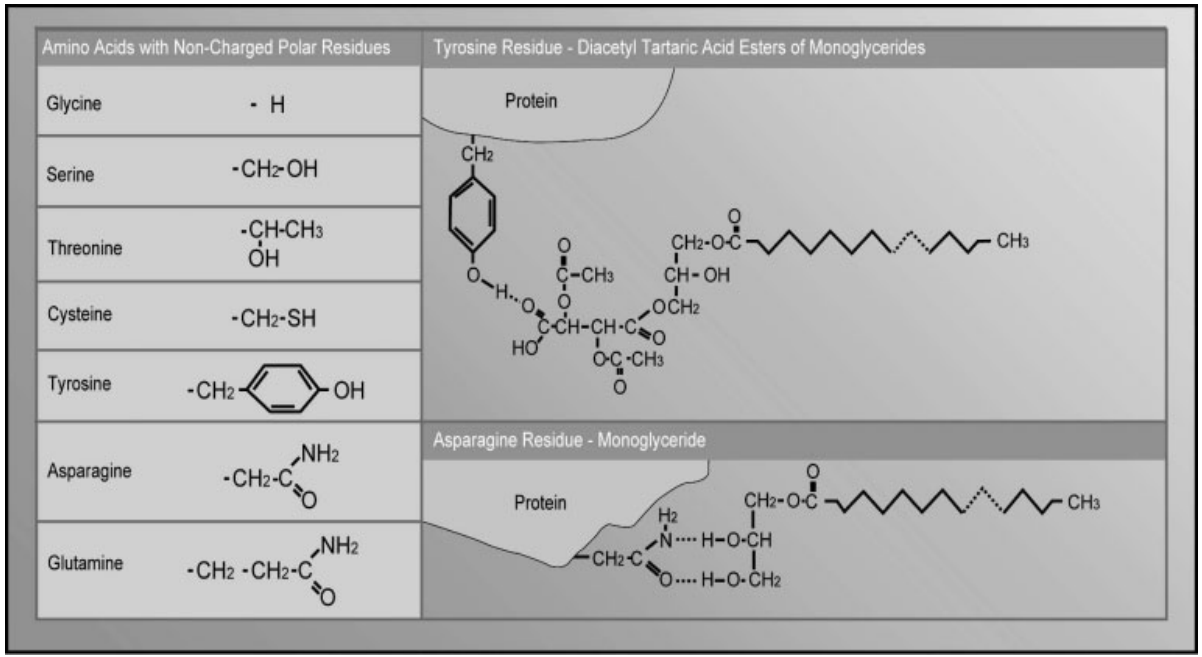


Fig. 4.11 Protein–emulsifier interaction in dough resulting in improved mixing tolerance, fermentation tolerance and volume.

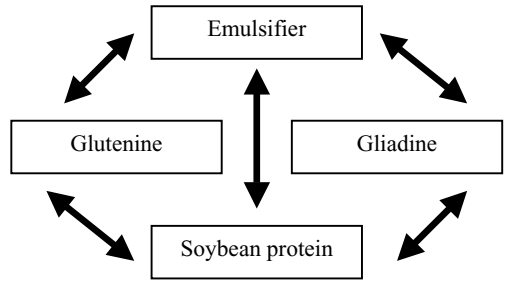


Fig. 4.12 Lipid–protein complexation (i.e. in gluten).

4.5.5 Interaction of DATEM with flour lipids

Emulsifiers are in competition with the natural flour lipids for the reactive groups in the dough [41]. This is proved by the observation of Jacobsberg *et al.* that the kneading of dough with DATEM within a nitrogen atmosphere significantly reduces the binding quality of lipids [47].

4.5.6 Use and action of DATEM during manufacturing and storage of baked goods

Emulsifiers and emulsifier containing preparations are established ingredients of any recipe for the manufacturing of baked goods. This is due to the improvements in processing and quality resulting from their use.

The emulsifiers can be added in liquid, paste or solid form directly into the dough. Other alternatives are to do this indirectly via an oily solution (shortening) or within an aqueous system (dispersed, jellified or as a paste) or bound to a carrier system within a compound. Here the emulsifier acts as a dough conditioner and is responsible for various effects. The most important ones, in combination with DATEM, will be:

- stabilisation of a soft crumb (delaying of the starch retrogradation) (Section 4.5.3) [48–50].
- dough performance during manufacturing (tolerance towards raw material quality, mechanical resistance, sticking to manufacturing equipment, mixing and fermentation tolerance)
- volume increase after baking (this will be the most objective parameter for the measurement of emulsifier efficacy) [50].

A study evaluating these results with dough conditioners for bread and fine baked goods, based on the use of lecithin and DATEM, confirmed the above-mentioned effects [51, 52].

Monoglycerides are very effective emulsifiers in bread manufacturing process. Using these emulsifiers the swelling of starch and release of water-soluble starch components during the baking process can be reduced. This will result in a softer bread crumb. Strandine explains this according to microscopic research that the formation of small particles of monoglyceride and shortening takes place during the kneading of the dough. So, these particles cover the surface of the starch grains and thus reduce the intake of water [53].

DATEM have been used in the US baking industry since 1948. They are often used in combination with monoglycerides which enhance their activity during bread manufacturing. In a synergistic way they offer, by their stronger hydrophility, an increased emulsification activity and a more homogenous distribution of the shortenings within the dough [54]. The efficacy of DATEM is extremely dependent on the quality of flour, resulting in different increases of volume of the resulting baked goods. This may be explained by an increased interaction of specific flour-lipids and extra-added lipids (baking fats) brought about by the DATEM molecules. So the retention of gas produced during the baking process is increased significantly [47, 55].

In comparison with other common food emulsifiers, DATEM offer very good dough conditioning properties. DATEM may partially substitute the use of shortenings and improve the dough consistency [56]. Storage stability of emulsifiers in flour blends is rather limited and depends largely on the water content of the flour. To guarantee proper efficacy after a storage period of maximum 6 months, the water content has to be lower than 5%. These results can be explained by the sensitivity of almost all esterified lipid derivatives towards hydrolysis [5].

The results described above are valid for the use of DATEM with wheat flour. Often rye flour in combination with wheat flour is used for bread making. Baking trials with rye-based bread have shown a certain efficacy of some emulsifiers (including DATEM) in terms of volume increase, which corresponds to their application concentration and the quality of the rye flour used [57].

Since the beginning of the last century, the idea of enriching wheat protein based bread with other high concentrated protein sources has been given importance [58]. The reason for this is rather simple, because world protein supply depends widely on cereal-based food. The most commonly used cereal here is wheat, which is rather low in total protein and especially low in lysine. Any addition of soybean flour, milk-based proteins, legume-derived proteins or other flours based on oilseeds would be the first choice to overcome this dilemma. It is a pity, but it has been proved that all these products show a negative influence on both dough properties and baking behaviour. This can be partially compensated by the use of emulsifiers. Here sodium-stearoyl-lactylate showed best results. The use of DATEM, depending on the baking process and the use of baking pans, seems to have limited influence on these parameters [5].

During storage of bread staling is the most important fact for the consumer because it influences the firmness of the crumb. Staling is not influenced by one

parameter, but reflects a number of different and parallel occurring processes. A few of these are:

- change in aroma and taste
- increase in crumb firmness
- darkening of the crumb
- getting more crumby
- increased crystallisation of starch in the crumb
- decreased absorption capacity of the crumb
- reduced soluble starch content

The most important parameter for all these changes is the retrogradation of the starch [39, 59]. The gluten fraction of bread seems to have some influence on staling as well. The speed of the 'redenaturation' of the gluten proteins is much slower compared to the speed of the retrogradation of starch [60]. Some authors consider the influence of the changes in gluten fraction as very important in the staling process [61]. Some other parameters, such as pentosans, lipids and water seem to have some influence as well [62–67].

One possible way to prolong the shelf life of baked goods is the use of emulsifiers. Due to their chemical structure they can interact with all substances discussed above and have an influence on the staling process [68]. Again the effects expected from the use of DATEM are rather limited. Nevertheless, a certain influence on volume and softness of the crumb are reported [69]. The most effective class of emulsifiers within this context seem to be monoglycerides [70].

4.6 Action of emulsifiers in fine baked goods

The use of emulsifiers or combinations of different emulsifiers in fine baked goods offer many advantages during processing and storage. The most important ones are:

1. simplification of the dough and/or baking mass preparation
2. reduction of baking fat
3. production of baking fat with an improved fat crystal structure
4. increase in the dough's fermentation tolerance
5. improved dough rheology
6. increase in the air intake into the baking mass during aeration
7. more reliable use of dried eggs in cake mix
8. reduction of water loss during baking
9. increase in the volume of the baked goods
10. improvement in constancy of shape and form of the baked goods

11. improvement in crumb texture
12. improvement in crumb softness
13. improvement in chewing and taste properties
14. delay in staling

DATEM are responsible for some of these effects. Their most important applications are discussed in the following sections.

4.6.1 DATEM in fine baked goods

Fine baked goods, in principle, are made with the similar flour qualities as bread. The main difference in their recipes is often a huge quantity of other ingredients. This fact may influence the efficacy of DATEM, or create some special application modalities. We will have a closer look at this issue.

Fruit bread. Here the use of DATEM in a concentration of maximum 0.5% on flour weight facilitates dough processing, improves the sensory properties, increases the volume and prolongs the freshness of the product [5].

Cookies and freshness. By the use of maximum 0.75% on flour weight of DATEM, the shelf life of such products can be prolonged [5].

Marie biscuits. The amount of fat in the recipe can be reduced by 20% with the use of 0.75% on flour weight of DATEM [71].

Short dough biscuits. A denser dough is obtained when emulsifiers are used. With the reduction of fat in the recipe such biscuits get harder. The use of DATEM reduces this effect and offers a better texture [72].

Batters with high fat content. The specific weight of the dough mass is not significantly influenced by the use of DATEM. In this case, use of ACETEM, LACTEM and polyglycerols is much more effective [5]. Figure 4.13 clearly illustrates this effect.

Various cakes. Here the use of emulsifiers shows some influence on the loss of water during the baking process. This process is due to the starch molecules sticking to each other. The water loss rate is normally reduced to 12–13 minutes. The presence of monoglyceride, diglyceride or DATEM significantly delays this region of stability, which corresponds to the sticking of the starch molecules. This has been shown using amylographic measurements of the sticking temperature and maximum viscosity. The influence of mono- and diglycerides is stronger in this case compared to the use of DATEM [73, 74].

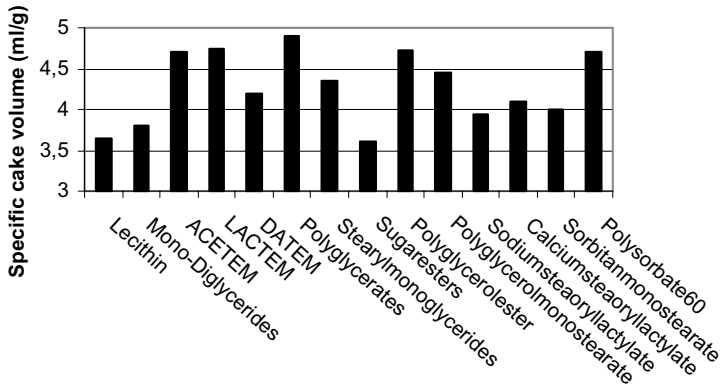


Fig. 4.13 Specific volume of batter cakes using different emulsifiers [82].

Figure 4.14 provides a short summary of all these effects that can be expected by the application of emulsifiers within or during the baking processes, starting from the mixing of dough through to the storage of the baked goods.

4.7 Summary and conclusions

The application of DATEM has a lot of advantages as a bread improving ingredient. The economics of its use is considered even more important than its organoleptic effect (softening of the bread crumb).

Since 1948 DATEM have been used in multiple applications within the US bakery industry [75]. Using some statistics from the US bread market may illustrate this fact. Approximately 8% of the daily bread production cannot be sold due to staling and is returned to the bakers. In 1969 this amounted to more than 50 million kg of bread, or 2600 million kg of wheat. This volume would be sufficient to feed more than 100 million people. Not included within these numbers is the microbiological deterioration of bread and bread products [76–81].

In addition to all the other bread improvers DATEM are one important part of this ingredient puzzle and guarantee proper bread manufacturing and consumer-orientated appearance.

Since the 1940s the use of DATEM has developed and changed dramatically. Details are shown in Table 4.2. Finally the effect of DATEM in rolls and on the stabilisation of high volume bread is illustrated in Figs 4.15 and 4.16.

The improved use of DATEM will continue in the future and we are keen to observe new interactions about this emulsifier within the ingredients portfolio to improve the properties of bread for better production of this essential food.

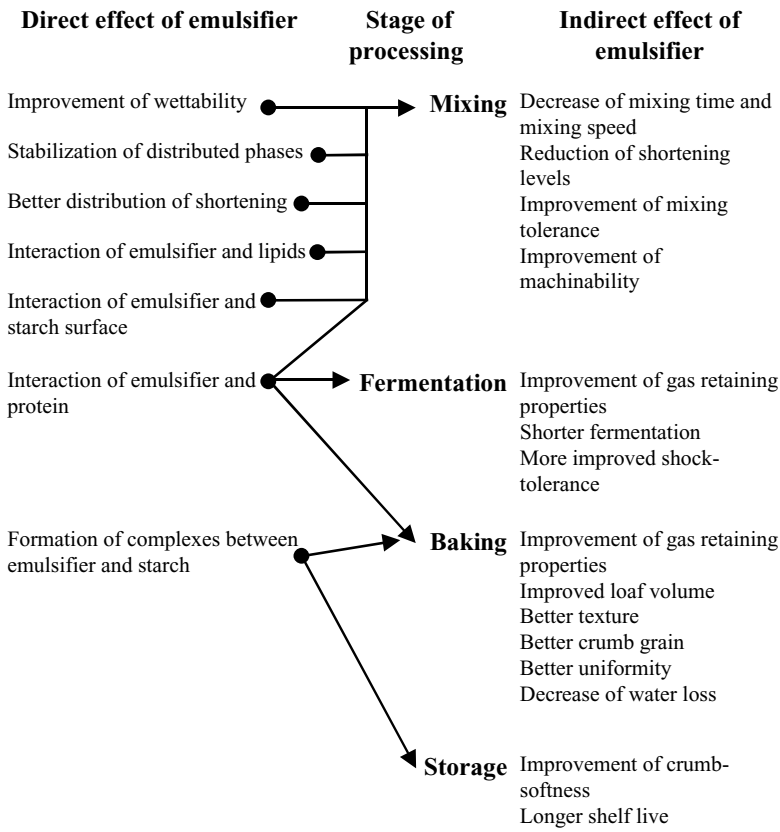


Fig. 4.14 Some effects resulting from the application of emulsifiers during bread processing (of which DATEM is responsible for some of the more important ones).

Table 4.2 Historic development of the application of bread improving ingredients

History	Fat
	Sugar
	Eggs (Lecithin!)
	Milk
	Malt
	Gypsum ($CaSO_4$)
	Sour dough
Early this century	Bromates
1940	Ascorbic acid, calcium peroxide, emulsifiers (mono- and diglycerides, lecithin)
1960	Azodicarbonamide (ADA), cystein, emuslifiers (DATEM, sodium stearoyl lactylate)
1970	Enzymes, emulsifiers

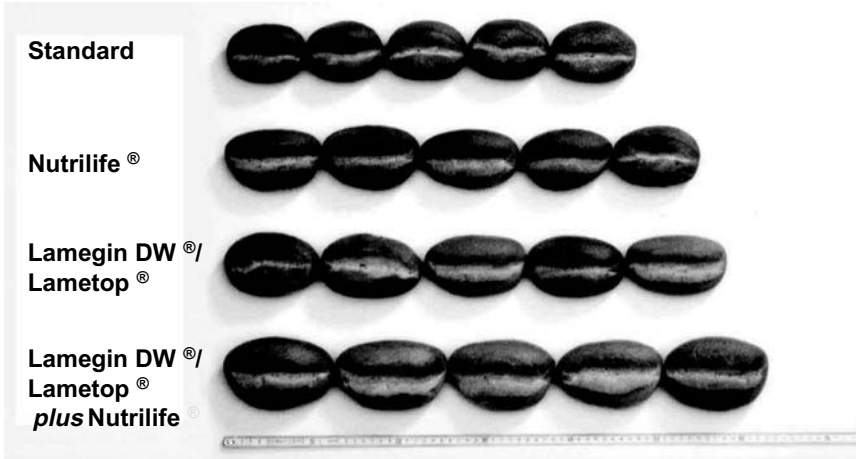


Fig. 4.15 Effects of emulsifiers (i.e. DATEM products out of the Cognis/Grünau Lamegin® and Lametop® ranges) and synergistic components, e.g. enzymes (i.e. products out of the Nutrilife® range).

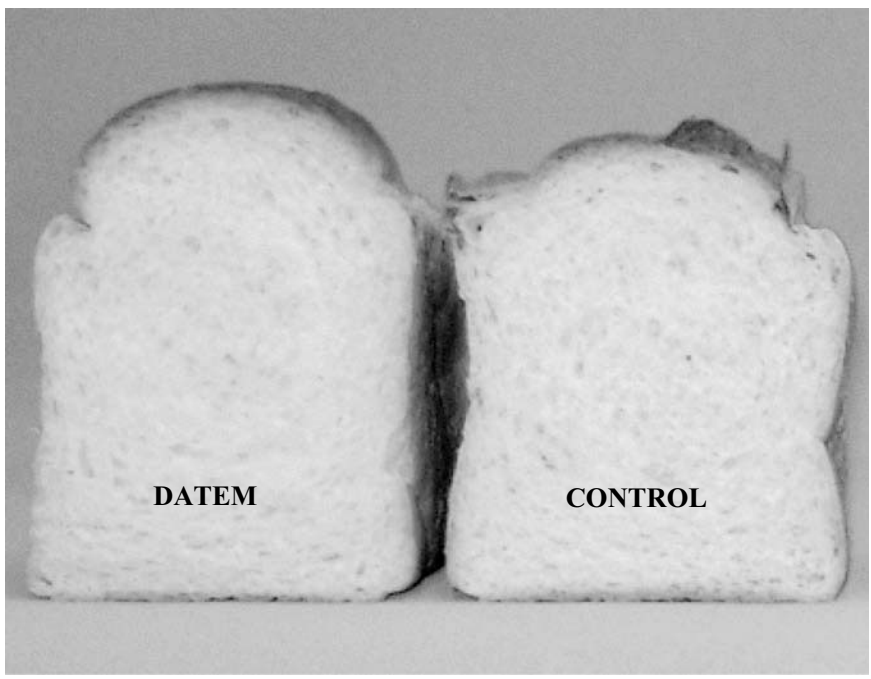


Fig. 4.16 Effect of DATEM on high specific volume tin bread.

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5 Polyglycerol esters

Viggo Norn

5.1 Introduction

Polyglycerol esters are a class of food emulsifiers used extensively within the food industry on account of their amphiphilic nature in various types of food. The esters (fatty acid esters of polyglycerol) exhibit characteristic interfacial properties due to the coexistence of hydrophilic and lipophilic moieties within the same molecule. The polyglycerol, which makes the hydrophilic moiety of the emulsifier, is a substance consisting of a series of oligomeric hydroxyethers of glycerol. The ethers are formed from an intermolecular condensation of glycerol – a reaction performed at high temperature, resulting in the formation of the alkoxy bonds between the glycerol moieties. The corresponding polyglycerol esters are produced from polyglycerol and fatty acids in a direct esterification of (or alternatively an inter-esterification between) triglycerides and polyglycerol.

The emulsifiers are of the non-ionic type and exhibit a broad range of polarity or hydrophilic-lipophilic balance (HLB) values (see Appendix 1), ranging from 6 to 11 [1], compared with many other food emulsifiers. The range of the polarity is due to several parameters derived from variations in the degree of the glycerol polymerization, types of esterified fatty acids or the degree of esterification (ranging from monoesters to polyesters). The diversity is reflected in the use of the emulsifiers, which are finding application in many different foods and technical process.

5.2 Legislation

The broad range of HLB values of the polyglycerol esters makes them a versatile emulsifier for food applications – national and international bodies have evaluated the polyglycerol ester as a food additive and have approved the emulsifier under legal reference numbers [2]. Numbers related to the polyglycerol esters are shown in Table 5.1, together with chemical abstract number (note that CAS has several entries for the polyglycerol and esters). Unesterified polyglycerol as a substance is not considered as a food additive.

Within the legislation of food additives, the polyglycerol ester is described, together with analytical parameters and other specifications. For example, within the EU the degree of polymerization is restricted to certain limits in relation to

Table 5.1 Reference numbers for polyglycerol and polyglycerolesters

	Chemical abstract	Einecs	EU	CFR
Polyglycerol	25618 55 7	No Einecs number	No number	No number
Polyglycerolester	9009 32 9	No Einecs number	E 475	172.854

the amount of the higher oligomers, and the specification will describe the degree of estrification, free fatty acid etc. The legislation often includes permission for food usage in the form of food categories and the maximum levels of addition of the emulsifier.

5.3 Synthesis of polyglycerol

Polyglycerols are substances consisting of oligomer ethers of glycerol. Depending on the degree of polymerization, the polyglycerols appear as more or less highly viscous, colourless or as yellow liquids. Polyglycerols are usually prepared from an alkaline polymerization of glycerol at elevated temperatures. Many patents have been published regarding this, see, for example, Christiansen and Norn [3]. The polymerization will yield a distribution of different oligomers [4] of which the major part is of linear structure, i.e. the form of polyglycerol which most authors refer to (see, e.g. McIntyre [5]). In addition to the linear configuration, a significant part of the polyglycerol is of the branched types, i.e. origin from 1,2- and 2,2-*O*-ether bonds between the glycerols. The kinetics of the reaction has been studied in more detail, and it has been proved [6] that the alkaline reaction of glycerol is of a consecutive character. An alternative to a homogeneous alkaline catalyst is the use of solid catalysts, for example, modified zeolites [7]. The solid zeolites are found to be more selective, but also show slower reaction rates. An acid catalyst such as sulphuric acid can be used, but it is difficult to control and gives in general a dark coloured polyglycerol.

Other possible processes for production of polyglycerol use reactive petrochemical substances such as epichlorinehydrine (1-chlor-2, 3-dihydroxypropane), which is allowed to react with glycerol in an etherification process [8]. This is a disadvantageous process as epichlorhydrine is a hazardous material and is difficult to handle. In addition, the purification of the polyglycerol adds further complications. Glycidol is also used for the production of polyglycerol [9]. The oxirane group easily reacts with glycerol or epichlorhydrine depending on the conditions of the reaction and the type of polyglycerol required. In addition to the toxic problems, these processes also have the disadvantage of using some of the chemicals that make the process non-competitive in relation to a glycerol based process (see Fig. 5.1).

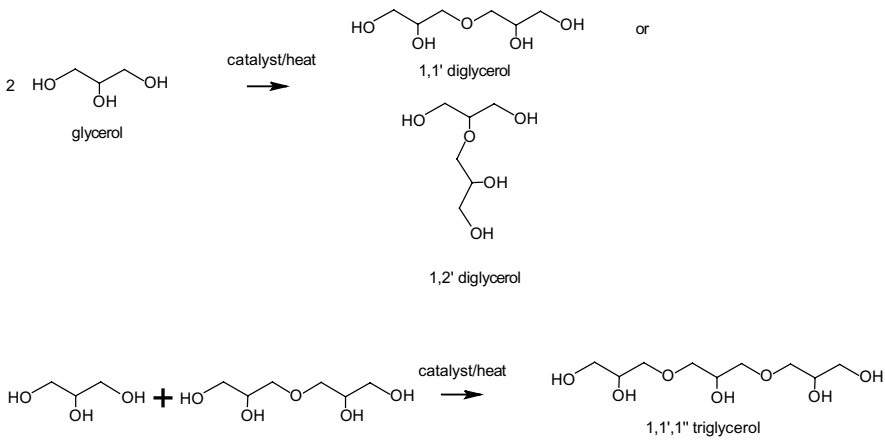

Fig. 5.1 Formation of polyglycerol.

Polyglycerols are a mixture of different oligomers and normally they exhibit a distribution between the individual structures [10] as with other polymers. This distribution can be analysed using GLC or HPLC techniques. Commercial polyglycerol esters are often marketed as esters of tetraglycerol, hexaglycerol or even higher decaglycerol as the hydrophilic backbone. Analysis of samples of commercial polyglycerol esters indicate the degree of glycerol polymerization being concentrated at the triglycerol and tetramer level, even for the esters claimed as decaglycerols. Figure 5.2 shows the formation of the individual polymers as the polymerization of glycerol progresses [3]. From the figure it can be seen that the glycerol content in the reaction mixture decreases as the formation of dimer increases. The diglycerol reaches a maximum and is then consumed, while the concentration of triglycerol and higher oligomers increases during the reaction.

Diglycerol is a special case, which can be produced from polyglycerol and requires distillation to be separated from the higher oligomers. To separate the higher oligomers by distillation the polyglycerol is first made into the corresponding acetal or ketal derivative and then it is fractionally distilled. The individually separated polyglycerols are obtained by removing the protection group [11,12].

Depending on the reaction conditions, polyglycerol appears as a yellow liquid with high viscosity. Although it quickly absorbs moisture, it is chemically stable in normal storage conditions. In some cases, the polyglycerol becomes cloudy after prolonged storage. The turbidity is derived from the formation of solid polyglycerols and the polyol becomes clear when heated. In cases where a colourless quality of polyglycerol ester is required, a purification can make transparent polyglycerol products.

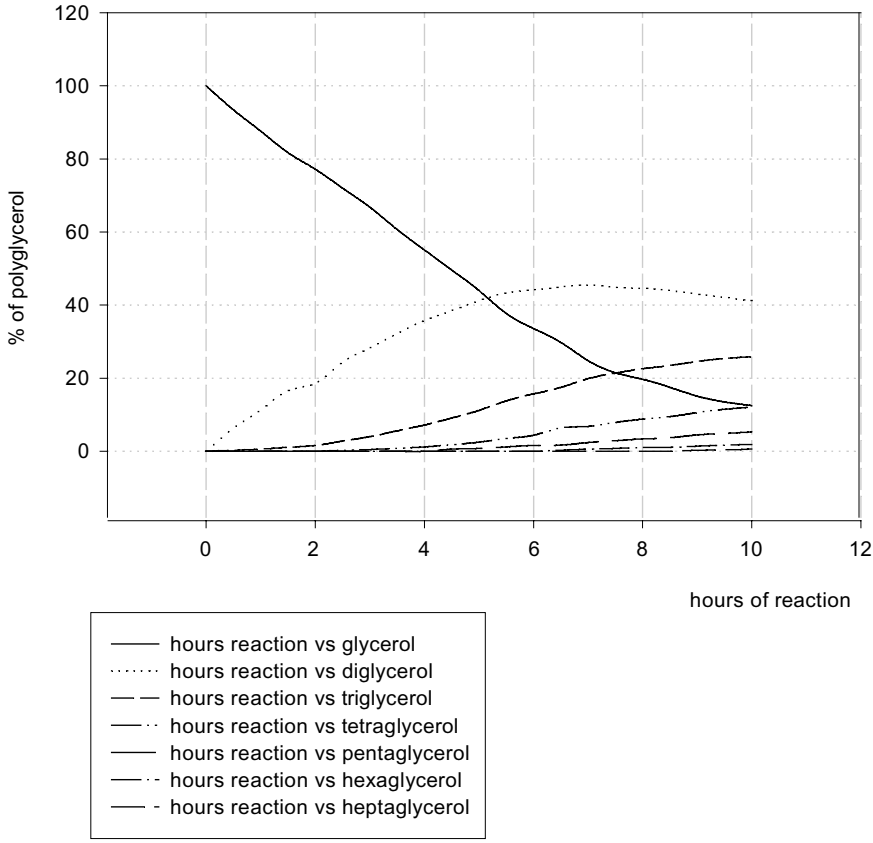

Fig. 5.2 Progress of polyglycerol formation.

5.4 Synthesis of polyglycerol ester

Polyglycerol ester can be produced by a direct esterification between the polyolether and the fatty acid at elevated temperatures and with removal of the water formed [13–16]. The esterification is generally done batchwise in a general-purpose reactor which allows reaction temperatures at plus 200°C, in combination with a reduced pressure to remove the water formed during the esterification [17]. Normally, the condition is alkaline and the process is terminated when the content of the free fatty acids is below a specified value. The esterification is stopped, for example, by adding an acid to neutralize the catalyst and then cooling the product to below 100°C. The emulsifier is often produced with a relatively high proportion of the polyol to get as much of monoester and diesters. This means that the product will contain a surplus unreacted polyglycerol. Part of

the unreacted polyglycerol can be removed by simple gravemetric settling. The polyglycerol ester will still contain some unreacted polyglycerol, the amount depending on the degree of its hydrophilic nature. This fraction can be removed from the ester by extracting with water combined with salts in a charge-wise separation process [18]. In addition to upgrading of the emulsifier by removing unesterified polyglycerol, in principle an inert material, the extraction also acts as a sort of deodorizing of the product, yielding an ester with a blander taste and smell. The polyglycerol dissolved in the water from the extraction can be recovered by evaporating the water and removing salt etc., thus yielding a polyglycerol which can be reused (see Fig. 5.3).

An alternative to the process mentioned earlier can be an inter-esterification between polyglycerol and triglycerides, a reaction carried out at a high temperature and under conditions similar to direct esterification. During trans-esterification no water will be evolved and the yield will be higher compared to the direct esterification. The resulting polyglycerol ester does not have a degree of polymerization as high as in the case of the direct esterified ester because the glycerol derived from the triglyceride will interact and form mono- and diglycerides as by-products. A further alternative is trans-esterification between polyglycerol and alcohol esters of fatty acids, for example, methylesters of palmitic and stearic acid [19]. During the trans-estrification, the methanol formed is continuously removed from the reactor. A reaction between glycidol and fatty acids forming polyglycerol esters with a content of 70% monoesters has been described [20]. The process includes a second step to reduce remaining unreacted oxirane oxygen.

The reactions mentioned above demand a high reaction temperature and in the case of heat-sensitive esters or fatty acid, the use of suitable solvents can improve the product with respect to colour, odour and smell. This has been described in a patent of Schou and Dreyer [21], who detail the use of tertiary butanol as solvent for low temperature inter-esterification.

5.5 Properties of polyglycerol esters

5.5.1 Stability

The polyglycerol esters appear as viscous liquids or solid powders with a somewhat waxy consistency and the colour of the emulsifier can vary from off-white to brownish. The colour of polyglycerol esters is dependent on the source of fatty acids but the polyglycerol will also add to the colour of the ester.

The organoleptic properties of the polyglycerol esters are characterized as bland to slightly sweet (glycerol like!) in taste and have a fatty mouthfeel. The smell will be neutral in good quality products, i.e. free from unreacted polyglycerol or deodorized in other ways, otherwise the emulsifiers can have a slightly pungent odour.

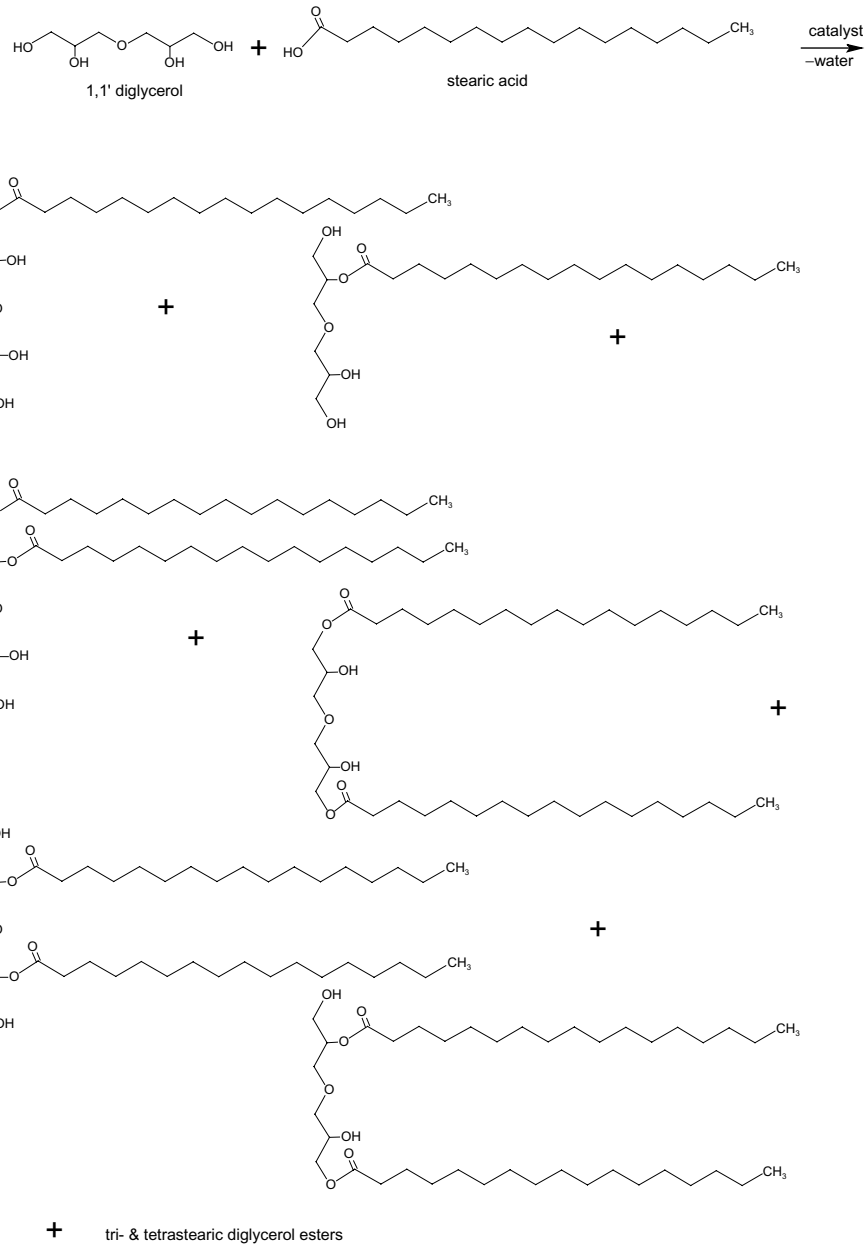

Fig. 5.3 Formation of diglycerolesters.

The thermal stability of polyglycerol esters under neutral conditions is relatively good and the esters can be considered as stable. This is also the case when kept in liquid form at temperatures below 100°C. The intramolecular and intermolecular migrations will be of minor importance under these conditions and the polyglycerol ester can be kept in bulk storage for a short period depending on the exact storage conditions. Alkaline substances like soaps and other chemical substances showing catalytic effect will decrease the stability of the esters dramatically. The instability will be further enhanced by elevated temperatures exceeding 100°C, and a migration towards di- or higher ester and the formation of free polyglycerol can take place.

The polyglycerol esters are comparable to monoglycerides with respect to hydrolysis and the emulsifier can be considered stable under normal conditions. In the presence of alkalis or acids the hydrolysis to free fatty acids or the corresponding soaps together with polyglycerol will speed up, but in general it is a trouble-free process when connected to food and food processes, even at elevated temperatures where application of the polyglycerol esters take place. In enzymatic systems lipases will hydrolyze the polyglycerol ester as seen in the case of other glycerides.

Only when the polyglycerol esters are based on unsaturated fatty acids, oxidation of the emulsifiers will have a significant influence on the quality of the product. Often the oleofinic bonds, which are accessible for oxidation from free radical oxygen, can be protected by addition of a suitable anti-oxidant to the emulsifier, preventing the formation of randicity.

5.5.2 Physical properties

5.5.2.1 Phase behaviour

The neat polyglycerol ester crystallizes from the melt in hexagonal sub-cells, i.e. the α-form, and the ester does not show any polymorphism [22]. The melting point of the polyglycerol ester will depend on the origin of the fatty acids and the proportion of polyols and, in general, the melting point will be in the range of 50–60°C for saturated types and lower for unsaturated types. Other thermodynamic parameters, such as boiling point, vapour pressure, heat capacities etc., are not reported in the literature. In relation to vapour pressure, it will only be relevant for the fractions of the polyglycerol ester consisting of monoglyceride and glycerol, as other components in a polyglycerol ester will be of very high boiling points. Table 5.2 lists some properties of a Palsgaard A/S polyglycerol and a related polyglycerol ester, Palsgaard 1007, a normal vegetable palmitic and stearic acid ester with a low content of unreacted polyglycerol.

The amphifilic properties of the polyglycerol ester of the emulsifier in water exhibit mesomorphic activities forming liquid crystalline structures, i.e. hydrates. The polyglycerol ester as a dipolar emulsifier will form aggregated bodies

Table 5.2 Melting point of polyglycerolester

	Melting point	δH melt	C_p	
			Below melting point	Above melting point
Unit	°C	kcal/kg	kcal/°C kg	kcal/°C kg
Polyglycerol 9001	Liquid		0.60	0.62
Palsgaard 1007	56.5	22.5	0.62	0.59

such as micelles at low concentration in the water. At higher concentration and at temperatures over the Kraftt point, the emulsifier in water will exhibit mesomorphism forming different lyotropic phases, i.e. liquid crystals. The polyglycerol ester will self-aggregate with the hydrophilic polyglycerol moiety oriented towards the surrounding water, and the fatty hydrocarbon chain packed in a more or less ordered form, away from the water. The structure of the liquid crystalline phase will depend on the chemical composition of the emulsifier. It means that the polymerization of the glycerol, the fatty acid composition and the content of monoester, versus higher esters. In addition to this, the concentration of the polyglycerol ester in the system, as well as the temperature, are fundamental parameters. Palmitic and oleic acid esters of primarily triglycerol and tetraglycerol have been reported [23] to form hexagonal bodies in certain concentration range and temperature level, while the alpha gel is observed at lower temperatures of the system. More hydrophilic esters are reported [23] to form lamellar mesomorphs in the form of alpha gels below the Krafft point, and above the point the hexagonal mesophase is limited to a certain range of concentration of emulsifier. When soaps, such as sodium or potassium salts of fatty acids, are present with the polyglycerol stearate, the hexagonal crystals will be replaced by a laminar structure. The nature of the fatty acid will interact and determine the structure of the lyotropic phase, and the polyglycerol moiety will also have an effect on the structure of the liquid crystal form. In a study of the influence of the polyglycerol, Ishitobi and Kunieda [24] found that lauric esters form hexagonal crystal structures with water. An ester with a broader polyglycerol distribution of the oligomers forms the hexagonal bodies at a higher concentration than an ester based on a narrower distribution of oligomers. This observation is explained from the tight packing the broadly distributed esters can form. In another work Kunieda *et al*. [25] report the phase behaviour of polyglycerol ester as a function of the polyglycerol chain length. As the number of glycerol units increases, the emulsifier becomes more hydrophilic and the structure of the liquid crystal changes from a laminar packing to a hexagonal crystal form and progresses further to a micellar form. For a series of diglycerolesters of increasing acyl chain length, the surface tensions between water/air have been recorded by Kumar *et al*. [26] and it is observed that the increasing chain length

increases the surface tension. In addition, the monoesters are found to reduce the surface tension more than the corresponding diesters.

Diglycerol esters have been specially examined and Ljusberg-Wahren *et al*. [27] report diglycerol monolaurate form elongated micelles in water, and when glycerol monolaurate or diglyceroldiester is added to the system a change to a lamellar liquid crystalline phase takes place. The authors conclude that the diglycerol esters are more comparable in their phase properties to the polyoxyethylene emulsifiers than to properties of glycerol monoesters of the corresponding fatty acids. In a work of Monduzzi *et al*. [28] diglycerol monooleate/glycerol monooleate and water is examined. In contrast, with short chain saturated fatty acid, no micelles are observed, and with water the diglycerolester forms lamellar phases together with a separate water phase, an observation explained from the possibilities for the diglycerol moiety to form intermolecular hydrogen bonds in coexistence with water. When the diglycerolester is combined with glycerol-monooleate the lamellar region expands and a cubic phase appears.

Depending on the concentration of the diglycerol ester of different fatty acids, lamellar phases or lamellar bodies are formed. Holstborg *et al*. [29] investigated the mesophases formed in emulsifier–water system using diglycerol monoester of myristic, palmitic, stearic and oleic acid, respectively. The capacity of swelling is rather restricted to a maximum water layer of approx 24 Å, which must be related to the forces from hydrogen bonds between the diglycerol moieties.

5.5.2.2 Solubility

Solubility of polyglycerol ester in organic solvents depends on the nature of the solvent and on the polarity of the ester, but generally the esters will show best solubility in protic and dipolar aprotic solvents, such as lower alcohols and dimethyl-sulphoxide. In some cases the solubility is above the Krafft point, e.g. polyols as 1, 2-propanediol. In triglycerides, such as soybean oil and other common edible oils and fats, it is generally found that the polyglycerol ester can be dissolved above the melting point.

In a ternary system of water, triglyceride and emulsifier, the polar polyglycerol esters with an HLB value between 6 and 11 reduce the surface tension between oil and water, and the polyglycerol esters in this way act as an oil-in-water emulsifier. The interaction is a consequence of minimizing the energy of the system and can be explained from effects associated with the adsorption of the emulsifier to the interfaces of water and triglyceride. Thus, the amphiphilic nature originates from the presence of a lipophilic moiety in the form of a fatty acyl group chemical connected to polyglycerol, the latter is a highly hydrophilic group, i.e. two fundamental different natures within the same molecule make the substance act as an emulsifier. In a system of two or more phases the polyglycerol ester will be associated to the interface of the different phases minimizing the energy of the system, i.e. decrease the interfacial tension by absorption to the boundary between the triglyceride and water.

The ternary system of soybean oil, water and polyglycerol ester has been elucidated by Hemker [23], who reports that the phase behaviour is very dependant on the temperature of the system, but the order of the component also plays a significant influence on the phases occurring in the system. The latter reflects the properties of the polyglycerol ester to form mesomorphic structures in the presence of water, as well as the ability to be more or less soluble in triglycerides, and in the two phase system to be associated with the interface between the hydrophilic and lipophilic phases. Both properties promote the emulsification and stabilization of an emulsion. Kumar *et al*. [26] reported that the short-chain lauric diglycerol ester is the most efficient emulsifier giving the best stability of a water and paraffin oil emulsion. In a work making monodisperse emulsions by using polyglycerol ester as emulsifier and using a straight-through extrusion filter technique, Kobayashi and Nakajima [30] found the emulsifier to make stable emulsions in comparison to sucrose esters, and the authors concluded that the rheological properties of the interface must be considered as a parameter in the stabilization.

The effect on crystallization of the lipid in dispersed systems, such as an oil-in-water emulsion, has been investigated by Awad and Sato [31]. They concluded that the emulsifiers are primarily absorbed at the interface as a thin film. The polyglycerol ester film at the interface will be crystallizing prior to the bulk lipid of the oil droplet. Thus, the crystallized film will act as a nucleus in a heterogeneous nucleation from the film and may in this manner promote and accelerate the overall nucleation of the triglycerides. In the study, it is also observed that the growth rate of the individual crystals formed was decreased by the presence of emulsifiers. The latter is interpreted as the crystals, which will inhibit the growing surface by absorbing the polyglycerol ester present in the liquid and blocking further crystal growth. The authors also report that the polyglycerol ester, in contrast to sucrose ester, does not seem to have the ability to form inverse micelles in the oil phase. The influence of the emulsifiers on the rate of crystallization of triglycerides, as well as the rate of polymorphic transformation, is also connected to the hydrophobic moiety of the emulsifier. In this case, triglycerol monostearate is reported [32] to stabilize the α-crystal form of tristearin, while some other emulsifiers such as monoglyceride and the monoglyceride-lactate esters enhance the transformation to the β-form, which is one of the important morphological properties in many food applications of the emulsifier.

5.6 Food applications of polyglycerol ester

There are a number of literature references to the application of polyglycerol esters in foods, cosmetic products etc., clearly indicating the versatile properties of the emulsifier. As mentioned earlier, it is the interface properties of the emulsifier which are useful. It is the potential to minimize the energy of a

multiphase system through associating at the interfaces between two different phases, combined with other parameters acting as catalyst, can be utilized in the crystallization of lipids which can be utilised. The ability of polyglycerol esters to form liquid crystals with water, which leads to the formation of film and can change rheological properties of a system, must also be considered as an important parameter in many applications.

5.6.1 Margarines

Margarines as food emulsions find extensive use in food and food preparation ranging from cooking, frying and baking to the use as spreads and thus a large number of different types of margarine are known. These include types of margarines developed for special applications or with special functional parameters or dietary properties. Margarines are characterized as water-in-oil emulsions where the proportion of water can vary from a low to a high content of water. The organic phase consists of triglycerides in the form of edible refined oil and fat. It can be pure oil as well, but it is mostly selections of different hydrogenated and/or fractionated fats and oils. The water phase can contain milk constituents, salt, pH regulator, in the form of edible acids and other ingredients. For making the margarines, emulsifiers are used in pure form or as mixtures of different types. Lecithins, monoglycerides or carboxyl ester of the monoglyceride or the polyglycerol esters are used in margarines. In the case of the polyglycerol esters, the applications are generally connected to special types of margarines where the emulsifier, in addition to the emulsification of the emulsion, will improve the functional properties of the margarine, e.g. the organoleptic properties of spreads, stabilizing or aerating of food.

Polyglycerol esters are reported [33] to improve the organoleptic properties of a margarine or low-fat spread by reducing the graininess of the lipid phase to yield a plasticity and elasticity of the margarine corresponding to natural butter. The polyglycerol ester used is composed of palmitic and stearic acid esters from an inter-esterification of primarily diglycerol and triglycerol. In low-fat spreads, polyglycerol ester is observed [34] to yield stable emulsions and in combination with unsaturated monoglycerides stabilizing the water-in-oil system by reducing the water separation in comparison with a low-fat spread based on monoglyceride only. Heinz *et al.* [35] also report that the addition polyglycerol ester to the emulsifier system of a pourable frying margarine will enhance the stability of the emulsion. In a study of the influence of emulsifiers on puff pastry margarines, Bandholm *et al.* [36] compared emulsifiers normally used for puff pastry margarine and it is concluded that the presence of polyglycerol ester in the formulations yielded margarines of excellent plasticity and a dry surface. Baking tests of the puff pastry margarines have resulted in a lift of the pastry equal to, or better, than the reference samples. The polyglycerol ester based margarines yield baked goods of much more regular lamination and with

clearly separate layers and a uniform expansion. The results are also found to be nearly equal for puff pastry margarines with an acid as well as a nearly neutral water phase. Addition of lecithin to the emulsifier system does not alter the results significantly.

Cake margarine is another type of margarine finding extensive application in baking industry. Here the margarine is used as a source of fat for the cake batter and therefore is an important part of the aeration of the batter. At the same time the use of a cake margarine or a cake shortening, due to the emulsifiers present, will simplify the manufacturing via an 'all-in process', i.e. all ingredients whipped together in contrast to the traditional process of two separate mixings, known as the creaming method.

In an aerated cake batter the system is a complex mixture of flour, water, egg, sugar and lipids plus a number of minor ingredients. The whipping causes a large number of small air bubbles suspended in a liquid phase. The latter is an emulsion/suspension in the form of a matrix comprising water as the continuous phase in which solids, e.g. flour particles and different crystals (sugar and fat), are suspended together with air cells and soluble matter in the form of carbohydrates, proteins and salts. Small oil globules of liquid triglycerides will also be present in the water phase. In the batter, the gas bubbles are stabilized against flocculation and coalescence by adsorption of fat crystals to the air–water interface [37], and at this stage the emulsifiers, in this case polyglycerol esters, interact as an interface-active component. The emulsifier will interact in the formation of the fat crystals of the shortening or margarine as it is absorbed on the surface of the fat crystal. In the case of polyglycerol ester, the fatty acyl chain of the emulsifier will be associated with the fat crystals, and the hydrophilic polyglycerol moiety will be oriented towards the area surrounding the crystal and can promote the adsorption of the fat crystals to the air–water interface. The amphiphilic nature of the emulsifier will at the same time cause an interaction with the proteins present in the batter and in this way the emulsifier can alter the interface properties of the proteins. Some of the polyglycerol esters will also be able to complex with the free water in the batter and form mesophases, i.e. liquid crystals. The latter structures have an affinity towards the air–water interface but the lyotropic phases will also result in an increase of the viscosity of the water phase and thus take part in the stabilization of the suspended gas bubbles [38].

In a work of Brooker [37] it is observed that the tips of the fat crystals are adsorbed into the air–liquid interface and the crystals are in contact with the air bubble. The lipid crystals are projected from the gas bubble and the emulsifier is thought to promote the projection of the fat crystal into the hydrophilic phase. During the baking process, the heat will melt the fat crystals and at the same time the gas will expand allowing the bubble size to grow. This expansion take place as the fat will now be a flexible oil film at the air serum interface, a film where polyglycerol ester and other interface-active components, such as proteins, will be present and stabilize the overall system.

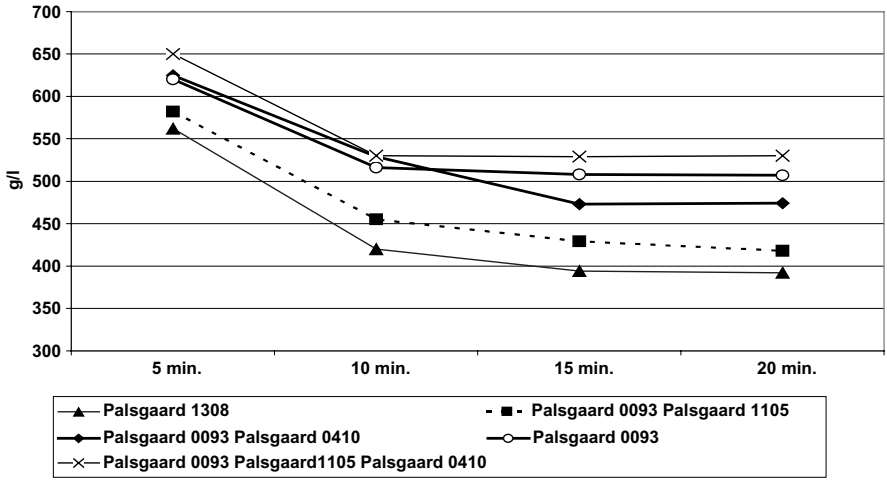

Fig. 5.4 Batter densities of pound cakes.

The advantages of formulating cake margarine with polyglycerol ester are increased batter volume and a stable batter. The latter makes handling much more easy and safe with respect to keeping the over-run intact. In addition, the presence of the polyglycerol ester will promote the distribution of the fat from the margarine or shortening through the batter, securing a uniform distribution of the fat in the dough. The baked goods i.e. cakes, obtain a better volume with a more uniform crumb structure and soft texture, while the shelf life of the cake will be longer due to decreased retrogradation of the starch [39]. In Fig. 5.4, two polyglycerol esters (Palsgaard 1105 and Palsgaard 1308) are compared with a monoglyceride (Palsgaard 0093) and a lactic ester (Palsgaard 0410) and all four emulsifiers are tested in pound cake formulations. The whipping tests are shown in the form of batter densities as a function of the whipping time. The volumes of the resulting baked cakes are shown in Fig. 5.5. From the two figures it can be seen that the batter and cake based on a margarine with polyglycerol ester (Palsgaard 1308) yields the lowest density of the batter and after baking produces the cake with the best volume.

In the formulation of low fat margarines, spreads and butter creams, the emulsifier plays a key role and a polyglycerol ester with erucic acid as the major fatty acid is reported [40] to give good stability. For pourable water-in-oil emulsions, with a high water content exceeding 50% and a very low content of solid fat in the lipid phase, a polyglycerol ester where the hydrophilic part is di-, tri- and tetraglycerols, oleic, and linolic acids as the two major acids but with erucic acid present as a minor constituent in the lipophilic part, yields emulsions with good stability in comparison to other types of emulsifiers as monoglyceride and esters of monoglycerides [41].

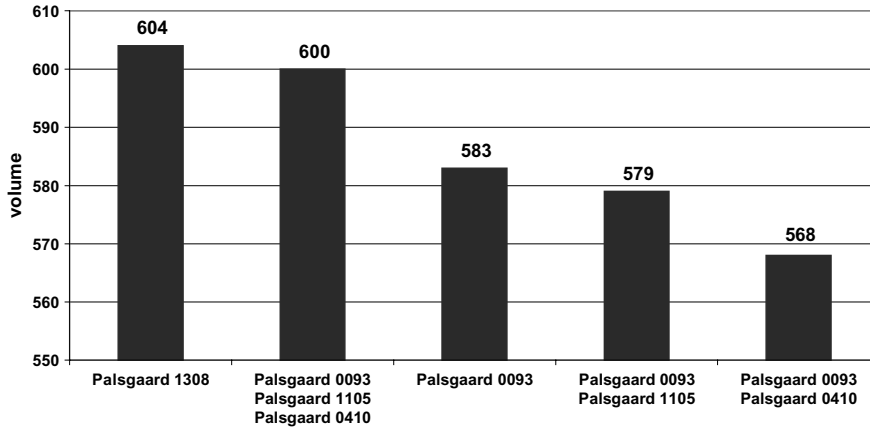

Fig. 5.5 Cake volume.

5.6.2 Cakes

An important application of the polyglycerol esters is in cake batters with little or no content of fat and oil, i.e. batters for sponge cakes, Swiss rolls and similar types of cake formulations that are based on egg, sugar and flour and/or starch. In the production of these types of cakes, the polyglycerol esters simplify the process from the two-step to a one-step 'all in whipping' of the cake batter. Due to the polyglycerol esters the batter, which actually is a foam, will be more uniform and incorporate a much higher number of small air cells when compared to a non-emulsifier batter. At the same time, the emulsifier-based batter has a more uniform foam structure. Due to the superior aeration, a lower specific weight is obtained, together with an increased viscosity of the whipped batter, which is important for easy and suitable handling. At the same time, as the emulsifier stabilizes the batter, the foam can be kept intact for a longer period without losing air. The polyglycerol ester can improve foam formation, which will result in a superior finished cake volume together with improved, uniform and thin walled, crumb structure, good handling and cutting properties and also an improved edible quality [42]. Compared to alternative emulsifiers, such as monoglycerides, the polyglycerol ester is found to have an advantage in providing long time stability of the whipping properties, making the emulsifier an excellent choice for cake mixes.

Polyglycerol esters for the use in cakes of the types mentioned above are formulated from saturated fatty acid and are waxy solid materials that cannot be used directly in a cake formulation. To make the emulsifiers more convenient, the polyglycerol esters intended for baked goods are normally marketed as paste or powder formulations developed for direct use in cake mixes or in batters. In

the case of paste formulations, the polyglycerol ester is hydrated at elevated temperatures together with a co-solvent such as sorbitol syrup and/or propylene glycol [42]. The mix, after cooling, yields a stable paste that can be used directly in cake production, together with the other ingredients.

A powdered polyglycerol ester, in comparison with a hydrated emulsifier, will offer big advantages in handling and can be used in flour and cake dry-mixes. Polyglycerol ester in powder form is normally formulated as 20% to 40% emulsifier combined with a carrier substance. This can be produced by spray drying an oil-in-water emulsion prepared from the polyglycerol ester and a combination of carbohydrates, e.g. maltodextrins and proteins dissolved in the water phase. The protein can originate from milk or vegetable sources [43]. An alternative to the spray-dried emulsifier is a product where the polyglycerol ester is added to starch to yield a fine and stable emulsifier powder [44]. In this case, the emulsifier is combined with the starch particles using extrusion technology and the resulting powder is an efficient whipping emulsifier for cakes marketed as Emulpals. TEM microscopic examination of the extrudate [45] shows the polyglycerol ester is present as a thin film (Fig. 5.6) surrounding the individual starch particles. This is in contrast to the spray-dried products

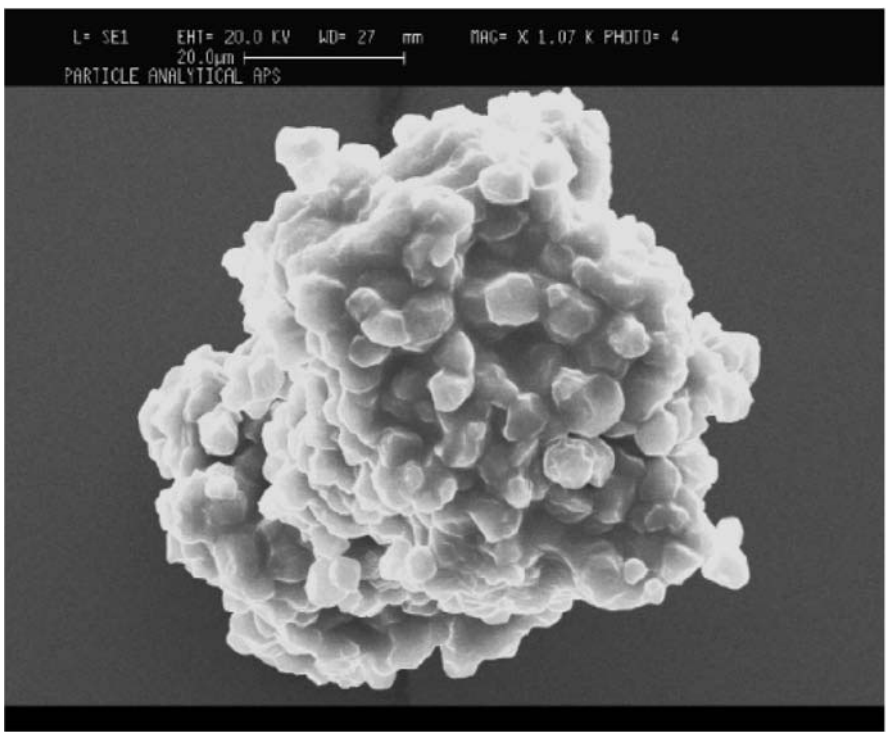

Fig. 5.6 TEM picture of Emulpals: a polyglycerol ester on a starch.

described earlier, in which the polyglycerol ester is enclosed in the matrix of the carrier material. Both types of powered emulsifier are very convenient and stable products, which can be incorporated in mixes with shelf life extending to 18 months without losing their functional properties. Often the polyglycerol ester is combined with other emulsifiers, e.g. lactylated monoglycerides to obtain formulations with properties optimized to a specific application. There seem to be no specific studies on the mechanism behind the properties of polyglycerol ester in the aeration of sponge cake batter, but it is likely that the emulsifier will compete with the film-forming protein from the egg at the air–liquid interface. In this manner, the polyglycerol ester stabilizes the interface, a stabilization is important during the baking process where heating causes the gas cells to expand, and a potential coalescence will cause loss of quality of the finished baked product. The displacement of the protein at the interface can be a direct substitution, but also a complexation between emulsifier and proteins is likely, thus altering the surface-active properties of the proteins. It must be considered that the polyglycerol ester as mentioned in Section 5.5.2.1 will form lyotropic phases with the free water present, which will increase the viscosity of the batter and in this way protect the cells during the whipping. However, it will also retard the movement of the air cells in the batter during the baking process and in this manner inhibit coalescence between the cells or liberation of the incorporated air.

The benefits of using polyglycerol esters in cake batters are a more simple and safe process together with better aeration, batter stability and better quality of the finished baked goods. Figures 5.7 and 5.8 show a comparison between a traditionally prepared sponge cake versus a formulation with addition of an emulsifier extrudate in the form of Palsgaard Emulpals polyglycerol ester in an ‘all in preparation’. The differences between the two sponge cakes are evident; the polyglycerol ester results in a smoother and uniform top surface of the cake as well as the walls which, during the baking, have been in contact with the baking tin. The emulsifier also gives a 45% higher volume of cake. Figure 5.8 shows the crumb of the sponge cakes where the polyglycerol ester based cake has obtained a much finer and uniform cell structure without any vertical channels. Tests in the form of monitoring the elasticity of the crumb and the force needed for making a defined deformation of the crumb confirm that the emulsifier based cake has better texture qualities and a significantly longer shelf life. The water activity of the cake with polyglycerol ester added is more stable during storage and has a delayed drying out in comparison to the reference sample.

5.6.3 Shelf life of baked products

The shelf life of starch based products, such as cakes and breads, is closely connected to the retrogradation of the starch, and it is well known that many food emulsifiers are able to complex with the amylose of the starch and thus inhibit or delay the retrogradation. In a comparative study of different food emulsifiers [46], tetraglycerol monostearate was found to be complex only moderately with

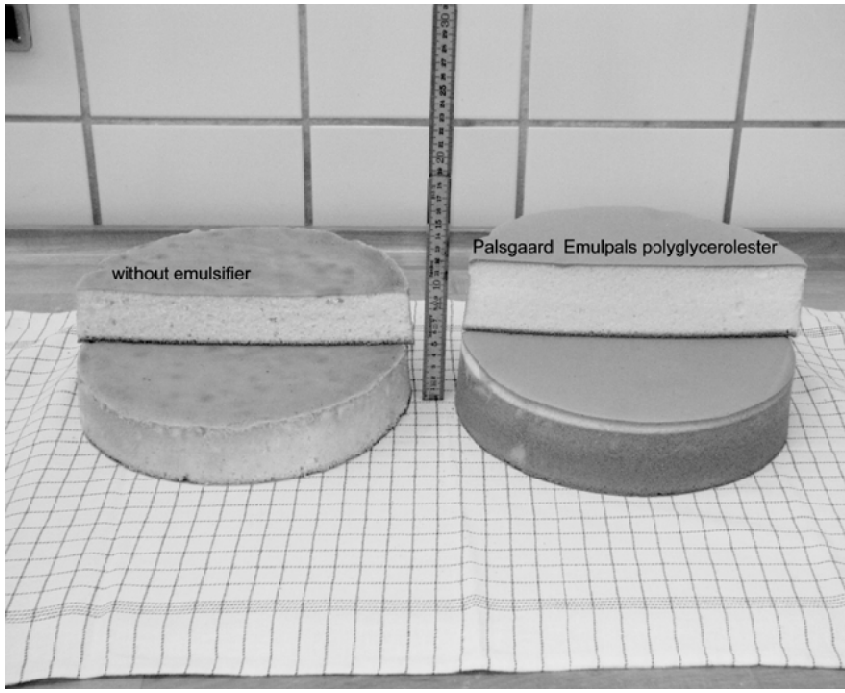

Fig. 5.7 Sponge cakes with and without polyglycerolester.

amylose, but it is likely that polyglycerol esters with other chain lengths of the hydrophilic moiety or with other ratios between mono- and oligoesters will complex to another degree, thus a polyglycerol ester has been found to increase the shelf life of maize-based products, such as tortilla, without changing the texture of the tortilla [47].

In fermented doughs for bread, polyglycerol esters are not found to be of much use. In a study by Garti *et al.* [48], polyglycerol esters with a high HLB value were found to improve doughs as well as the finished breads, and the authors found that polyglycerol ester in some cases can replace sodium stearoyl lactylate, a food emulsifier with widespread use in fermented bread doughs.

5.6.4 Creams and toppings

The air-incorporating properties of polyglycerol esters have also found application in products like whipping cream substitutes. These are products are formulated from dairy proteins, such as caseinate, carbohydrates and fat, together with an emulsifier [49]. Different polyglycerol esters combined with lecithin are reported [50] to give a reduced fat-imitation cream with improved freeze- and acid-resistance properties, while a patent [51] describes the use of polyglycerol

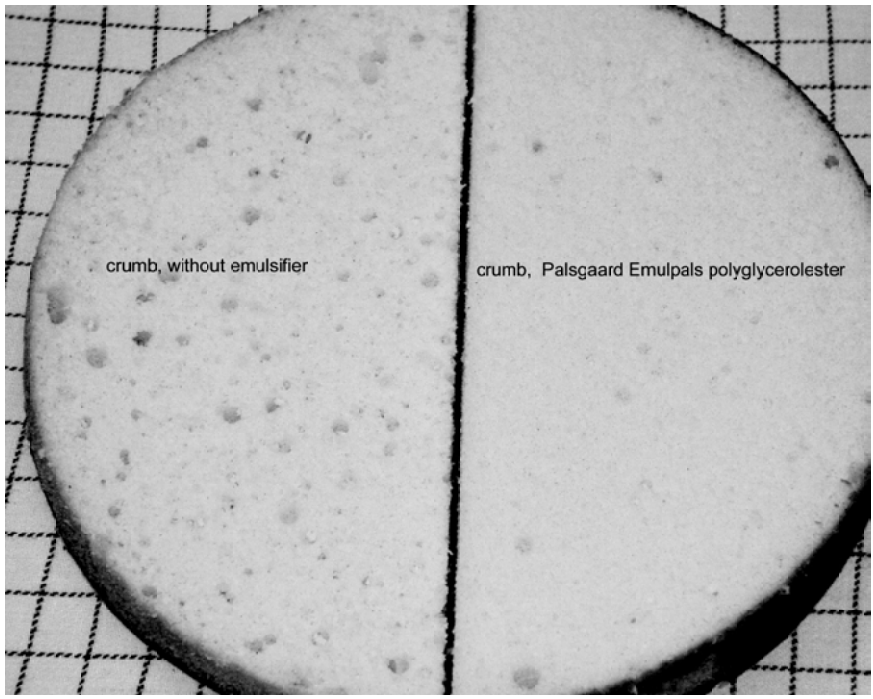

Fig. 5.8 Crumb of sponge with and without polyglycerolester.

ester in spray-dried formulations. The powder is claimed to be useful in a range of different aerated foods, such as toppings, puddings, ice creams etc. In a study comparing different emulsifiers in ice cream formulations, polyglycerol ester has been found to give results comparable to mono- and diglyceride with respect to over-run (air incorporation) and melt down properties. Sensory evaluation of ice cream incorporating polyglycerol esters has reported more creaminess together with a good texture [52].

Polyglycerol esters are also reported [53] to be used for aeration of non-aqueous lipid systems, e.g. peanut butter and compound chocolate, and it has been found that triglycerol monostearate can reduce the specific gravity of this type of food down to approximately 0.5.

5.6.5 Fats

Special types of polyglycerol esters are used as crystallization inhibitors in the oil and fat industry. In a study comparing different crystal inhibitors, Idris *et al.* [54] report that a polyglycerol ester has been observed to give the best results. In the case of crystallization of wax from sunflower oil [55], the inhibition effect is

explained as existing because the polyglycerol ester favours nucleation and thus forms a larger number of crystals. This nucleation decreases the amount of wax available for further crystal growth, thus preventing the formation of turbidity of the sunflower oil during storage. Oxidation of triglycerides in oil-in-water emulsions has been investigated by comparing sucrose ester and polyglycerol ester as emulsifying agents. Here the polyglycerol ester is reported [56] to enhance the stability against oxidation more than in the case of the sucrose esters under the same conditions.

5.6.6 Other applications

A potentially different application from that of being an interface active emulsifier is polyglycerol ester as a food preservative, a property suggested and tested by Razavi-Rohani and Griffiths [57] and later by Plocková *et al*. [58]. In both works, the lauric esters have been tested. Here the biocide effect of the fatty acid combined with the solubility or dispersibility of the polyglycerol ester is the object, and a preservative effect is observed. The preservative effect of the capric and other short-chain polyglycerol derivatives is described in two patents [59, 60].

Other food applications of polyglycerol esters, which do use the interfacial properties of the emulsifier, is used as a fat substitute, i.e. a low calorie fat substitute in food, a subject described in a number of works and patents [61–63].

In addition to the above applications of polyglycerol ester in food, there are many other uses of the emulsifier in the food industry. Polyglycerol esters have also found applications in the pharmaceutical and cosmetic industries.

5.7 Conclusion

The study of polyglycerol esters and the interaction of emulsifiers with other food components on a molecular level give some knowledge about how the emulsifiers interact with the chemical substances present in the food. This knowledge can explain about forces or parameters that are the basis for the macroscopic effects of the esters, which are useful in many applications. Even though the polyglycerol esters have been known for many years and a lot of work has been done on the emulsifier, many questions concerning the nature of these compounds are still open for future scientific research and applied studies.

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6 Sucrose esters

Bianca A. P. Nelen and Julian M. Cooper

6.1 Introduction

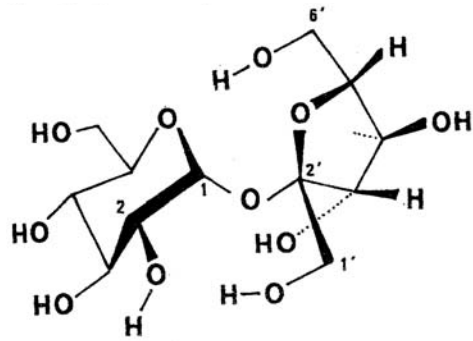
Carbohydrates are polyhydric alcohols which, when reacted with non-polar fatty acids, produce a diversity of surface-active materials which find uses as emulsifiers and/or fat replacers.

One such example, sucrose, is a low cost carbohydrate which is readily available and has the world's highest production of any single, pure, natural, organic chemical [1].

Sucrose esters are non-ionic compounds synthesised by esterification of fatty acids (or natural glycerides) with sucrose. Sucrose (α-D-glucopyranosyl β-D-fructofuranoside) is a polyhydric alcohol with eight hydroxyl groups (Fig. 6.1.): there are three primary hydroxyls – C6, C1′, C6′ – and five secondary hydroxyls. The three primary hydroxyls on the sucrose molecule (C6, C1′, C6′) are the most reactive and are the easiest to substitute with fatty acids, forming mono-, di- and tri-esters. Hence compounds ranging from mono- to octa-esters are theoretically possible, and different ester substitutions can determine the properties of the resultant sucrose esters.

The type of fatty acids that are reacted with the hydroxyl groups on sucrose can also influence the properties of sucrose esters. Varying the number of fatty acids from one to eight and the chain length of the fatty acid creates an extensive family of sucrose esters. Fatty acids in the C8–C22 range can be reacted to form esters with sucrose. In general, long chain fatty acids of palmitic acid (C16), oleic acid (C18) and stearic acid (C18) are preferred, but only sucrose esters with the saturated fatty acids (lauric, palmitic and stearic) are currently available in Europe [2]. Sucrose esters based on primarily lauric, palmitic or stearic acid will be referred to as, sucrose laurate, sucrose palmitate and sucrose stearate. Typical fatty acids combined with sucrose are detailed in Table 6.1.

The higher substitution esters, e.g. hexa, hepta and octa (see Section 6.9.2), find use as fat replacers, the lower substitution esters, e.g. mono-, di- and tri-esters, find use as oil-in-water as well as water-in-oil emulsifiers, this offers advantages over other commercially available emulsifiers. Sucrose esters can have a very wide range (1 to 18) of hydrophilic–lipophilic balance (HLB) (see Section 6.6.1). The different HLB values can be obtained by changing the degree



Hydroxyls	Glucose	Fructose
Primary	C6	C1′, C6′
Secondary	C2, C3, C4	C3′, C4′

Fig. 6.1 Structure of sucrose.

Table 6.1 Fatty acids

Fatty acid	Chain length	Number of double bonds
Lauric	C12	0
Myristic	C14	0
Palmitic	C16	0
Stearic	C18	0
Oleic	C18	1
Behenic	C22	0
Erusic	C22	1

of substitution as illustrated in Fig. 6.2. Low ester substitution provides high HLB, with higher substitutions delivering lower HLB values. Low HLB value sucrose esters find applications in stabilising water-in-oil emulsions and high HLB value sucrose esters can stabilise oil-in-water emulsions. The wide range of emulsification properties, other functional properties and applications of sucrose esters will be discussed at length later in the chapter.

This chapter will focus on the uses of sucrose fatty acid esters as emulsifiers. If the readers are interested in the applications of sucrose fatty acid esters as fat replacers, a study in [3] provides a good review on carbohydrate polyesters as fat substitutes.

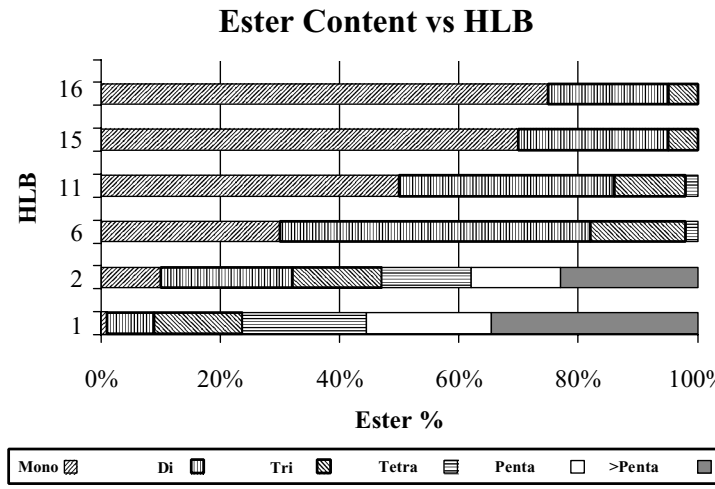


Fig. 6.2 Ester substitution and its effect on HLB.

6.2 Early history of sucrose esters

In 1880, Herzfeld wrote an article in *Berichte der Deutschchen Chemischen Gesellschaft* describing the preparation of sucrose octaacetate [4]. This is the first mention of a sucrose ester. It is intensely bitter in taste and is used as a denaturing agent for industrial alcohol [5].

Haworth and co-workers [6, 7] reported the production of similar esters from a range of disaccharides – cellobiose, lactose and melibiose. Hess and Messner synthesised and examined the properties of sucrose octapalmitate and sucrose octastearate in 1921 [8].

Early attempts to produce sucrose esters used direct esterification using the acid chloride or anhydride of the fatty acid reacted directly with sucrose. The major problem was ensuring thorough mixing of the two dissimilar materials. Most early production routes involved toxic solvents, e.g. pyridine, and it usually produced low yields of the required esters which required extensive clean-up procedures.

In 1924 Rosenthal patented a classical condensation reaction of the acid chlorides of the fatty acids of drying oils (linseed) with sucrose, in the presence of pyridine, to produce highly substituted sucrose esters [9]. Rheineck *et al.* patented a similar process to produce esters of sucrose and other polyhydroxy compounds, e.g. mannitol [10]. These two routes gave low yields of highly coloured crude mixtures.

In 1939 Cantor patented a production route to fatty acid esters from starch factory by-products (mainly glucose) [11]. He claimed the products could be

used as fats or emulsifying agents. The synthesis is achieved using a direct esterification using either the anhydride or acid chloride of fatty acids isolated from refinery mud, reacted with the mother liquor from dextrose crystallisation. The process requires the use of pyridine with either chloroform or carbon tetrachloride to facilitate mixing of the reactants.

The major advancements in the manufacture and determination of the properties of sucrose esters were achieved in the early fifties, when Foster Snell and co-workers were asked by the Sugar Research Foundation to investigate the feasibility of attaching fatty acids to sucrose to make sucrose esters [12, 13]. This research programme produced several mono- and di-esters of sucrose and resulted in processes that have been commercially developed to produce sucrose esters today.

6.3 Production routes to sucrose esters

The reactions that produce sucrose esters can also produce a multitude of co- and by-products; the routes to manufacture have all attempted to maximise the yield and selectivity of the reactions to produce the desired product. The major problems associated with sucrose ester manufacture are as follows:

- Lability of sucrose under the conditions of reaction, e.g. high temperature
- Degradation of the start materials, e.g. caramelisation and saponification
- Solubility of the reactants and products in different reaction phases
- Production of by-products, e.g. soaps, glycerides
- The production of flavour and colour during the process by caramelisation and maillard reaction products.Use of toxic solvents in both reaction and purification stages necessitating stringent downstream processing.
- Different manufacturing process patents have endeavoured to address these issues. Several routes can produce sucrose esters and three major ones have been reported to produce materials on a commercial scale:

  (i) Direct esterification using either the fatty acid chloride or anhydride
  (ii) Interesterification using alcohol esters (e.g. methyl) of the fatty acids
  (iii) Enzymatic methods

As seen earlier attempts using route (i) resulted in low yields of crude mixtures using toxic solvents and were not considered viable as production routes to food grade materials.

The use of enzymes to manufacture selective sucrose fatty acid esters is very attractive due to the ‘cleaner’ specific reactions associated with enzymatic synthesis. Early attempts by Seino *et al.* to use enzymes in aqueous media to carry out direct esterification of sucrose with fatty acids were unsuccessful, resulting in poor selectivity and low yields [14].

Early pioneering studies by Klibanov at the Massachusetts Institute of Technology discovered the use of hydrolytic enzymes in dry organic solvents [15]. Lipases and proteases were found to catalyse esterification and transesterification when used in organic solvents. Recently, this approach has been employed to explore the production of sugar fatty acid esters using lipases [16]. However, this route to large scale production of sugar esters is not commercially viable at present.

The interesterification route has proved to be the principal method for production of sucrose esters on a commercial scale. Their manufacture via interesterification can also be achieved via three routes:

(i) *Solvent process.* This reacts sucrose with a fatty acid ester in a homogeneous system using a mutually compatible solvent, e.g. dimethylformamide (DMF) or dimethyl sulphoxide (DMSO). The reaction takes place at moderate temperature using alkaline catalysts, e.g. potassium carbonate.

(ii) *Emulsion process.* This route uses emulsion processes and typically sucrose is dissolved in water or a similar solvent, e.g. propylene glycol, prior to dispersion with the fatty acid ester, using a soap or emulsifier. The interesterification reaction is achieved by removal of the water and solvent.

(iii) *Melt process.* The melt route either melts sucrose and reacts the melt with fatty acids methyl esters, or uses soaps to produce an emulsion that is heated to drive off the water and thus produces a homogeneous melt.

A large number of patents have been published on the manufacture of sucrose esters; the following is not intended to provide a comprehensive review, but aims to provide the reader with an appreciation of the different routes that have been attempted to simplify and improve the commercial production of these versatile emulsifiers.

The manufacturing processes for sucrose esters were developed from the early research carried out by Foster Snell and his co-workers [12, 13]. The first process for sucrose ester production sometimes referred to as the Hass–Snell process, used DMF as the solvent for solubilising both the sucrose and the methyl esters of the fatty acids. This was described in the early work funded by the Sugar Research Foundation and was later patented by Hass *et al*. [17].

In the patent, Hass and his co-workers reacted sucrose and other carbohydrates with the esters of fatty acids with lower monohydric alcohols (typically methyl or ethyl) in the presence of an alkaline catalyst, all solubilised in a suitable solvent (the preferred solvents were DMF and DMSO). Examples of the application of this process include the reaction of sucrose with oils and fats (tri- and di-stearin, tallow and coconut oil) and with methyl esters of fatty acids in the presence of sodium methoxide solubilised in DMF. The reaction conditions

were relatively harsh – temperatures up to 180°C for 8–15 hours and resulting yields were low, 25–50%.

The use of DMF and other expensive and exotic solvents was the major obstacle to commercialisation of sucrose ester from this process. The presence of toxic solvents and the smell from the solvent meant that in the USA and Europe products derived from the DMF route were not acceptable for use in food products.

Research commissioned by the State Government of Nebraska into uses for surplus tallow resulted in the development by Osipow and Rosenblatt of the Nebraska–Snell process. This method relied on the development of a micro-emulsion of sugar in propylene glycol plus the addition of a fatty acid methyl ester in the presence of potassium carbonate to produce sugar fatty acid esters [18]. They reported a yield of 85% of the mono-ester and the work resulted in a patent in 1969 [19]. The examples included use of propylene glycol to dissolve the sucrose and an emulsion is formed with the methyl ester of the fatty acid and a catalyst, typically sodium methoxide. The propylene glycol is then distilled off from the mixture, which results in the trans-esterification and production of the sucrose fatty acid ester. This route was used to make mono- and di-esters of sucrose with stearic, lauric and oleic acids.

A process which was essentially solvent-free was developed by Feuge and his colleagues at the United States Department of Agriculture (USDA), Southern Regional Research Center (SRRC) [20]. This so-called USDA method involved a reaction between molten sucrose and methyl esters of fatty acids in the presence of alkali soaps that act as solubilisers and catalysts. A similar method called the Zimmer method was developed in Germany [21].

The major problem associated with both these methods is the temperature which is employed. At the very high temperature used (175–185°C) the sucrose undergoes very rapid degradation before it can react with the methyl esters of the fatty acids and this results in rapid colour formation and increased downstream processing.

Yamagishi *et al.* [22] improved on the USDA method in 1974, by first dissolving sugar in a fatty acid soap solution and them adding a mixture of fatty acid methyl ester plus an alkaline catalyst to the mixture. Water was driven off to produce a dehydrated, homogenous melt in which the trans-esterification reaction proceeded at temperatures between 110 and 175°C. They reported relatively high conversion rates of 85–95% with different levels of mono- (28–52%) di- (29–31%) and tri- (9–41%) ester composition.

Many attempts [23, 24] to improve this process have been patented in recent years but not many have superseded these initial processes. Tsuyoshi *et al.* have used ion-exchange resins with alkali earth and alkali metal counter ions to catalyse the interesterification reaction [23]. Clark and Lemay have used an organotin-based acylation promoter to selectively synthesise sucrose-6-esters [24].

6.4 Purification methods for sucrose esters

As mentioned above, there have been many attempts to produce sucrose esters on a commercial scale. The main stumbling block to commercialisation has been an effective route to purification from both a functionality requirement, and more specifically a food safety perspective.

The work patented by O'Boyle is typical of early attempts to purify reaction mixtures from trans-esterification reactions. To obtain high levels of mono-esters it is necessary to have high levels of sucrose in the starting mixture thus resulting in high levels when the reactions have almost reached completion. O'Boyle used secondary solvents (e.g. alcohols and mixtures with xylenes and toluene!) to recover unreacted sucrose from the reaction mixture [25]. A second patent [26] provides details of the use of fluxing solvents (e.g. propylene or ethylene glycols plus organic acids) to improve the removal of distillable impurities–residual reaction solvents (DMSO or DMF) and the purification solvents. A third patent teaches the use of alkane hydrocarbons which are added as wash solvents, in which the extraneous solvent is soluble but the polyhydric ester has limited solubility [27]. This results in a series of solvents to remove solvents!

Other multiple purification systems are not uncommon. Mizutani *et al.* patented a process(es) for recovery of sucrose esters of fatty acids [28]. The researchers used a series of processes, either singly or in combination, to effect the purification of sucrose esters from reaction mixtures. The processes were (i) addition of an acid or acid salt to give a pH of 3.5–5.0 (the sucrose ester can be recovered using liquid/liquid extraction), (ii) the sucrose ester can be recovered by the formation of a double decomposition salt with by the addition of the salt of a metal and (iii) adding a water soluble 'substance' to recover the sucrose ester by precipitation. Thus, an organic or mineral acid is used to drop the pH to the desired range. Solvents such as methyl acetate, ethyl acetate are used to separate sucrose and water-soluble materials into an aqueous layer. The double decomposition salts of the surface-active materials are precipitated from the solution, leaving the purified sucrose ester in the liquid layer, which is then isolated by salting out with potassium or sodium chloride. Again a multi-stage process using a range of reactants that must be recovered and re-used for process economy.

More recently Dai Ichi Kogyo Seiyaku Co Ltd has published a series of patents [29] that have used ultrafiltration, reverse osmosis and spray drying to effect the commercial purification of sucrose esters. The two companies currently producing sucrose esters on a commercial scale for food emulsifier applications are Mitsubishi Chemical Industries Ltd (Ryoto Sugar Esters) and Dai Ichi Kogyo Seiyaku Co Ltd (DKS) (DK Esters), both from Japan. Several authors have reported the processes they use for manufacture. Bekkum and Lammers [30] report that Mitsubishi use DMSO as a solvent and that DKS use

the micro-emulsion process. However, authors from the two companies are less open about the precise process employed [21, 31].

Mitsubishi report an annual production capacity of 3000 tonnes with DKS reporting 2000 tonnes, giving a total figure of some 5000 tonnes worldwide. Sisterna B.V. is a joint venture between DKS and Royal Cosun U.A. (of which Suiker Unie is the major part) formed to service the western hemisphere with sucrose esters.

Two similar products which include sucrose esters have been developed – however, sucroglycerides and sucrose ester detergents have had limited commercial success.

6.5 Sucroglycerides and sucrose ester detergents

Sucroglycerides are produced by a trans-esterification reaction between a natural triglyceride (e.g. palm oil or coconut oil) and sucrose. They are mixtures of mono- and di-esters of sucrose with mono- and diglycerides as defined by the e-number E474. The regulations state that sucroglycerides permitted for food use must contain at least 40% sucrose esters and at least 40% glycerides. The functional properties of the resultant mixture are determined by the starting triglyceride. Most sucroglycerides are lipophilic, fat soluble and only sparingly soluble in an aqueous solution. Typically, they are supplied as a paste and have to be dispersed in the fat phase of a product or melted down to produce a pre-emulsion. Several routes have been proposed for their manufacture [32]. The main application for sucroglycerides has been in animal feed and principally as calf milk replacers [32]. Rhone-Poulenc planned to install a factory manufacturing up to 2000 tonnes per annum of their Celynol^{TM} sucroglycerides [32]. However, these products are not commercially available at present.

Similarly, Tate and Lyle attempted to produce sucrose ester based detergents [1] to compete with petroleum-based surfactants with the added advantage of biodegradability. The product was a mixture of sucrose mono-ester (27%) with higher esters, sucrose, mono-, di- and triglycerides with potassium soaps (30%). However, due to process difficulties TAL^{TM} detergents were never commercialised.

6.6 Functional properties of sucrose esters

6.6.1 Emulsification

Sucrose esters offer advantages over most other commercial emulsifiers. By selection of the ester composition, it is possible to obtain sucrose esters having a hydrophilic–lipophilic balance (HLB) over the range 1 to 16 (Fig. 6.3). Low and high HLB value sucrose esters are functional in water-in-oil (w/o) and

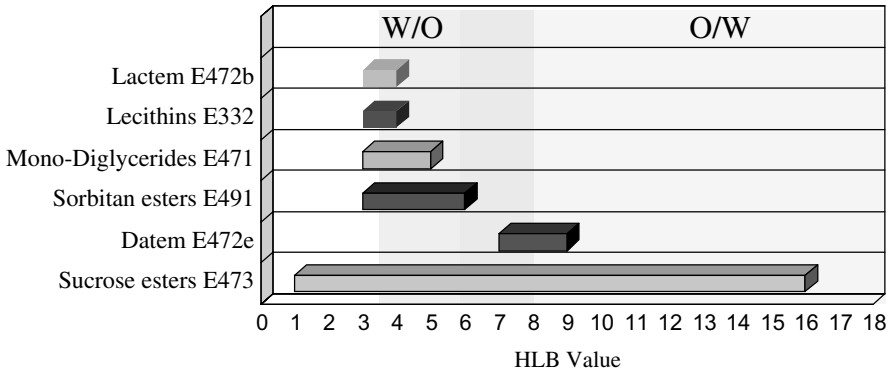


Fig. 6.3 Typical HLB values of emulsifiers.

oil-in-water (o/w) emulsions, respectively. Functionality of sucrose esters in foods is complex due to multiple interactions with starch, proteins, sugars, oils and fats, which are the major components of food products [34, 35].

The HLB value can be calculated mathematically or can be measured, the scale ranges from 0 to 20. Emulsifiers in the 3.5 to 6.0 range, tend to be most suitable for use in water-in-oil emulsions and from 8 to 18 for oil-in-water emulsions [35]. Commercial sucrose esters are mixtures of mono-, di- and tri-esters, the HLB value is closely related to the mono-ester content; the more the mono-ester content, the higher the HLB value [36]. The fatty acid chain length has a secondary effect on the emulsifying capacity, the shorter the fatty acid chain length the higher the HLB value. As seen in Fig. 6.3, sucrose esters are unique in the high HLB values; this means that sucrose esters have special benefit in o/w emulsions. With sucrose esters having an HLB value of 12 to 16, it is possible to obtain an emulsion with a very small droplet size, thus increasing stability and a creamy mouth feel (Fig. 6.4). Sucrose esters with a medium HLB value, 6 to 11, stabilise the fat globules in an o/w-emulsion.

6.6.2 Interactions with proteins (gluten, dairy proteins)

The binding mechanism of sucrose esters with proteins is not fully understood, but it is postulated that it is due to the interaction between sucrose esters and the amino acid side groups within the protein molecule. The type and strength of the specific interaction depends on the polarity of the side groups and the pH of the system.

Although different interactions are possible, it is thought that the principal one is hydrophobic bonding, similar to 'Van der Waals' interactions. In the presence of water a hydrophobic bond can be formed between the non-polar side groups of the amino acid and the fatty acid chain of the sucrose ester molecule. The

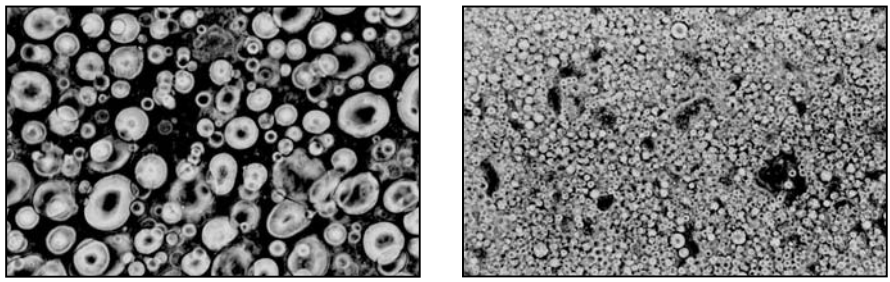


Fig. 6.4 Comparison of droplet size of 20% oil dressing.

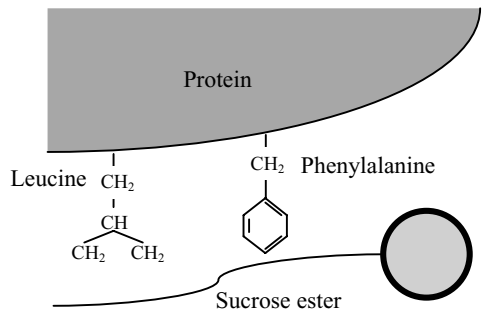


Fig. 6.5 Hydrophobic binding between proteins and sucrose esters.

individual hydrophobic parts have the tendency to group together and repel the surrounding water (see Fig. 6.5).

As a result of this binding mechanism, the hydrophilic sucrose part of the sucrose ester molecule will be localised at the protein surface, increasing the surface polarity of the protein. Thus, the protein becomes more soluble and far less susceptible to aggregation and coagulation.

Other interactions can also occur, for example, hydrophilic binding, forming hydrogen bonds between the non-charged polar side groups of the protein and the hydrophilic part of the sucrose ester molecule. By electrostatic binding, the sucrose ester will interact with the charged polar amino groups from the protein to form loose bonds. These binding mechanisms will occur to a lesser extent compared to the hydrophobic binding and thus will have a limited effect on the end product.

Sucrose esters can bind to specific places on ß-lactoglobulin and a more random binding to ß-casein and casein micelles [37, 38]. Enzymes like lipoxygenase can also be strongly inhibited by the interaction of high HLB value sucrose esters at the active site [39].

Sucrose esters with high mono-ester content (high HLB value) interact most strongly with proteins. Specific effects are obtained in different food products:

- in dressings and sauces, sucrose esters protect the dairy proteins against coagulation denaturation or maillard reactions from heat or acids leading to more stable emulsions (see Section 6.8.1)
- in gelatin-based confectionery, the interaction with sucrose esters results in a more tender structure and an increased shelf life (see Section 6.8.2)
- in bakery products, a more flexible gluten network is obtained which better resists the mechanical forces applied during intensive kneading, thus ensuring maximum gas retention (see Section 6.8.3).

6.6.3 Interactions with starch

Many emulsifiers are able to complex with amylose or amylopectin [40–45]. There are various methods to measure starch complexation:

- Differential scanning calorimetry (DSC) [46]
- iodine binding capacity (IBC) of amylose [47]
- Rapid Viscosity analyser (RVA) [48]
- gluco-amylase digestibility or X-ray diffraction.

Starch complexation with emulsifiers can result in a change in peak gelatinisation temperature and gelatinisation enthalpy, DSC and RVA measure these effects. Peak temperature and gelatinisation enthalpy can differ depending on the type of emulsifier and the starch source.

The interaction between starch and sucrose ester varies with the mono-ester level and the saturation and chain length of the fatty acid. The peak temperature for gelatinisation rises with longer chain length and degree of saturation of the fatty acids. Starch gels containing mono-esters of long chain fatty acid are more resistant to retrogradation [49, 50].

Sucrose fatty acid esters react mainly with the amylose molecule to form helical complexes during gelatinisation. These helical complexes of amylose inhibit retrogradation, which is accelerated by the interaction of amylose helices. As a result, retrogradation of starch is prevented with the existence of complex-forming agents [51]. Usually, starch gels with high amounts of sugar or emulsifiers are weak, resulting in a softer crumb [52].

Various studies underline the starch complexing abilities of sucrose esters. Buck and Walker [46] examined the DSC of wheat starch–sucrose ester combinations and showed an increase in peak gelatinisation temperature and a decrease in gelatinisation enthalpy as sucrose ester concentration increased. With a maize–sugar ester combination, the enthalpy significantly decreased. Sucrose palmitate and stearate slowed the retrogradation rate of rice starch, with the sucrose palmitate being more effective [44].

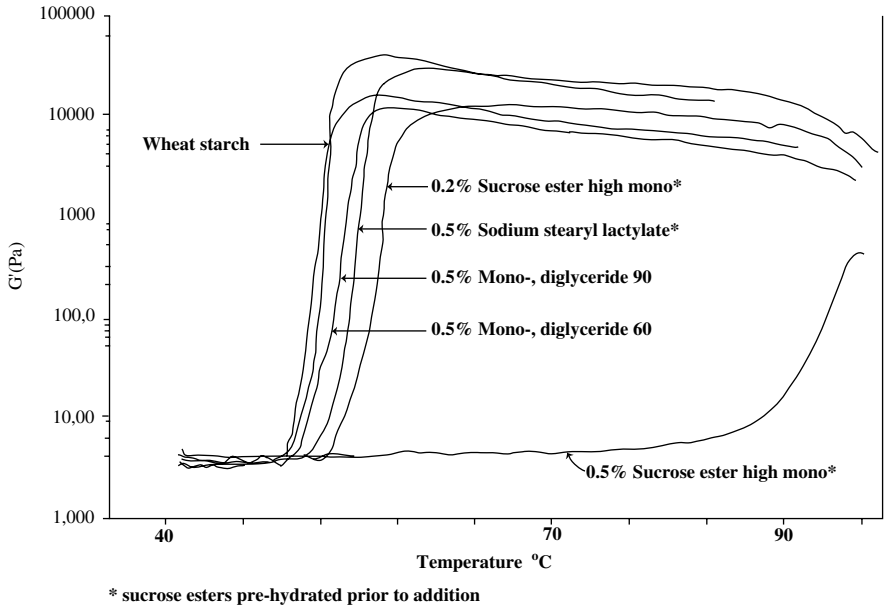


Fig. 6.6 The effect of emulsifiers on the peak gelatinisation temperature of wheat starch.

An unpublished report from the Cosun Food Technology Centre [53] outlines the effect of a sucrose stearate (SE) with HLB 15, glycerol monostearates (GMS) (mono-stearate 60% and 90%) and sodium stearyl lactylate (SSL) on the peak gelatinisation temperature and viscosity of wheat starch and flour in a watery solution. The sucrose ester increased the peak gelatinisation temperature and decreased the viscosity more effectively than the other emulsifiers (Fig. 6.6). In this study, the sucrose esters were pre-hydrated before addition (attempts to celebrate the other emulsifiers were unsuccessful). An addition level of 0.2% pre-hydrated sucrose ester gave a similar effect to 0.5% addition of the other emulsifiers.

6.6.4 Control of sugar crystallisation

Surfactants have no real effect on the growth rate of sugar crystals. In a massecuite (mass of crystals and mother liquor) sucrose esters do promote secondary grain and prevent agglomeration by enhancing the lubrication. The net result will be reduced boiling time and more consistent crystal size [54]. It is speculated that the polar sugar part of the sucrose ester molecule interferes in the primary crystallisation directly after cooling down. The crystal lattice is disrupted, thus preventing the formation of big sugar crystals.

The non-polar fatty acid of the sucrose ester will move from the polar sugar solution to the (less polar) sugar crystal. The sugar crystals will be covered with

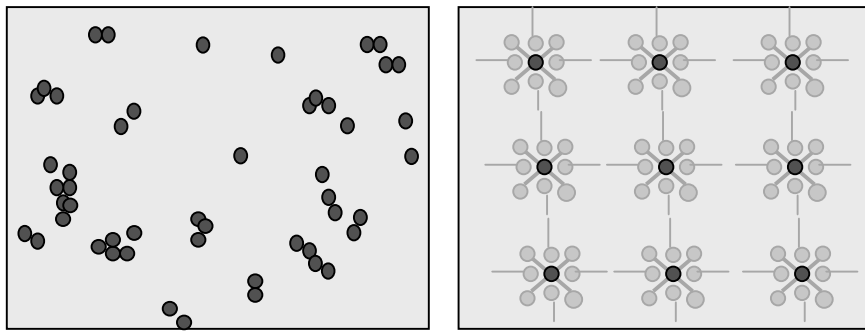


Fig. 6.7 Sugar crystal surrounded by the fatty acid chain from a sucrose ester.

a layer of sucrose esters, the fatty acids will partly point to the sugar crystals and partly to the water phase.

The (fatty) sucrose ester layer surrounding the sugar crystal prevents further crystal growth. Re-solubilisation and re-crystallisation of the sugar crystal will thus be inhibited. As illustrated in Fig. 6.7, the sucrose ester coat stabilises the water shell around the crystal and prevents evaporation of water from mixed sugar systems, e.g. fondants; this will also lead to a reduction of crystal growth and the resultant gritty mouth feel. Sucrose stearate (HLB 6) is most suitable to reduce viscosity of molasses during sugar production [55]. In application areas such as confectionery (see Section 6.8.2) and icings (see Section 6.8.4) sucrose stearate (HLB 6–11) results in improved product quality [56, 57].

6.6.5 Aeration and foam stabilisation

Many foods are aerated and therefore foam formation and stabilisation are of major importance. Foam formation is a matter of incorporating air into a product, which may include water, fat, proteins, hydrocolloids and other ingredients. The surface tension of water makes it difficult to disperse and retain air in a product. Emulsifiers can lower the surface tension, thus enabling incorporation and retention of air in a product. The more an emulsifier can lower the surface tension, the easier it is to obtain and maintain an effective foam [58, 59]. Emulsifiers with a high HLB value are the most effective at the formation and stabilisation of foams. Sucrose esters with a low substitution degree (high mono-ester) are hydrophilic with an HLB value up to 16, they are the most effective at lowering surface tension. Table 6.2 summarises the effects of sucrose esters with differing HLB values on foam characteristics, e.g. surface and interfacial tensions and foam height. High HLB (11–16) sucrose esters are able to lower the surface and interfacial tensions and produce stable foams.

Table 6.2 Effect of different sucrose esters on foam characteristics

Emulsifier	Mono-ester %	HLB value	Surface tension[a] (mN/m)	Foam height[b] (ml)	
				0 min	5 min
Sucrose laurate	70	15	28.5	127	124
Sucrose palmitate	75	16	34.0	29	26
Sucrose stearate	70	15	34.5	31	29
Sucrose stearate	50	11	36.7	12	9
Sucrose stearate	30	6	46.8	4	2
Distilled water	–	–	72.8		

All tested in 0.1% solutions.
[a] Du Nouy method.
[b] Ross & Miles method.

It is well known that the presence of fatty materials will have a destabilising effect on aqueous foams. The water film around the air pocket will be squeezed away from the fat and the aqueous film will become thin, resulting in the collapse of the air bubble [61]. If the fat in the emulsion is properly emulsified, it will be covered by a layer of surface-active material and will not be able to interfere with the film around the air bubble. The surface-active material should cover the fat globule surface sufficiently and stabilise the fat globules, so that they do not break upon aeration of the emulsion. Emulsifiers with a lipophilic character (low HLB value) stabilise fat better, but do not produce good oil-in-water emulsions, a hydrophilic emulsifier (high HLB) is well equipped for oil-in-water emulsions, but results in less stabilisation of the fat globule. Sucrose esters with a hydrophilic character, but a medium HLB value (6–11) are well equipped for oil-in-water emulsions and have the benefit that they can stabilise the fat globule as well. Thus, these sucrose esters can be used to stabilise foams containing fats more effectively than other emulsifiers.

6.6.6 Anti-microbial properties

Sugars and other solutes (e.g. salt) can be used as preservatives in foodstuffs. The solutes alter the water activity (aw) by increasing the osmotic pressure. This mechanism is used in products like jam. Fatty acids also have an anti-microbial effect, which is related to the chain length and the number and position of the double bonds (*cis* or *trans*), C12, C16:1 and C18:2 are most effective [62–64]. In general, gram-positive bacteria are more susceptible to fatty acids than gram-negative bacteria. Fatty acids cannot be used as broad spectrum preservatives, due to the fact that the inhibitory effect differs from species to species; different fatty acids also have differing effectiveness in preventing microbial growth with the same species.

The effectiveness of (non-inhibitory) fatty acids can be increased when esterified to sucrose, but the anti-microbial spectrum of the sucrose fatty acid ester, however, decreases. Very similar micro-organisms can demonstrate a wide variation of susceptibility to comparable sucrose esters [65]. Di-esters of sucrose appear to be more active than mono-esters, with sucrose dicaprylate having the highest activity [66–68]. The degree of substitution is of extreme importance since the proportion of mono- and di-esters determines the effectiveness of sucrose esters.

The anti-microbial mechanism of sucrose ester involves interaction with the cell membrane causing autolysis. This mechanism can also explain the difference in inhibitory effect on gram-positive, gram-negative bacteria and yeast and fungi. From different studies it is evident that sucrose esters can have an additive or synergistic effect when combined with other food preservatives. A multi-barrier approach for preservation may demonstrate important future applications.

The anti-microbial properties of sucrose esters are not fully utilised in many food systems. The complex matrix of food tends to decrease the anti-microbial properties of the sucrose ester by interactions with fat, starch and proteins. The one area where the anti-microbial properties of sucrose esters are employed is in canned milk coffee served from hot (50–60°C) vending machines in Japan. Sucrose esters act against bacteria causing flat sour spoilage [69].

The selective anti-microbial properties of sucrose esters can be used in fermented foods. Sucrose stearate was tested against a variety of common lactic acid bacteria: *Lactobacillus acidophilus*, *L. bifidus*, *L. lactis*, *L. casei* and *L. plantarum*, *Saccharomyces cerevisiae*, *S. lactis*, *S. cremoris*, *S. diacetylactis*, *S. faecalis* remained unaffected [70].

6.7 Physico-chemical properties of sucrose esters

Sucrose esters are off-white, free-flowing powders, with low taste and odour. Upon ingestion, they are hydrolysed by the bodies' digestive enzymes to their components, sugar and fatty acids, which are metabolised by the body in the normal way. They are non-toxic, non-sensitising and have low irritancy. Sucrose esters are biodegradable and are produced from sustainable and renewable feedstocks. Sucrose esters have a consistent and reusable quality, even though they are derived from natural raw materials.

6.7.1 Solubility

Sucrose esters with HLB $>$ 6 are (partly) soluble in water but have poor oil solubility; those with a lower HLB $<$ 6, i.e. higher di- and tri-ester content have poor water solubility but good oil solubility. For maximum activity, sucrose esters must be first dispersed in cold liquid and then heated to 60–80°C to achieve

Table 6.3 Solubility of sucrose esters in different solvents [58, 71]

		Glycerol		Propylene-glycol		Water		Oil		Ethanol	
Sucrose ester	Mono-ester %	20°C	70°C	20°C	70°C	20°C	70°C	20°C	70°C	20°C	70°C
Sucrose palmitate	75	PS	S	PS	S	PS	S	I	I	S	S
Sucrose stearate	70	PS	S	PS	S	ST	S	I	I	S	S
Sucrose stearate	50	PS	PS	PS	S	PS	PS	I	I	S	S
Sucrose distearate	30	I	PS	PS	PS	PS	PS	I	PS	PS	S
Sucrose distearate	01	I	I	I	PS	I	I	PS	S	PS	S

S = Soluble, ST = Soluble translucent, PS = Partly Soluble, I = Insoluble.

full solubility. Table 6.3 illustrates the differing solubility characteristics of a range of sucrose esters in different solvents [71, 72].

6.7.2 pH stability

Sucrose esters are stable at pH values between 4 and 8. This means that they can be used as emulsifiers in virtually all foodstuffs. At pH values higher than 8, saponification of the ester bond may occur, while under acid conditions inversion of the sucrose moiety is possible. Also acid aggregation may occur at very low pH and high salt concentration.

6.7.3 Thermal stability

Sucrose esters melt at temperatures between 40°C and 60°C, depending on the degree of esterification and the type of fatty acid. Heating to temperatures up to 185°C can be achieved without any deleterious effects on functionality. However, at temperatures above 140°C, some colour formation can occur due to caramelisation of traces of free sucrose present in the product.

6.7.4 Preparation of sucrose ester solutions

To obtain the full functionality of sucrose ester solutions, the powder must be fully hydrated and dissolved. This can be most effectively achieved by using the following guidelines [72]:

(i) Choose the most appropriate solvent for the grade of sucrose (see Table 6.3)
(ii) Disperse the sucrose esters in cold solvent (water, oil, other) – this will prevent lumping

(iii) Heat to 60–80°C, at these temperatures sucrose ester solubility is at a maximum
(iv) If dissolution in warm solvents is required, first wet the sucrose ester with ethanol or propylene glycol to improve solubility. Lumping can be reduced by premixing with easy soluble ingredients like sugars
(v) Upon emulsification the remaining undissolved sucrose esters will dissolve at the oil/water interface
(vi) Incorporation of air into sucrose ester solutions will produce very stable foams, which can influence functionality and increase viscosity. The design of stirrers and tanks used for preparation of sucrose ester solutions should ensure that air is not incorporated into the mixture
(vii) Sucrose ester concentrations of 10–15% can increase the viscosity of solutions considerably
(viii) Stock solutions of sucrose esters are susceptible to microbial attack, so the use of preservatives or pasteurisation should be considered if solutions are to be stored for more than 24 hours

It is also important to consider the other ingredients that will be combined with the sucrose esters. If there are high levels of acids or salts, these can degrade the sucrose esters. With these types of products it is essential to prepare the emulsion using the sucrose ester before addition of the salts and acids.

6.8 Food applications

6.8.1 Dressing and sauces

6.8.1.1 Sterilised emulsified sauces

Mushroom and cheese sauces are examples of emulsified sauces with a pH higher than 4.5. In order to improve shelf life the sauce is sterilised. Difficulties such as instability and colour formation occurring upon sterilisation can be minimised by using sucrose esters with HLB 15. Sucrose esters will improve the emulsion, ensuring small oil droplet size. This will not only improve shelf life stability but also the appearance (whiteness) and the creamy mouth feel will be enhanced. During sterilisation of the sauce, proteins can react with reducing sugars causing colour formation (maillard reaction). Sucrose esters interact with proteins (see Section 6.6.2) thus reducing the reactivity of the proteins with the sugars and hence the sauce will retain its natural colour [73].

A high HLB sucrose ester can be used to stabilise a carbonara sauce. Figure 6.8 compares a sauce stabilised with protein and a high HLB sucrose ester. The sauce stabilised with the sucrose ester does not show signs of protein flocculation.

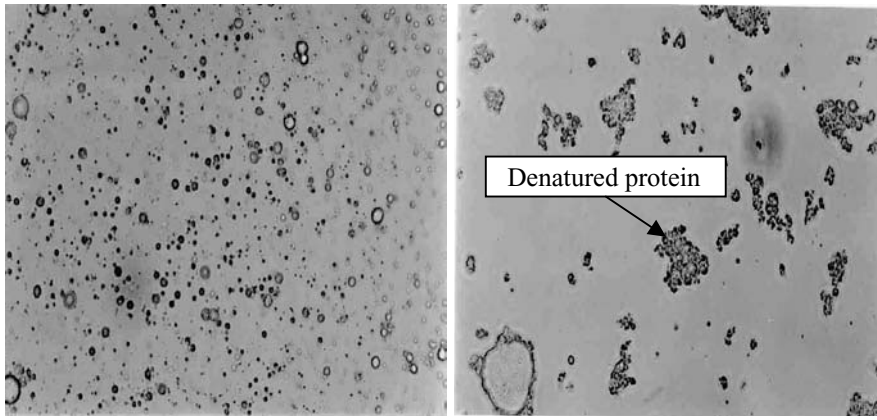


Fig. 6.8 Carbonara sauce with 1% high HLB sucrose ester and 1% protein [74].

6.8.1.2 Mayonnaise-like products and dressings

In traditional mayonnaise, egg yolk is used as the natural emulsifier. Egg yolk is a natural raw material that is subject to fluctuations in price and quality and is not always preferred due to its cholesterol content, the risk of salmonella and its allergen potential. Using sucrose esters to replace egg yolk, it is possible to produce cholesterol-free mayonnaise-like products. High HLB sucrose esters are more suitable for producing oil-in-water (o/w) emulsions like mayonnaise than lecithin (emulsifying component in egg yolk) with its low HLB value (see 6.6.1 emulsification).

Light mayonnaise products (40–55% oil) are relatively unstable; the lower the fat content the less stable the emulsion. In order to produce a stable, light mayonnaise (55% oil) combinations of egg yolk and high HLB sucrose esters can optimise viscosity and decrease oil droplet size. This combined with a high homogeniser rotational speed (8000 rpm) and long emulsification time (5 min) enable the production of stable emulsions [75]. Pasteurised light mayonnaise (20% oil) with 1% high HLB sucrose esters, emulsified for 4 minutes in a colloid mill, resulted in a product with an average droplet size of 3 μm (Malvern Mastersizer) and good shelf-life stability (1 month at 42°C) [76].

Sterilised, light mayonnaise (50% oil) emulsified with sucrose esters (1%) compared to the standard with whey proteins (1%) have a smaller average oil droplet size and better reflection (whiteness) (see Table 6.4). The emulsions were produced using a colloid mill; average oil droplet size was measured with Malvern Mastersizer, and the reflection was measured with a photovolt (green filter).

Table 6.4 Reflection and average oil droplet size in sterilised light mayonnaise [77]

	Sucrose esters	Whey protein
Reflection before sterilisation	72.1	69.8
Reflection after sterilisation	69.6	62.4
Average oil droplet size (μm)	2.36	9.81

Cold processing is also possible using sucrose esters; high HLB sucrose esters are completely soluble in water, and even reasonably soluble in cold water. In sauces with more than 40% fat, the water phase will contain high levels of salts and acids. Sucrose esters are sensitive to elevated levels of salts and acid, therefore it is advised to first make the emulsion and add the salts and acids afterwards (see Section 6.7.4).

6.8.2 Confectionery

Sucrose esters can be used in various confectionery products; they are used primarily as emulsifiers and stabilisers but can also inhibit crystal growth of sugar and fats, and facilitate aeration and increase lubrication.

6.8.2.1 Caramels and high boils (candies)

Fats and oils can separate from the caramel mixture in the final stages of boiling (ca 125°C). The use of an emulsifier will not only prevent the separation of fats and oils, but also prevent adhesion to moulds or die cutting machinery. The emulsifier can also reduce adhesion to wrapping materials and reduce stickiness at high temperature and humidity. The use of sucrose stearate at 5–10% on the oils is effective.

At the higher boiling temperatures (130–150°C) of high boils (candies), the dispersion of fats and oils is difficult using either mono-glycerides or sorbitan esters. The addition of sucrose esters (with HLB 7–13) produce good results in these products [78, 79].

6.8.2.2 Chocolate

During the manufacture of chocolate, sucrose esters with a low HLB value lower viscosity by reducing the friction between the components, and also inhibit the growth of cocoa butter and sugar crystals (bloom). In chocolate coating for confectionery, sucrose esters effectively emulsify and disperse fats, cocoa and sugar [79, 80]. Sucrose esters with high levels of di- and tri-esters can be used as effective alternatives to soya lecithin; the effect on the viscosity of the chocolate mass is similar to that of lecithin.

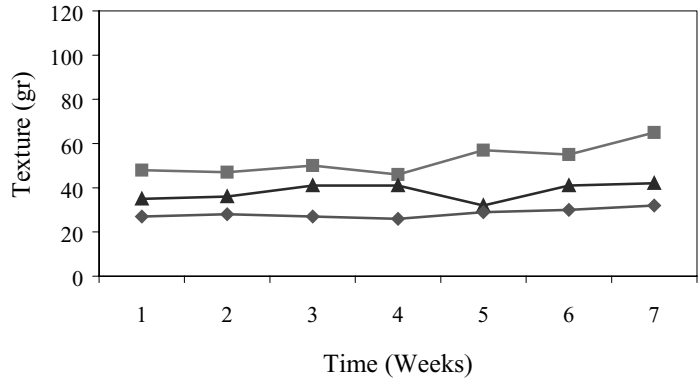


Fig. 6.9 Texture of marshmallow with 0.05% sucrose ester, stored at 20°C and 60 ERH in closed bags.

6.8.2.3 Marshmallow

Aerated products, such as marshmallows, tend to become hard during storage. Research shows that the water content of the product remains constant during storage but the change in texture is mainly due to sugar crystallisation. Marshmallow is a mixture of different sugar (syrups), water, gelatine and a whipping agent that is cooked and then mixed with flavours, colours and additional glucose syrup. This mixture is whipped and upon further cooling, gelation traps air in the matrix, contributing to the texture. Sucrose esters with an HLB value of 6–15 act as whipping agent and texturisers in marshmallows; the product has a softer texture and will remain softer for at least seven weeks (Fig. 6.9) [81].

6.8.2.4 Tablets

Confectionery and pharmaceutical tablets are usually produced by means of compression. In Europe, magnesium stearate is generally used for lubrication of the mould, thus maximising production capacity on high-speed tabletting machines. Lubricants also effect pressure transmission, disintegration and dissolution of the tablet. Sucrose esters with a high substitution degree (low HLB) can be used to replace magnesium stearate in tablets for the Japanese market where magnesium stearate is not permitted. Compared to magnesium stearate, sucrose esters do not react with actives or other ingredients, they are also neutral in taste and show better disintegration and dissolution properties. Typical usage rates are 0.5–3.0% of sucrose ester [82].

6.8.3 Bakery

Many studies have been carried out using sucrose esters in bakery applications. In Europe, the use of sucrose esters is not permitted in bread, but they can be used in bakery wares (see Section 6.9.1). The main uses include improvements in texture and shelf life in products such as cakes or fat reduction in biscuits and other products.

6.8.3.1 Sponge cakes

Sponge cakes are typically low fat cakes that rely on incorporated air for volume and texture. Sucrose esters alter batter specific gravity, cake volume, crumb firmness and the texture of sponge cake. Pierce and Walker [83] used sucrose esters with HLB values 11–16 in sponge cakes. This resulted in slightly larger volumes than the control. However, when the esters were pre-hydrated (see Fig. 6.6), the resultant increases in volume were much improved. The pre-hydrated sucrose esters at 2.5 and 4% concentrations on the flour also greatly improved both initial tenderness and texture at 2 weeks shelf life. In this study, the reference emulsifier was a commercial α-mono/diglyceride in the plastic form [83]. Unpublished results from Somers compared the use of four emulsifiers in sponge cakes [84]. The sucrose ester was pre-hydrated and all emulsifiers were used at 4% on flour weight. The sucrose ester gave a softer texture and a greater cake volume when compared to mono- and diglyceride (MDG), polyglycerolester (PGE), polyglycerol monstearate (PGMS) and a mixture of MDG and PGE (see Fig. 6.10).

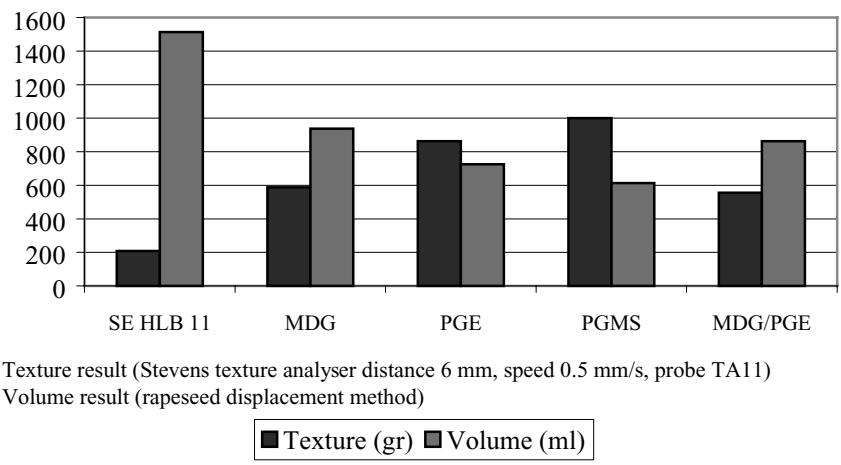


Fig. 6.10 Sponge cakes with 4% emulsifier (sucrose ester hydrated in water).

6.8.3.2 Biscuits

Attempts to lower fat (by 25–50%) in biscuits usually result in increased hardness and major changes in dough characteristics. Increased attention on fat reduction in food products has resulted in the use of sucrose esters and other emulsifiers to produce acceptable biscuits containing a reduced fat level. The hardness resulting from a reduction in fat in biscuits is attributed to sugar agglomeration. The fat reaches a minimum where it cannot fully coat all the available sugar and this results in increased sugar agglomerates and increased hardness. Sucrose esters can reduce the formation of sugar agglomerates by working in two ways: The emulsifying properties of the sucrose esters ensure that the reduced amount of fat is dispersed in the matrix as efficiently as possible. The second effect is on the sugar particles. The sucrose ester molecules reduce sugar crystal growth and ensure that agglomerates do not readily form. Breyer and Walker investigated the use of sucrose esters in biscuits and demonstrated that there was little difference in the dough characteristics [85].

6.8.3.3 Bread

As mentioned earlier sucrose esters cannot be used in bread in Europe, however this application has been utilised in the USA. Bread quality depends on factors such as volume, texture and rate of staling. As already discussed sucrose esters interact with both starches and gluten to influence texture and starch retrogradation. Higher HLB (16) sucrose esters are most effective in improving loaf volume when used at moderate concentrations; they are also effective in improving initial softness. Long-term softness, however, was improved more by mid-range HLB (11) sucrose esters [85].

Frissen compared the use of sucrose esters alone and in combination with gluten in bread [86]. Figure 6.11 illustrates the comparison of the bread prepared using gluten and the addition of sucrose esters. Sucrose stearate with high HLB (0.2 % on flour) improved the volume over the reference loaf. In combination with gluten (5.1% gluten plus 0.2% sucrose stearate on flour) there was also an improvement over the gluten addition (5.3% on flour).

6.8.4 Icings and fillings

Icings and fillings play an important role in bakery products. Emulsifiers and, in particular, sucrose esters provide the potential to improve product quality and shelf life. Important requirements for icings are emulsion stability, inhibition of fat and sugar crystals growth as well as good air incorporation and stabilisation. These requirements are of increasing importance in frozen products. In general, sucrose esters with medium HLB value (11) at a dosage of 0.1% will be beneficial in icing, see Fig. 6.12 [87].

Sucrose esters can be used in a wide range of icing-type products [88] as illustrated in Fig. 6.12. and Table 6.5.

Fig. 6.11 Pictures of bread:1. standard, 2. plus gluten, 3. plus gluten and sucrose ester 4. plus sucrose ester.

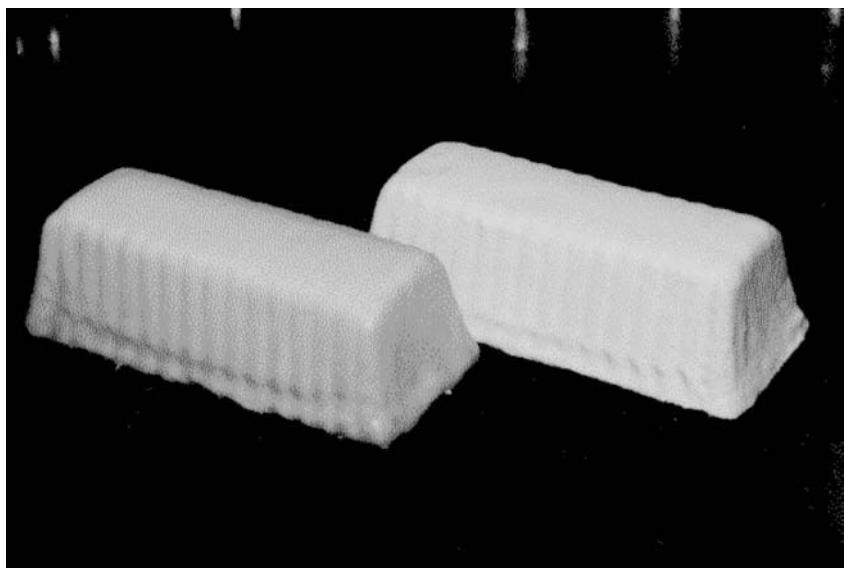


Fig. 6.12 Pound cake glazed with icing. Front standard glaze; Back plus medium HLB sucrose ester (0.1%). Photographed after 5 weeks storage [87].

Table 6.5 Average crystal size of standard icing and icing containing 0.1% medium HLB sucrose ester [87]

	Average crystal size (μm) (Malvern Mastersizer)	
	Standard	0.1% sucrose ester
Day 0	291	300
Week 5 (stored at 20°C)	480	410
Week 5 (stored at –35°C)	365	250

6.8.4.1 Flat icings

Also termed as water icings or glazes these are based on sugar syrups to which are added colour and/or flavours. The whiteness and freeze stability are important features. The whiteness of the product is largely dependent on the small sugar particle size directly after production, and also after storage at ambient temperature or under frozen conditions. The use of sucrose esters results in icings having a superior white colour without the need for any whitening agents (e.g. titanium dioxide). The sucrose esters also prevent crystal growth (see Section 6.6.4) on storage and thus reduce the gritty texture associated with larger crystals. Table 6.5 details average crystal sizes in standard icings with and without the addition of a medium HLB sucrose ester.

6.8.4.2 Butter cream icings

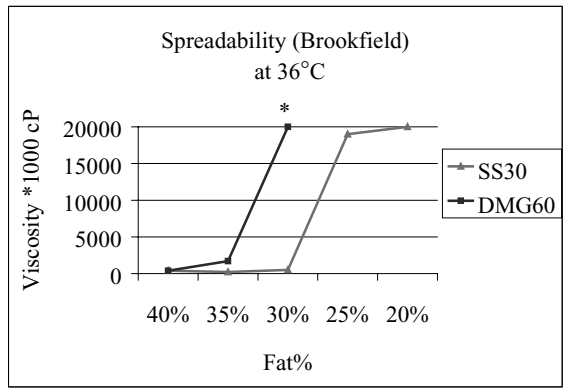
Butter cream icings are basically flat icings with butter oil emulsified in the sugar syrup. The emulsified butter oil gives a creamier mouth feel and a softer texture to the icing. The basic o/w emulsions are obtained by dissolving sucrose esters in the sugar syrup and heating to at least 65°C. The butter oil is then added while mixing thoroughly. Stable emulsions will thus be obtained which can be stored for long periods at low temperatures.

6.8.4.3 Fluffy icings

Fluffy icings are aerated varieties of the two icings mentioned above. These icings are lighter with respect to eating properties while still giving a sweet and creamy mouth feel. In fluffy icings, sucrose esters are of special benefit since they facilitate air incorporation. In general, the foams obtained using sucrose esters as the aerating agent can be characterised by their small air cell size and long-term stability at low temperatures.

6.8.4.4 Fat fillings

Fat fillings and aerated emulsified fat fillings are high caloric components in bakery products. Incorporation of air and/or reduction of fat can lower the calorie content of the fillings, however, product quality is usually adversely affected. By



* Measurements above 2,000,000 cP were not possible with the equipment

Fig. 6.13 Spreadability of fat fillings with 40% to 20% fat and raising dosages (0.3%–0.6%) of sucrose ester and distilled monoglyceride [92].

lowering the amount of fat from 40% to 20% in fat fillings, the proportions of sugar, milk powder and dextrose is automatically raised. This increase of solids in the fat matrix results in a reduction of spreadability as measured by viscosity. Addition of emulsifiers with a low HLB value, such as sucrose stearate HLB 6 or distilled monoglyceride, can retain the spreadability when the fat content is lowered. Voermans investigated a range of fat fillings containing 40% to 20% fat, and levels of 0.3% up to 0.6% emulsifier [89]. A 30% fat emulsion with sucrose stearate (0.4%) resulted in a similar spreadability (viscosity) to the standard fat filling with 40% fat (ca: 400 00 cP) (see Fig. 6.13.).

Reducing calories in emulsified oil-in- water fat fillings can be achieved by lowering the fat content and the density. These fillings contain 5–20% fat, milk powder, sugar (syrups), a mixture of hydrocolloids and a minimum of water to maintain a low water activity. Hydrocolloids or fibres such as inulin partially replace fat and improve the viscosity and body of the product. This type of emulsion tends to be very difficult to aerate due to the hydrocolloids that increase the viscosity of the aqueous phase and make emulsification difficult to achieve and maintain. Emulsifiers with a high surface activity, such as sucrose esters with HLB value 6–15, will incorporate the fat into the viscous water phase and also lower the surface tension to a level where aeration can be easily achieved. A combination of sucrose esters is best suited to this application. The ratio of low mono-ester (HLB 6), high mono-ester (HLB 15) depends on the amount of fat in the formulation and the required finished product density. Low fat content and low product densities require higher levels of high mono-ester emulsifier. If higher fat levels are employed low mono-esters are more beneficial.

6.8.5 Ice cream

Ice cream is the classic product requiring the use of emulsifiers—it is an aerated emulsion that requires high performance emulsifiers to achieve good product quality and shelf life. Emulsifiers are used to decrease freezing time, improve whipping quality and to produce a dry ice cream with a fine, stiff texture that melts slowly and uniformly [90].

Emulsifiers lower the surface tension of liquid ice cream. This will result in smaller fat globules at similar homogenisation pressures. Immediately after homogenisation and during aging various entities compete for position at the oil–water interface such as proteins, emulsifier, lipoproteins, caseins [91]. Upon aeration and freezing of ice cream, the following changes take place: The collision frequency of fat globules increases and ice crystals force the fat globules into smaller spaces, resulting in shape distortion. Freezing of water can dehydrate adsorbed protein films thereby disrupting the protein–emulsifier complexes. The surface viscosity and crystallisation of fat globules may cause the lipophilic portion of the emulsifier to be immobile. The overall membrane characteristics change, i.e. increased brittleness and an increased tendency to rupture.Upon rupture, liquid oil flows out of the fat globule and a part of it promotes agglomeration of partly damaged globules. A certain amount of fat destabilisation is desirable to coat air cells with liquid oil, while at the same time retaining enough clusters of intact fat globules to provide a continuous matrix of protein in the serum phase. A balance between agglomeration of ruptured and intact fat globules produces the desired properties in ice cream.

Hydrophilic emulsifiers encourage fat agglomeration in ice cream due to a weak protein–emulsifier film formed around fat particles. Because the film is weak, freezing and agitation readily destabilises the emulsion, causing agglomeration. Unsaturated emulsifiers form stronger films leading to firmness, structure and stability. Saturated emulsifiers form weaker and more rigid films, and increasing levels of unsaturation increase fat destabilisation. Also, short-chain fatty acids tend to promote fat destabilisation more than long-chain fatty acids [91]. Changing the proportions of different types of emulsifiers can lead to the desired properties in ice cream.

Evaluating sucrose esters in ice cream, Buck *et al.* clarified that ice cream produced with high mono-sucrose ester (70%) produced the highest overrun of $>180\%$ compared to samples produced with mono- and diglyceride (MDG) $<120\%$ and the standard $<120\%$ overrun. High mono-sucrose esters having the highest overrun is also confirmed by El-Dairy *et al.* in a comparison between ice cream with lecithin and different grades of sucrose esters [92].

Depending on dosage, sucrose esters show similar destabilisation (coalescence, clusters) upon freezing as emulsifiers being used traditionally. The sensory evaluation was in favour of ice cream produced with sucrose stearate having medium HLB of 11 at a dosage of 0.25% [91]. In other ice cream combinations sucrose palmitate having a HLB of 16 at a dosage of 0.2% was favoured [92].

6.9 Legal status

6.9.1 Europe

The use of food additives such as emulsifiers is limited to the European Union and the legislation is published in the European Parliament and Council Directive No 95/2/EC on food additives other than colours and sweeteners (OJ L61, 18.3.1995) of 20 February 1995. According to this directive, all sucrose esters with less than 7% of tetra- and higher ester are registered under E473.

The ADI for sucrose esters is 25 mg/kg body weight and therefore the use of sucrose esters is limited to specified applications/product types and the quantities that can be used are also specified in Annexes to the Directive. These are detailed in Table 6.6.

6.9.2 USA

Sucrose fatty acid esters (SFAE) are approved by the FDA (CFR 172.859) and are more or less in line with European legislation.The FDA have recently (effective 20 August 2003) amended the food additive regulations to provide for the safe use of sucrose oligoesters referred to as SOE (sucrose esters of fatty acids with an average degree of esterification ranging from 4–7) as emulsifiers or stabilisers, at a level not exceeding 2.0%, in chocolate and butter-substitute spreads.

Table 6.6 European Parliament and Council Directive No 95/2/EC on food additives, Annex IV

Bakery wares	10 g/kg
Fat emulsions for bakery wares	10 g/kg
Beverage whiteners	20 g/kg
Dairy based beverages	5 g/kg
Edible ices	5 g/kg
Deserts	5 g/kg
Sugar confectionery	5 g/kg
Chewing gum	10 g/kg
Sauces	10 g/kg
Soups	2 g/kg
Bouillon	2 g/kg
Dietetic foods	5 g/kg
Food supplements	q.s.
Canned coffee	1g/l
Non-alcoholic anisette, almond drinks, coconut drinks	5 g/kg
Powder for the preparation of warm beverages	10 g/kg
Heat treated meat products (on fat)	5 g/kg
Surface treatment, fresh fruits	q.s.
Spirituous beverages (excl. beer and wine)	5 g/kg
Cream analogues	5 g/kg
Sterilised cream (with/without a reduced fat content)	5 g/kg
Baby food	120 mg/l

6.9.3 Canada

Sucrose esters approval is expected in 2004 and is expected to be similar to the European legislation.

6.9.4 Japan

Sucrose esters are generally approved in foodstuffs and have been used in Japan for over 30 years.

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7 Sorbitan esters and polysorbates

Tim Cottrell and Judith van Peij

7.1 Introduction

Emulsifiers used in food applications are dominated by mono- and diglycerides and their derivatives. However, another group of compounds derived from sorbitol rather than glycerol make up the group of emulsifiers known as sorbitan esters, which can further be modified to polysorbates. Sorbitan esters and polysorbates in non-food industry are often referred to as non-ionic surfactants, where emulsifier is the term preferred for these same compounds in the food industry. While perhaps accounting for less than 15% of the food emulsifiers used, this group of unique emulsifiers plays an important role in the production of industrialized food products.

This chapter will describe the means of production and the unique chemical and physical properties of sorbitan esters and polysorbates. A description of the structure/function relationship will correlate the chemical and physical properties of these compounds with their properties in solutions and in emulsions, as well as with their properties in their main applications in food. A brief summary of the EC and US regulations, together with the toxicological issues, will also be discussed.

7.2 Historical development

Atlas Powder Company – the predecessor of what is now ICI America – was initially an explosives company. Nitrated mannitol was found to be a highly effective material for blasting caps. In the 1930s, researchers found that mannitol, which occurs naturally in small amounts, could be more efficiently synthesized by the electrolysis of sugar. However, during the chemical synthesis of mannitol, four times the amount of a related isomer, sorbitol, was produced. A commercial application of sorbitol was required. Since sorbitol had many similar properties to glycerol, it was soon introduced directly into food and cosmetics applications as an alternative. It was also found that sorbitol could be converted readily into vitamin C, or reacted with fatty acids to create esters, which proved to be valuable emulsifiers for foods and other applications. In 1938, the Atlas Powder Company introduced commercial sorbitan fatty acid esters under the trade name

'Span'. Around the same time, knowledge surrounding ethylene oxide and its reactivity with active hydrogen atoms coupled with its commercial availability initiated the development of polyoxyethyene derivatized emulsifiers. By 1942, the polyoxyethylene (20) sorbitan esters or polysorbates were commercialized under the trade name 'Tween'. Although Span and Tweens are registered trade names for sorbitan esters and polysorbates respectively, the terms are still often used as common names or used interchangeably in literature. Sorbitan esters and polysorbates are amongst the most universally recognized, safe, regulatory approved, high performance emulsifiers used not only in food industry but also in personal care, cosmetic, textile and pharmaceutical industries.

7.3 Production

7.3.1 Production of sorbitan esters

Sorbitan esters of fatty acids are derived from a reaction of sorbitol and a commercial grade fatty acid. Sorbitol, the starting material for sorbitan esters along with mannitol, was originally produced from the hydrogenation of sucrose. However, currently a more economic and pure form of sorbitol is produced commercially from D-glucose which itself is derived from corn syrups (maize) or tapioca. D-glucose is reacted with hydrogen gas under pressure in the presence of a catalyst such as nickel phosphate [1] or ruthenium dichlorotriphenyl phosphine [2]. The product of this hydrogenation process is D-glucitol, or what is commonly known as sorbitol. Commercial grade sorbitol typically contains minor amounts of other polyols such as mannitol. Sorbitol belongs to a group of compounds called sugar alcohols or polyols, which have all the properties similar to that of glycerol.

Similarly, commercial grade fatty acids are not pure compounds but mixture of other fatty acids. The purity of the acid can vary considerably depending on the original raw material source as well as the manufacturing process. For example, commercially available stearic acids have true stearic acid (C18:0) contents varying from below 40% for single pressed quality to above 95% for high purity grades. Fatty acids from C8:0 to C22:0 can be used. However, most common fatty acids for food application are the products based on C18:0 (stearic acid) and C18:1 (oleic). High oleic fractions of the fatty acids that are low in polyunsaturated fatty acids (e.g. C18:2, C18:3) are used for oxidative stability and flavor/odor of the emulsifier as well as the finished product. Fatty acids derived from vegetable sources such as palm oil, soybean oil, canola oil and sunflower oil are used almost exclusively over animal derived fatty acids.

The popular method for producing sorbitan esters (Fig. 7.1) is the direct fatty acid esterification of sorbitol with fatty acids [3]. Blends of both an acidic catalyst such as phosphoric acid and a caustic soda type catalyst are used together to drive the reaction. The acid catalyzes the dehydration of sorbitol, resulting in a

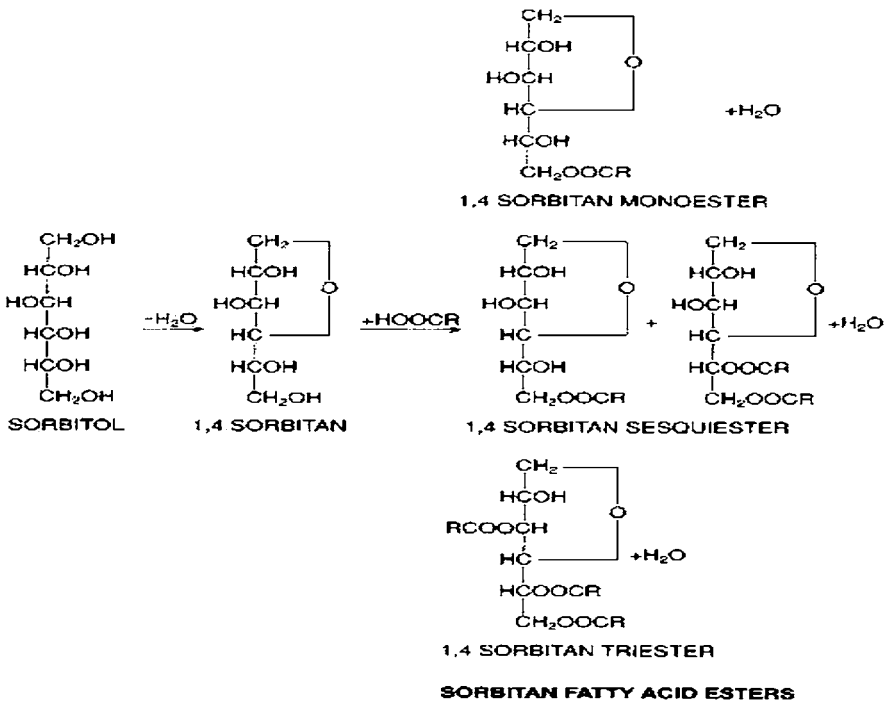

Fig. 7.1 Direct fatty acid esterification of sorbitol with fatty acids.

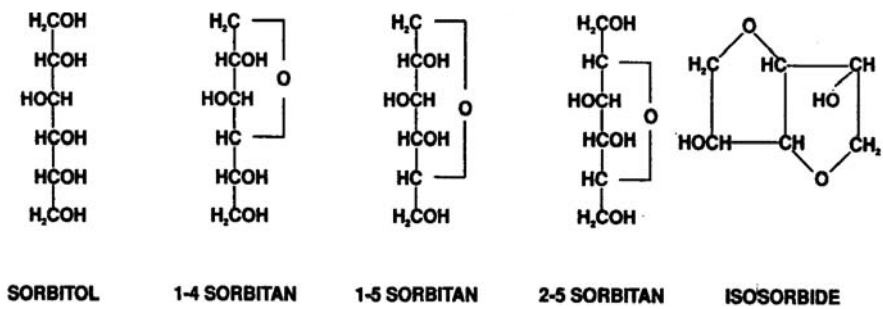

Fig. 7.2 Common sorbitol derived components found in sorbitan esters.

mixture of linear sorbitol, 1,4-sorbitan, 1,5-sorbitan, 2,5-sorbitan and isosorbide (Fig. 7.2). The caustic catalyst directs the esterification reaction [4].

However, in most commercial processes the dehydration of the sorbitol and the esterification reactions occur concurrently. The unique blends of catalyst systems, the reaction temperatures and specific reaction conditions, all contribute

to a manufacturers' proprietary process. One method of producing lighter colored sorbitan esters uses a two-step addition of the catalyst [5]. The acid system is used in the first stage, creating the mono- and dianhydrides or cyclic compounds. The cyclic compounds are less sensitive to darkening when further reacted with the fatty acid under caustic conditions resulting in a lighter colored product. Conversely, in a faster direct method, hydrogen peroxide can be used following production to reduce color bodies.

The most common sorbitan ester, sorbitan monostearate, is the product made from equimolar concentrations of fatty acid and sorbitol. Sorbitan tristearate is made from 3 moles stearic acid to each mole of sorbitol. The sorbitan esters of stearic, lauric, oleic and other fatty acids can all be further reacted with ethylene oxide to produce the polyoxyethylene sorbitan esters or polysorbates. Usually, the high melt point stearic (and palmitic) acid esters of sorbitol are finished by a spray chilling process that congeals the product into a micro-bead or coarse powder. Although the actual composition of each ester product is poorly characterized, they do conform to defined specifications (Table 7.1). Generally, but not always, specifications as outlined in the Food Chemical Codex, European and US Pharmacopoeias as well as the National Formulary, conform to one another. Due to the variety of components in the reaction mixture and the commercial process, the final sorbitan ester product is not a pure compound

Table 7.1 EU regulations for several common sorbitan esters

	Sorbitan monolaurate	Sorbitan monostearate	Sorbitan tristearate	Sorbitan monooleate
E No.	E493	E491	E492	E494
FDA reference	–	21CFR172.842	Self-determined GRAS	–
Sorbitol, sorbitan and isosorbide content	Min 95%	Min 95%	Min 95%	Min 95%
Acid value	Max 7	Max 10	Max 15	Max 8
Saponification value	155–170	147–157	176–188	145–160
Hydroxyl value	330–358	235–260	66–80	193–210
Water	Max 2%	Max 2%	Max 2%	Max 2%
Sulfated ash	Max 0.5%	Max 0.5%	Max 0.5%	Max 0.5%
Arsenic	Max 3 mg/kg	Max 3 mg/kg	Max 3 mg/kg	Max 3 mg/kg
Heavy metals (as Pb)	Max 10 mg/kg	Max 10 mg/kg	Max 10 mg/kg	Max 10 mg/kg
Lead	Max 5.0 mg/kg	Max 5.0 mg/kg	Max 5.0 mg/kg	Max 5.0 mg/kg
Mercury	Max 1 mg/kg	Max 1 mg/kg	Max 1 mg/kg	Max 1 mg/kg
Cadmium	Max 1 mg/kg	Max 1 mg/kg	Max 1 mg/kg	Max 1 mg/kg

From Commission Directive 98/86/EC of November 1998 amending Commission Directive 96/77/EC laying down specific purity criteria on food additives other than colors and sweeteners.

but is a heterodispersed 'soup' of components, all related but dissimilar. It is not surprising that differences in raw materials and proprietary processes can result in apparent differences in color, flavor and physical properties between sorbitan esters from different suppliers.

7.3.2 Production of polysorbates

Ethylene oxide, a compound derived from the petrochemical industry, is one of the major building blocks used in the production of polysorbates. In commercial production, the oxidation of ethylene is brought about using a silver-catalyzed air based or oxygen based process [6]. Polysorbates are made by further modifying the sorbitan esters with ethylene oxide in a specialized pressure vessel referred to as an autoclave. Small amounts of a basic catalyst, such as potassium hydroxide, are used during the process [7]. The exothermic ethoxylation reaction requires constant agitation and cooling to maintain a reaction temperature between 120 and 140°C. The ethylene oxide pressure is maintained at 40–80 psig during the reaction. Ethylene oxide demands caution when handling, as it is both physiologically damaging and a highly explosive compound. Controls are in place during manufacture to limit the amount of residual ethylene oxide and 1,4-dioxan in the final product. During the reaction the original esters are rearranged, resulting in a product with an assortment of positional isomers. The polysorbates are made from a reaction of an average of 20 moles ethylene oxide to one molecular weight equivalent of the sorbitan ester. The linear chain of 20 moles polymerized ethylene oxide comprises the hydrophilic portion of the emulsifier. There are a number of related compounds all made in a similar fashion. Twenty moles of ethylene oxide can be reacted with low alpha monoglycerides to produce ethoxylated monoglycerides. Ethoxylated monoglycerides are made from glycerol esters of stearic and palmitic acid and are commonly referred to as polyglycerate 60. It is also possible to react ethylene oxide directly with a fatty acid such as the polyoxyethylene (8) stearic acid. Block copolymers, a group of compounds made by polymerizing long chains of ethylene oxide attached to long chains of polymerized propylene oxide, are products with exceptional surfactant activity and find applications in many industries. Ethylene oxide can be reacted with various other alcohols to produce a variety of compounds.

Although these ethoxylated emulsifiers are all related compounds, this discussion is limited to the ethoxylated sorbitan esters or polysorbates that have direct application in food products. The commercial polysorbate products are not chemically pure compounds but are statistical polydispersed compounds [8]. That is, the product is a mixture of chemical compounds all closely related with properties and structural distribution clustered around a mean molecular weight (MW).

Table 7.2 Nomenclature and physical characteristics of sorbitan esters

Generic name	Common name	Physical form (25°C)	HLB* (±1)
Sorbitan monolaurate	Span 20	Liquid	8.6
Sorbitan monopalmitate	Span 40	Solid	6.7
Sorbitan monostearate	Span 60	Solid	4.7
Sorbitan monooleate	Span 80	Liquid	4.3
Sorbitan tristearate	Span 65	Solid	2.1
Sorbitan trioleate	Span 85	Liquid	1.8

HLB* = Hydrophyle–Lipophyle Balance.

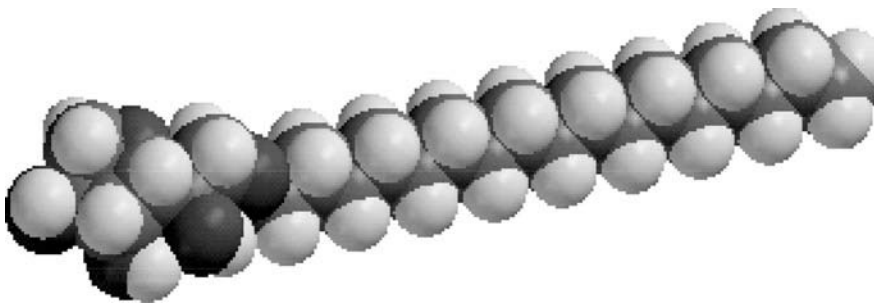

Fig. 7.3 Chemical structure of sorbitan monostearate.

7.4 Physicochemical properties

Sorbitan esters of fatty acids are non-ionic, low HLB lipophylic emulsifiers. The hydrophilic/lipophylic properties of the sorbitan ester depend on the degree and type of fatty acid esterified. The shorter the chain length of the fatty acid, the lower the HLB (Table 7.2) Sorbitan monostearate shares some characteristics with the related monoglyceride counterparts, such as glycerol monostearate.

However, because of the bulky hydroxylated sorbitan ring, sorbitan monostearate (Fig. 7.3) is slightly more hydrophilic than glycerol monostearate. More important, sorbitan monostearate is monomorphic. Sorbitan tristearate has no surfactant properties and is ineffective for stabilizing emulsions. Sorbitan tristearate has a molecular structure (Fig. 7.4) very similar to that of a triglyceride [9] but with dissimilar crystallization properties. While triglycerides are polymorphic, that is they can exist in one of several crystalline phases, sorbitan tristearate is stable in one phase, i.e. the alpha crystalline phase. The shorter chain and oleic sorbitan esters are of limited importance for food systems since they are restricted from use in most markets. These esters are primarily used

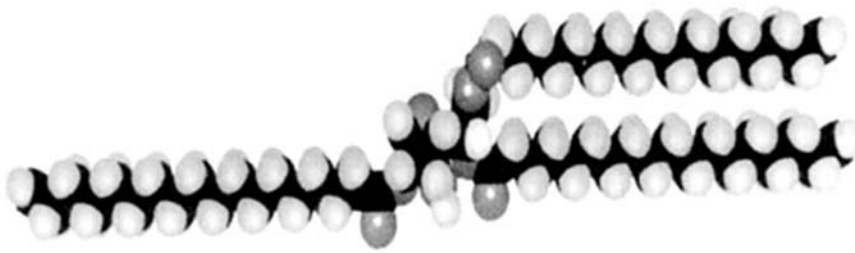

Fig. 7.4 Chemical structure of sorbitan tristearate (Reproduced by permission from [9]).

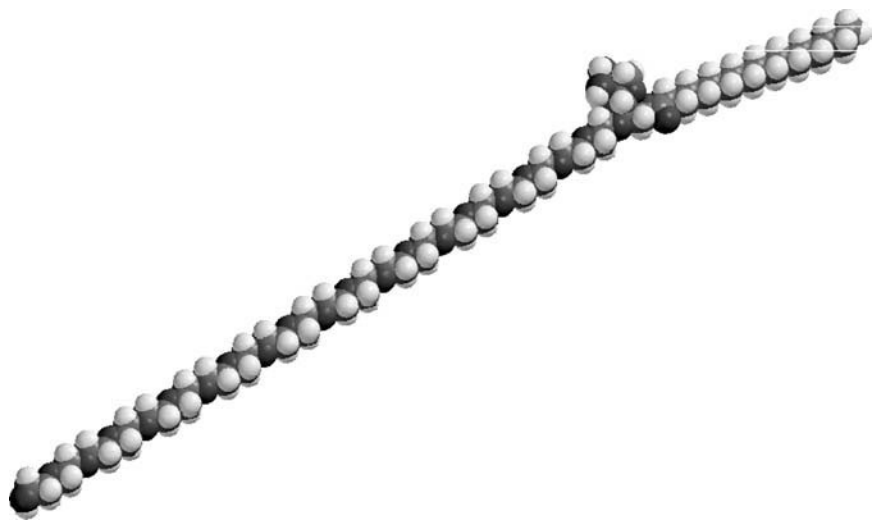

Fig. 7.5 Chemical structure of polysorbate 60. Note: for illustrative purposes the polyoxyethylene chain (20 moles of EO) is located on a sole hydroxyl group. Typically, the polyethylene chain (20 moles of EO) may be associated with one or more of the three available hydroxyl groups.

as intermediates for the polyoxythylene derivatives that have greater food application.

The polysorbate family of products is amongst the most hydrophilic or water soluble emulsifiers allowed in foods, due to the long polyoxyethylene chain (Fig. 7.5). The unique qualities of each polysorbate is attributed to the different fatty acid used in each product as the ethylene oxide chain length, controlled at an average of 20 moles and it does not change between products. Polysorbate 60 and the other monoesters may have the ethylene oxide chain located on more than one hydroxyl groups of the 1,4-sorbitan. However, the polysorbate 65 and polysorbate 85 triester products have a single hydroxyl site for ethoxylation.

Table 7.3 Nomenclature and physical characteristics of ethoxylated esters

Generic name	Common name	Other name	Moles of EO/ester	Physical form (25°C)	HLB* (±1)
Polysorbate 20	Tween 20	Polyoxyethylene (20) sorbitan monolaurate	20	Liquid	16.7
Polysorbate 40	Tween 40	Polyoxyethylene (20) sorbitan monopalmitate	20	Liquid	15.6
Polysorbate 60	Tween 60	Polyoxyethylene (20) sorbitan monostearate	20	Gel	14.9
Polysorbate 80	Tween 80	Polyoxyethylene (20) sorbitan monooleate	20	Liquid	15.0
Polysorbate 65	Tween 65	Polyoxyethylene (20) sorbitan tristearate	20	Solid	10.5
Polysorbate 85	Tween 85	Polyoxyethylene (20) sorbitan trioleate	20	Liquid	11.0
Polglycerate 60	Ethoxylated mono and diglycerides	Polyoxyethylene (20) mono- and diglycerides of fatty acids	20	Liquid	13.0
	Myrj 45	Polyoxyethylene (8) stearate	8	Gel	11.1

All 20 moles of ethylene oxide are in a single chain, which results in a strongly polarized structure. The short-chain fatty acid polysorbate 20 has the highest HLB at 16.7 followed by the other longer chain products (Table 7.3). All polysorbates, however, are considered hydrophilic and are truly water soluble.

7.5 Emulsifiers in solution

7.5.1 Emulsions

The hydrophile–lipophyle balance (HLB) system was designed to assist the formulator to select appropriate non-ionic emulsifiers, such as sorbitan esters and polysorbates, in making emulsions. As most food applications of emulsifiers do not directly involve stabilizing emulsions, there is limited relevance for the HLB system in foods. Nevertheless, the HLB system is an excellent way of characterizing emulsifiers. A detailed description of the HLB system is discussed by

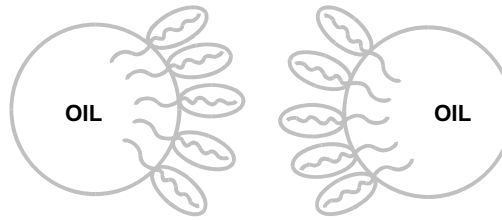

Fig. 7.6 The hydrated polyoxyethylene chains provide a steric barrier between approaching oil droplets in o/w emulsions.

Griffin [10] and reviewed by Friberg [11]. Experience has shown that combinations of two emulsifiers work best for stabilizing emulsions. Because of the closely related chemistries, polysorbates and sorbitan ester perfectly complement each other. When used together, the two emulsifiers can pack more densely along the interface and this results in a film of greater mechanical strength.

Dispersions can be stabilized by electrostatic or steric mechanisms. The nonionic polysorbate emulsifiers have no effect on electrostatic stabilization. However, polysorbates are powerful steric stabilizers. Consequently, these emulsifiers are valuable for preparing emulsions or concentrates that must be diluted by water of unknown hardness. The bulky hydrated polyoxyethylene chains of polysorbate repel each other (Fig.7.6). The attractive van Der Waals forces, active at close distances, are kept in check by the repulsive forces of the polyoxyethylene chains of polysorbates. It turns out that the 20 moles of EO used in polysorbate products are just about the minimum required for effective stabilization [12]. Longer chain products of 50–100 moles EO are more effective emulsion stabilizers but are not allowed in food products.

7.5.2 Molecular arrangement and critical micelle concentrations (CMC)

Sorbitan esters and other low HLB emulsifiers are not water soluble. However, the significance of these emulsifiers concerning their interaction with water has spurred much interest. There is far more work published concerning the dispersion states of glycerol esters than for sorbitan esters. Sorbitan monostearate in water exhibits similar phase behavior to glycerol monostearate. Above the Krafft point a lamellar phase is formed. Upon dilution of the lamellar phase with water, a dispersion is formed. Cooling the lamellar phase or dispersion phases below the Krafft point results in the slightly more viscous meta-stable gel phase. The sorbitan monostearate gel is quite stable, as the emulsifier does not go through the transition to beta crystals, as occurs with glycerol monostearate gels. This illustrates a significant advantage of sorbitan monostearate over monoglycerides in stabilizing emulsions. The hydration force in monoglyceride is eventually lost in emulsions because of a polymorphic crystal transition that

Table 7.4 Approximate molecular weight (MW), and critical micelle concentrations (CMC) of polysorbate emulsifiers at 25°C

	MW (average)	CMC (mM)	CMC (%)
Polysorbate 20	1228	0.059	0.07
Polysorbate 40	1284	0.027	0.03
Polysorbate 60	1312	0.025	0.03
Polysorbate 80	1310	0.012	0.015

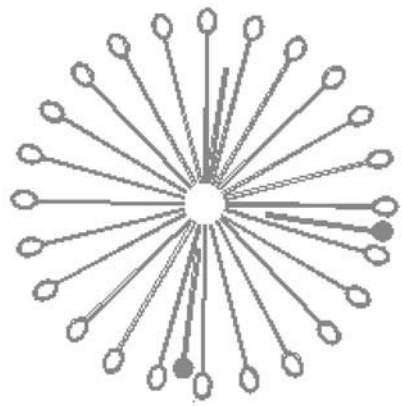

Fig. 7.7 Micelle showing possible location of solubilizate.

consequently destabilizes the emulsion [13]. In sorbitan monostearate stabilized emulsions, there is no polymorphic transition over time and the hydration force is maintained.

Polysorbates are water soluble, so the interaction of polysorbates with water is dramatically different from that of sorbitan monostearate. The addition of small amounts of polysorbate emulsifiers to water results initially in a dramatic decrease in interfacial tension. Once the solution is saturated with emulsifier, additional emulsifier will exist in micelles with very little further effect on interfacial tension. The emulsifier concentration above which micelles are formed is the Critical Micelle Concentration (CMC). This is the concentration at which the polysorbate can form a monolayer. The concentration of emulsifier above the CMC governs its performance. The CMC for various polysorbates are a function of the length of the fatty acid chain (Table 7.4) and decreases with decreasing temperature. Micelles are small (0–50 Å) spherical droplets or liquid particles (Fig. 7.7). The inner core of the micelle is totally non-polar due to the orientation of the individual emulsifier molecules. In a practical sense the micelle is more soluble in the aqueous phase than the emulsifier itself.

7.5.3 Effect of temperature

The type and stability of emulsions prepared using polysorbates is strongly dependant on temperature. Although considered hydrophilic, polysorbates become increasingly lipophilic with increasing temperature. As the temperature increases, the polyoxyethylene chain is dehydrated and takes on a more non-polar quality [14]. Both the surface activity and the 'powerful' steric stabilizing nature of polysorbates is highest following cooling.

Under high temperature conditions the polysorbates form reverse micelles, swollen with water (w/o) with their ethoxylated chains directed inward and the non-polar fatty acid chains directed outward [15]. As temperatures decrease, the polysorbate forms aqueous micelles that can hold oil (o/w). The transition temperatures where both w/o and o/w microemulsions occur are of great technical interest as the microemulsion can solve both oil and water. Polysorbate-type microemulsions typically have a limited temperature range compared with microemulsions made with ionic emulsifiers. The temperature where the oil, water and microemulsion phases all coexist is called the 3-phase temperature, or phase inversion temperature (PIT), or sometimes the HLB temperature. W/O macroemulsions are stable above the PIT and o/w macroemulsions are stable below the PIT [16]. As a rule of thumb the best o/w emulsion stability is achieved 20–50°C below the PIT. However, the finest dispersed phase is achieved close to the PIT. Consequently, the ideal emulsification procedure involves preparing the o/w emulsion just below the PIT and cooling rapidly [17].

7.5.4 Protein emulsifier interactions

The interaction between proteins and non-ionic emulsifiers such as sorbitan monoesters and polysorbates is weak in comparison with ionic emulsifiers such as sodium stearoyl 2-lactylate or SDS [18]. The low protein interaction of polysorbates appears to be a function of the low CMC. Weight for weight polysorbates are capable of reducing the interfacial tension far more than proteins [19]. Proteins are excellent emulsifiers but quite different in application from polysorbates. Low molecular weight polysorbates are about 1/25th the size of higher molecular weight proteins. As a result they are far more mobile and faster at getting to the interphase. The highly surface-active polysorbates will generally displace proteins from an interface, an important effect that is exploited in the ice cream industry. Researchers [20] have shown that Tween 20 added to β-lactoglobulin stabilized emulsion decreases the surface activity of the protein–Tween 20 complex leading to protein displacement. However, it is thought that low levels of polysorbate can also assist protein stabilized emulsions if the complex causes unfolding of the protein and therefore increased hydrophobic. Polysorbates may also improve stability by allowing more efficient

Table 7.5 Weight of various polysorbate products required to solubilize several common flavor oils

	Weight (g)		
Lipophile	Polysorbate 20	Polysorbate 60	Polysorbate 80
Peppermint oil	5	8	7
Clove oil	6	4	5
Lemon oil	3	5	6
Menthol	4	7	6
Spearmint oil	10	12	8
Eucalyptus oil	5	5	6
Pine oil	7	4	4

Reference Uniqema Technical Bulletin Solubilization and Solubilized Systems 1999.

packing of the protein at the interface [21]. The physical and chemical properties of proteins can be altered by polysorbates as micelle-like clusters of polysorbate form at previously hydrophilic sites of the protein. The altered conformation of a protein through these complexes may have reduced enzymatic activity or surface activity. There is also a competitive adsorption between the two molecular species and if the protein is at a sufficiently high concentration, compared with the polysorbate, it may still win and stabilize the emulsion.

7.5.5 Solubilization and microemulsions

Polysorbates form micelles at relatively low concentration levels. The micelle can dissolve a host of lipophilic substances that are normally insoluble in water. The appearance is an isotropic (transparent) solution that is thermodynamically stable. Depending on the nature of the compound to be solubilized (solubilisate), the compound will be located in the core, amongst the carbon chains or between the oxyethylene chains [22]. Indeed, this process is the key to many non-food industrial applications, such as cleaning, soil removal, oil recovery and dry-cleaning. It also has great relevance in foods. In the manufacture of liquid aqueous smoke preparations, the extremely polar flavor compounds of smoke are effectively solubilized using high levels of polysorbate 80. In similar fashion, dill flavoring and color are stabilized by polysorbate 80 in the processing of pickles and oil soluble vitamins in concentrated vitamin solutions.

Various flavor oil compounds can be solubilized using this technique (Table 7.5). Often a blend of two emulsifiers may allow a lower total level of emulsifier to be used. For example, a blend of 5 parts Tween 20 and 3 parts Tween 60 can solubilize 1 g of lemon oil where it requires more of each emulsifier individually (Table 7.6). Microemulsions, similar in principle to solubilization, are thermodynamically stable suspensions that more closely resemble swollen micelles than conventional macroemulsions (Fig. 7.8).

Table 7.6 Blends of polysorbates required to solubilize 1 g of lemon oil

	% Weight		
	A	B	C
Lemon oil	1	1	1
Polysorbate 20	10	–	5
Polysorbate 60	–	12	3
Water	89	87	91
HLB	16.7	14.9	16.0

Reference Uniqema Technical Bulletin Solubilization and Solubilized Systems 1999.

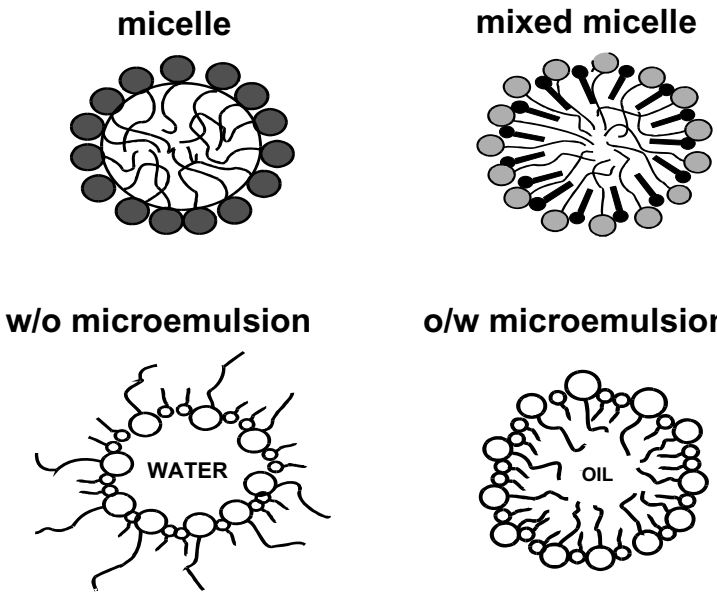

Fig. 7.8 Schematic representation of a micelles, mixed micelle and microemulsions.

There has been limited success using sorbitan monoesters along with other emulsifiers to prepare w/o microemulsions [23]. Polysorbates offer the greatest potential for microemulsions with application in the food industry. Most work in food microemulsions has involved flavor oils, vitamins or antioxidants. An excellent example is the fortification of milk with a microemulsion solubilized form of vitamin A [24]. However, Parris *et al.* [25] were successful in preparing microemulsions of triglycerides using ethoxylated monoglycerides. Long carbon chain triglycerides such as sunflower oil prove difficult in microemulsions,

possibly because the carbon chains are too bulky to penetrate and negatively affect the ideal curvature of the interface [26]. Greater success may be achieved with medium chain triglycerides. Polysorbate 20 has been used as part of a surfactant blend in another soy oil triglyceride microemulsion [27].

7.6 Applications

Sorbitan esters and polysorbates are regulated emulsifiers. In North America, the market where they are most popular, the specific applications for these compounds in foods is defined and the use level is controlled. Most sorbitan esters and polysorbates end up in bakery goods. However, there are applications in dairy, oil processing, confectionery and many other end uses. The flavor of sorbitan esters is typically considered bland with a profile similar to that of hard monoglycerides or fats. Polysorbates on the other hand have a unique bitter flavor that can linger and is not easily forgotten. Certain individuals seem more sensitive to the flavor associated with polysorbates. The flavor profile of polysorbates can vary slightly amongst suppliers. It appears that certain people are more sensitive to the threshold flavor of polysorbates. Polysorbates should not be tasted neat. Screening polysorbate products for flavor is typically accomplished by 20 to 30 times dilution in whole fat milk. Although no polysorbates taste pleasant, the stearate based polysorbate 60 has the mildest flavor compared with the polysorbate 20 and 80 products. In most dairy and bakery applications, polysorbates are used below 0.3%. In full fat traditional formulations, there is typically sufficient fat to mask the flavor of polysorbate. In low and no fat formulas, the characteristic polysorbate flavor can become more apparent. One challenge that food product formulators periodically find themselves facing is in finding a suitable alternative to polysorbates when they must be removed from formulations due to regional regulations or preferences. Other similarly high HLB candidates are limited in the portfolio of emulsifiers allowed in foods. However, specialty sucrose esters and polyglycerol esters may provide some similar effect but usually at an additional cost.

7.6.1 Fine bakers wares

Commercial co-mingled blends of emulsifiers have taken advantage of the hydrophilic, highly dispersible nature of polysorbate 60 to aid in the dispersion of low HLB emulsifiers such as monoglycerides or sorbitan esters.

Developed in the 1940s, sorbitan esters and polysorbates are still current cost effective emulsifiers for making quality baked goods. Hi-ratio cakes made with emulsified shortening (containing mono- and diglycerides) are improved by the use of sorbitan monostearate and polysorbate 60 [28]. The cake batter whips to a lower specific gravity faster, developing less gluten, resulting in softer cakes

with uniform fine cell structure. In practice, this is accomplished by using commercial blends of approximately 70 parts sorbitan monostearate and 30 parts polysorbate 60, dispersed in water with other minor components. The best commercial hydrates are prepared under controlled cooling and shear in specialized equipment called a votator (scraped surface heat exchanger). The votated products have unequalled dispersability in batter systems, resulting in a cost effective delivery of active emulsifiers. Although the sorbitan monostearate/polysorbate hydrate works best for high ratio shortening type cakes, the hydrates made from polysorbate 60 with mono- and diglyerides are more effective in low or no fat sponge-type cakes. The hydrates are prepared at low pH and with antimicrobial agents to maintain product safety. Polysorbates themselves have antimicrobial activity and will control the development of microbes in these hydrates to some extent.

Similarly, icings and cream-type fillings made with emulsified shortening are improved by the incorporation of a dispersible form of sorbitan monostearate and polysorbate 60 [29].

7.6.2 Bread

Emulsifiers are added to yeast-raised baked goods for a variety of reasons. While monoglycerides are predominantly added to delay firming, DATEM, SSL, sucrose esters and polysorbate 60 are added as dough strengtheners to improve the baking performance of dough. These emulsifier strengtheners have a dramatic effect, stabilizing the dough during the late proofing and early stages of baking, where there are great stresses on the inflating cells within the dough. The use of the strengthener polysorbate 60 results in larger loaves with fine uniform crumb structure, compared with loaves made without a dough strengthener. Baking researchers have proposed several different mechanisms concerning the interaction of emulsifiers with dough components. Researchers [30] reported that baking performance of dough is related to at least three different rheological characteristics:

(i) resistance to deformation
(ii) extensibility
(iii) strain hardening

In a test comparing the effect of various dough conditioners during dough inflation, it has been shown that polysorbate 60 had the highest strain-hardening index coupled with high failure strain of any dough strengthener available [31]. Many emulsifiers are limited in their applications by their dispersability. Polysorbates do not suffer this limitation in most applications due to their water solubility. In fact, polysorbates act as co-emulsifiers improving the dispersion of more

polar emulsifiers, such as monoglycerides or sorbitan esters. Furthermore, small amounts of polysorbate 60 is used to break nuisance liquid crystal structures formed when pure monoglycerides come in contact with hot water and are difficult to disperse. The polysorbate 60/monoglyceride mixture with water forms a uniform lamellar phase [32].

7.6.3 Active dry yeast

Sorbitan monostearate is used in the processing of active dry yeast. High active dry yeast is treated with sorbitan monostearate prior to drying. The sorbitan monostearate treatment protects the yeast cells during the drying process and aids in the eventual rehydration of cells. For optimum cell viability and gassing power of the active dry yeast, it is critical that the individual yeast cells are uniformly coated with sorbitan monostearate which can be used at up to 1.0% on the dry weight of the yeast (Fig. 7.9). To ensure uniform coverage, the dispersible gel formed from cooling a lamellar phase of sorbitan monostearate is incorporated with the fresh yeast crumb prior to drying. The sorbitan monostearate molecules

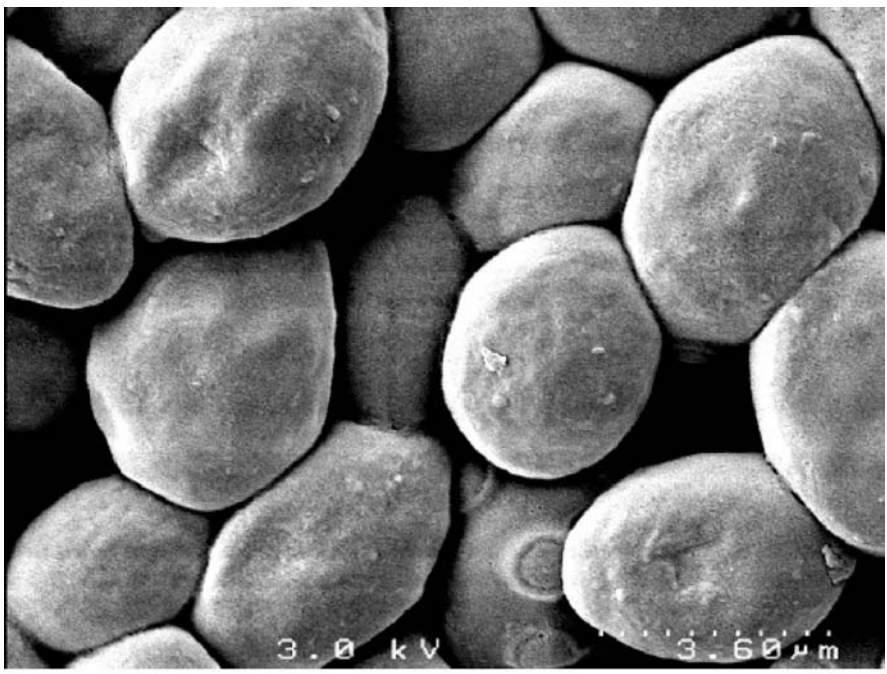

Fig. 7.9 Active dry yeast coated with sorbitan monostearate.

migrate to the surface of the yeast cell, where the alpha crystalline network supports the membrane and prevents rupture during dehydration and subsequent rehydration.

7.6.4 Beverage

Although polysorbates and sorbitan esters offer potential as emulsifiers in beverage emulsions and beverage products, their inherent flavor limits their use in commercial products [33]. There are, however, niche applications for polysorbates in the beverage industry. The polysorbates are used in combination with other emulsifiers as flavor adjuvants. Blends of polysorbate 60 with monoglycerides are effective at suspending insoluble fine powdered forms of calcium. Polysorbate 60 is used extensively in alcoholic mix preparations to emulsify flavored components such as coconut milk and as a foaming agent in mixed alcoholic drinks.

7.6.5 Dairy

Polysorbates, rather than sorbitan esters, are used predominantly in the dairy industry. Milk proteins are powerful emulsifiers for dairy based emulsions. The synthetic polysorbate emulsifier is generally added to dairy systems to destabilize rather than stabilize the emulsion. There is a plethora of work reported over the years in the literature investigating ice cream, perhaps because the bench work is so delicious. Many reports in the literature have discussed the effect that emulsifiers (including polysorbate) have on ice cream quality. It is generally believed that during the preparation of the ice cream mix, the proteins native to milk efficiently emulsify milk fat. Following appropriate ice cream processing conditions, including cooling/freezing, agitation and ageing, the synthetic emulsifiers migrate to the fat globule interface, displacing the protein. With the proteins removed from the interface, neighboring fat globules which are primarily solid fat crystals can partially agglomerate and a stiff microstructure is formed that can trap air. Researchers have consistently shown that emulsifiers such as polysorbate 80 contribute to the textural characteristics of ice cream, such as the stand-up ability or the ability that molded ice cream has in retaining its shape [34]. This ability to retain shape is absolutely necessary for wrapping operations and when filling soft serve cones. The stand-up quality correlates with a dry surface appearance in comparison with a glossy or wet-looking sloppy product with poor stand-up ability. The stand-up quality of ice cream also appears to be highly correlated with destabilization of the fat emulsion [35]. The ability of various emulsifiers to destabilize the fat emulsion has been reviewed by Knightly showing that polysorbate 80 has the greatest effect at the lowest concentration [36]. Although, polysorbate 80 is highly effective in promoting stiffness in ice cream, stearate-based monoglycerides were able to produce ice

cream with higher over-run than that made with polysorbate 80. Knightly proposed that the highly effective destabilizing activity of polysorbate 80 created an agglomerated mix that could only retain limited amounts of air. Consequently, the ice cream industry often uses a commercial blend of 20 parts polysorbate 80 to 80 parts mono- and diglycerides to produce an ice cream product with good over-run, combined with excellent stand-up qualities.

A similar destabilizing mechanism facilitated by polysorbate 80 is found in whipped cream and non-dairy cream alternatives. Although it is possible to whip these products at room temperature, improved whipping is achieved in chill-aged product where there is increased surface activity of the polysorbate. There is evidence that polysorbate 80 promotes sharp fat crystals that penetrate through the fat globules surface and assist in bridging the gap between fat globules and agglomeration [37].

Non-aerated liquid cream type products can also benefit from the use of polysorbates. Large interfacial areas are created during high-pressure homogenization. If there is insufficient protein available to cover the new fat globule surface created, clusters will form as protein molecules share two adjacent fat globules [38]. Clusters present a problem as they cannot be easily broken down by stirring. Polysorbate 60 is effectively used at levels around 0.3% to prevent aggregation of the fat globules. It is thought that clusters form when proteins are too slow at getting to the interface immediately during droplet break-up in the homogenizer. Neighboring droplets collide, coalesce and cluster. As polysorbates are smaller and therefore faster compared with larger proteins, they can adsorb far quicker than proteins to the interface and prevent coalescence and clustering [39].

7.6.6 Margarine and spreads

Sorbitan tristearate has no surface activity. Its chemical structure is more similar to triglyceride fat than to an emulsifier. Sorbitan tristearate is used in several fat-based products such as margarine where it has a dramatic effect on the crystalline nature of the bulk fat. In certain margarine formulations, typically made from single oil sources (e.g. 100% soy or 100% canola), a textural defect can occur over only a short period of time when the fine needle-like beta prime crystals shift to the more stable beta form. The large platelet structures of beta crystals with higher melt points have a gritty texture. Sorbitan monostearate, because of its similar structure to fats, is able to co-crystallize in a growing fat crystal. Although similar to fat, because of the bulky sorbitan head group, sorbitan tristearate is also different enough from the bulk fat in structure and it effectively terminates the crystal growth. As a result, the beta crystals can grow only to the point where they are terminated by a sorbitan tristearate molecule. If the beta crystal size is below the threshold of perception, the beta prime stabilized margarine texture is maintained.

7.6.7 Chocolate and confectionery coatings

In poorly tempered chocolate and coatings a defect called 'bloom' is common where low melt point fats migrate to the surface and re-crystallize in an unappealing dull gray film. Over time and accelerated by temperature cycles, a gradual transition of the fats occurs from metastable to more stable forms. As the bulk fats of the coating realign to crystallize in their lowest energy form, lower melting fractions are squeezed out from the matrix.

A blend of polysorbate 60 and sorbitan monostearate, as well as sorbitan tristearate, is used in some chocolate and confectionery coatings. Blends of 60 parts sorbitan ester/40 parts polysorbate 60 used at up to 1% produce the best initial gloss and resistance to bloom [40]. The emulsifiers are melted with the mass well above their melt point at 71°C with sufficient mixing to assure complete dispersion. Polysorbate seems to act as a wetting agent assisting in the dispersion of the sorbitan ester. The sorbitan esters inhibit migration of fat fractions to the coating surface. The use of these emulsifiers at higher levels can have a marked impact in delaying crystallization, which can be used to the processors' benefit [41]. Slow crystallization can be overcome by seeding at 31°C with a percentage of pre-crystallized mass.

Similarly, sorbitan tristearate has found application in controlling the crystalline characteristics of chocolate-type compound coatings. Sorbitan monostearate when dispersed thoroughly in the matrix will again terminate the undesirable crystal growth and prevent the fat bloom.

7.7 Regulations

Polysorbates and sorbitan esters are allowed in foods in many countries around the world. However, several countries in the Middle East and Japan have not yet approved these products. Even where allowed, the sorbitan esters and polysorbates are regulated so the application and use levels are clearly restricted. In the United States, sorbitan monostearate is the only sorbitan ester listed in the CFR as a direct food additive. Sorbitan tristearate has a self-determined GRAS status filed with the FDA for limited use up to 0.5% by weight in margarine. Polysorbate 60, polysorbate 80 and polysorbate 85 are all listed as direct food additives in the Code of Federal Regulations published by the US Food and Drug Agency. It is intriguing why the ethoxylated version of sorbitan monooleate (polysorbate 80) is allowed and the non-ethoxylated sorbitan monooleate is not. In the EU, a wider range of polysorbates and sorbitan esters are allowed. However, in practice, they are not as commonly used as in North America. Tables 7.7 and 7.8 summarize the US FDA and EU regulations concerning the use of sorbitan esters and polysorbates in foods [42]. Regulatory agencies should be consulted before using sorbitan esters or polysorbate in a new application to ensure that the food product is within compliance of local regulations.

Table 7.7 Food Chemical Codex specifications for several polysorbates

	Polysorbate 20	Polysorbate 60	Polysorbate 65	Polysorbate 80
E No.	E432	E435	E436	E433
FDA reference	–	21CFR172.836	21CFR172.838	21CFR172.840
Content (anhydrous base)	97.3–103.0%	97.0–103.0	96.0–104.0	96.5–103.5
Oxyethylene content	70.0–74.0%	65.0–69.5	46.0–50.0	65.0–69.5
Acid value	Max 2.	Max 2.0	Max 2.0	Max 2.0
Saponification value	40–50	45–55	88–98	45–55
Hydroxyl value	96–108	81–96	44–60	65–80
Fatty acids	15–17 g/100 g as lauric acid	21.5–26.0 g/100 g as stearic and palmitic acids	42–44 g/100 g as stearic and palmitic acids	22–24 g/100 g as oleic acid
Water	Max 3.0	Max 3.0	Max 3.0	Max 3.0
1,4 dioxane	Max 10 mg/kg	Max 10 mg/kg	Max 10 mg/kg	Max 10 mg/kg
Residue of ignition	Max 0.25%	Max 0.25%	Max 0.25%	Max 0.25%
Heavy metals (as Pb)	Max 10 mg/kg	Max 10 mg/kg	Max 10 mg/kg	Max 10 mg/kg

From Food Chemical Codex Fourth Edition, 1996.

7.8 Toxicology

Extensive toxicological work concerning food emulsifiers, including the sorbitan esters and polysorbate products, was performed before the 1970s. The results of much of this work were summarized and reported in the Seventeenth Report of the Joint FAO/WHO Expert Committee on Food Additives, World Health Organization Technical Report Series, 1974 (No. 539); FAO Nutrition Meeting Report Series, 1974 (No. 53) and reviewed again in 1982. Feeding trials including metabolic studies and acute oral toxicity were carried out on many animal species. Those interested in specific toxicological data from short-term or long-term feeding trials of sorbitan esters and polysorbates are referred to this summary, Joint FAO/WHO document, for detailed results and extensive referenced work on the subject. Early results showed that there were some deleterious effects of polysorbates at high dosage, which was believed to be due to large amounts of free polyol (sorbitol), which caused diarrhea. From these trials the estimate of acceptable daily intake for man was set at 0–25 mg/kg bw.

More recently, the European Commission, Scientific Committee on Food has been concerned with the impurities of ethylene oxide and related compounds in food additives [43]. Although the polymerized forms of ethylene oxide used in polysorbates have been shown to be safe, the unreacted free-ethylene oxide has been classified as 'carcinogenic to humans (Category 1)' by the International Agency for Research on Cancer [44,45]. Several other related impurity

Table 7.8 EC Purity specifications for several polysorbates

	Polyoxyl(40) stearate	Polysorbate 20	Polysorbate 40	Polysorbate 60	Polysorbate 65	Polysorbate 80
Water	max 3% (Karl Fischer)	max 3% (Karl Fischer)	max 3% (Karl Fischer)	max 3% (Karl Fischer)	max 3% (Karl Fischer)	max 3% (Karl Fischer)
Acid value	max 1	max 2	max 2	max 2	max 2	max 2
Saponification value	Not less than 25 and not more than 35	Not less than 40 and not more than 50	Not less than 41 and not more than 52	Not less than 45 and not more than 55	Not less than 88 and not more than 98	Not less than 45 and not more than 55
Hydroxyl value	Not less than 27 and not more than 40	Not less than 96 and not more than 108	Not less than 90 and not more than 107	Not less than 81 and not more than 96	Not less than 40 and not more than 60	Not less than 65 and not more than 80
1,4-Dioxane	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg
Ethylene oxide	Not more than 0.2 mg/kg	Not more than 0.2 mg/kg	Not more than 0.2 mg/kg	Not more than 0.2 mg/kg	Not more than 0.2 mg/kg	Not more than 0.2 mg/kg
Ethylene glycols (mono- and di-)	Not more than 0.25 mg/kg	Not more than 0.25 mg/kg	Not more than 0.25 mg/kg	Not more than 0.25 mg/kg	Not more than 0.25 mg/kg	Not more than 0.25 mg/kg
Arsenic	Not more than 3 mg/kg	Not more than 3 mg/kg	Not more than 3 mg/kg	Not more than 3 mg/kg	Not more than 3 mg/kg	Not more than 3 mg/kg
Lead	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg	Not more than 5 mg/kg
Mercury	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg
Cadmium	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg	Not more than 1 mg/kg

From Commission Directive 2003/95/EC (27 October 2003).

compounds such as 1,4-dioxane and ethylene chlorohydrin and mono- and dieththylene glycol are being questioned. Purity criteria levels for ethylene oxide in all polysorbates have been set by the Commission Directive 2003/95/EC at $\leq$2 mg/kg (SCF 2003). As is often the case with impurities in food, the allowable levels are set by achievable limits of detection. Recent improvements in detection now allow for potential tighter control. It should be noted that the Commission puts the potential risk in perspective by calculations of an unrealistic worst-case scenario. If 1 kg food is consumed daily, all of which contains the maximum allowable level of polysorbate with the highest level of free ethylene oxide proposed, the intake would equate to 5 μg ethylene oxide per day. The significance of this recent concern may be put into better perspective when one considers a realistic diet, the loss of ethylene oxide during cooking/baking and the fact that intestinal bacterial flora produce a greater amount approximately 15–20 μg ethylene oxide per day [46].

Although the potential risk of impurities in polysorbates is low, a responsible food manufacturer should be aware of these concerns. Food producers would be prudent to source their polysorbates from a reputable supplier.

Sorbitan esters and polysorbates have been used safely in food products for over half a century. The products have an impressive safety record that is supported by volumes of toxicological data so sound that they are used as a bench mark by which other food and pharmaceutical ingredients are measured.

7.9 Concluding remarks

This chapter presented a general view of sorbitan esters and the related ethoxylated derivates. As the development of new emulsifier chemicals has slowed to a virtual halt due to increased regulatory restrictions and reduced funds for basic research, new interest is being focused on existing chemistries. New demands are made on food emulsifiers resulting from public opinion or changes in economic and political climates. Properties overlooked during initial development of these may now have far greater relevance. The truly superior steric stabilizing power of polysorbates should be grounds for new or novel applications using this exceptional group of compounds.

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8 Propylene glycol fatty acid esters

Fleming V. Sparsø and Niels Krog

8.1 Introduction

Fatty acid esters of propylene glycol (1, 2-propanediol) have been known to the food industry for about 40 years. Their development began in the early 1960s in connection with the use within the bakery industry of emulsified shortening for cake mixes, sponge cakes, etc. [1–3]. Furthermore, the specific crystalline properties of distilled propylene glycol monostearate (PGMS) and its ability to stabilise the meta-stable α-crystal form of distilled monoglycerides are beneficial in many aerated products, such as non-dairy desserts, whipping creams, powdered toppings and cake emulsifiers.

Due to its α-crystalline properties, distilled propylene glycol monostearate also enhances the functional effects of other emulsifiers, e.g. monoglycerides, leading to interactions with water and forming gel structures at low temperature. The swelling of PGMS crystals in shortenings, speciality fats for toppings or whipping creams is a unique functional property.

8.2 Chemistry and physical properties

Propylene glycol fatty acid esters are lipophilic, oil-soluble emulsifiers with specific crystalline properties. This melting/crystallisation behaviour is related to the chemical composition in respect of fatty acid chain length, monoester content and positional isomers. The chemical structures of the components present in commercial propylene glycol fatty acid ester products are shown in Fig. 8.1.

8.2.1 Pure, synthetic propylene glycol fatty acid esters

The crystallisation properties of the two positional isomers 1-propylene glycol monostearate (1-PGMS, stearic acid 2-hydroxy-propyl ester) and 2-propylene glycol monostearate (2-PGMS, stearic acid 1-hydroxy-propyl ester) and 1-propylene glycol esters of myristic, palmitic, arachidic and behenic acid were studied by Martin and Lutton in 1965 [4]. They found that pure, synthetic 1-PGMS shows a polymorphism, and may exist in four different crystal forms, referred to as forms I, II III and α.

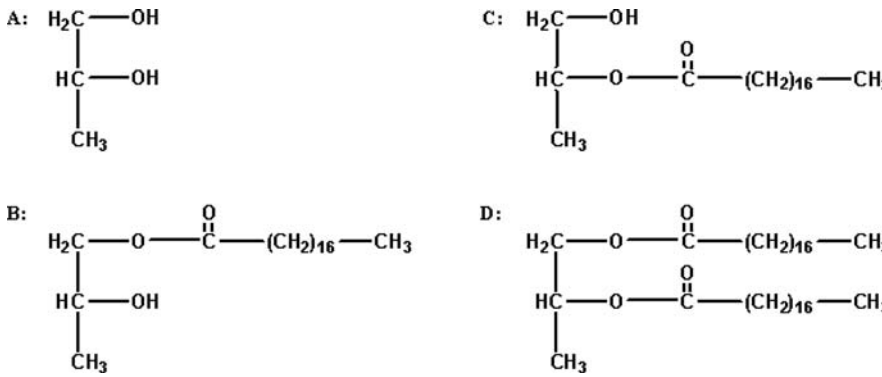

Fig. 8.1 Propylene glycol and esters with stearic acid. A: Propylene glycol; B: 1-Propylene glycol monostearate; C: 2-Propylene glycol monostearate; D: 1, 2-Propylene glycol distearate.

The most stable crystal form of 1-PGMS (Mp. 56°C) was termed form II and is formed by the transition of the meta-stable α-like crystal form during storage at room temperature. X-ray diffraction analysis indicated that the molecules are packed in a single-chain length (SCL) mode, and this crystal form has several short spacings. This crystal form has also been referred to as a β'-crystal form [1], when following the standard crystal form nomenclature for triacylglycerides, as defined by Larsson [5]. However, no single-crystal structure data is available for propylene glycol esters, and the use of the crystal nomenclature for glycerides such as propylene glycol esters is basically incorrect but generally accepted.

Some of the preliminary results were refined and the polymorphism of 1-propylene glycol monopalmitate (1-PGMP) and 1-PGMS published by Lutton *et al*. in 1972 [6]. The melting points of the crystal forms of pure 1-PGMP and 1-PGMS are shown in Table 8.1. For comparative purposes, the melting point of a commercial, distilled PGMS is also included. From melt via rapid cooling to 0°C, both pure, synthetic propylene glycol esters crystallise in an intermediate form III, which transforms to an α-like crystal form on heating to a temperature above its melting point. The α-form may transform to a higher melting, stable

Table 8.1 Melting points and crystal forms of pure 1-PGMP and 1-PGMS

	Melting points, °C			
	Form III	α-form	Form I	Form II
1-PGMP	31.0	37.5	42.0	47.8
1-PGMS	42.0	47.2	52.5	55.3
Distilled PGMS*	–	40.0	–	

* Based on palmitic and stearic acid, ratio 1:1.

form II on storage. Both forms I and II can be obtained by crystallisation from solvents (hexane) at different speeds. However, after a lengthy storage period, the stable form II is the predominant crystal form of pure, synthetic 1-PGMP and 1-PGMS.

The polymorphism of synthetic propylene glycol esters is affected by fatty acid chain length as well as purity with regard to positional isomers and minor contents of other lipids (e.g. monoglycerides). Form II has not been found in propylene glycol esters of arachidic acid (C20) or behenic acid (C22), which are stable in the α-crystal form.

8.2.2 Commercial mixed fatty acid esters of propylene glycol

Commercial distilled propylene glycol esters, with a monoester content of minimum 90% are mixtures of the positional isomers of the monoester and propylene glycol diesters and have mainly a mixed fatty acid profile. The typical fatty acid composition of distilled propylene glycol esters is a blend of palmitic and stearic acid, which may vary from 60:40 to 30:70 in the C16:C18 ratio. Such products may still be referred to as propylene glycol monostearates (PGMS) or propylene glycol monoesters (PGME). Figures 8.2a and 8.2b show the composition of (a) a commercial propylene glycol monodiester containing the equilibrium mixture of monoesters and diesters after removal of free propylene glycol after the esterification process, and (b) the composition of a distilled propylene glycol monostearate.

The mixed composition of commercial PGMS products changes the crystallisation behaviour to a simple monomorphic pattern, where a stable α-like crystal form crystallises from melt. X-ray diffraction analysis of distilled PGMS shows a long spacing of about 50 Å, indicating a double chain length packing mode similar to monoglycerides. The short spacings are dominated by a strong peak at 4.15 Å, but several other low intensity X-ray spacings are present in PGMS. In spite of such differences from the standard nomenclature for the crystal forms of fats and monoglycerides, the crystal form of PGMS is commonly called an α-form. The X-ray data of a distilled PGMS is shown in Fig. 8.3.

The so-called α-tending properties of propylene glycol esters were first studied by Kurt *et al.* [1] and Kurt and Broxholm [2], who studied combinations of monoglycerides and propylene glycol esters and their ability to stabilise the effective α-crystal form of monoglycerides. The aim of this study was to stabilise the functional meta-stable α-crystal form of distilled monoglycerides for use as an aerating agent in sponge cakes, fruit preparations and so on. When using a freshly prepared dispersion of distilled, saturated monoglycerides, it was found that such preparations lost their aerating capacities very quickly due to a crystal transition from the α-form to the more stable, high-melting β-crystal form. For this reason, studies were conducted on the effect of combining related emulsifiers with distilled monoglycerides, with the aim of retaining the α-crystal form

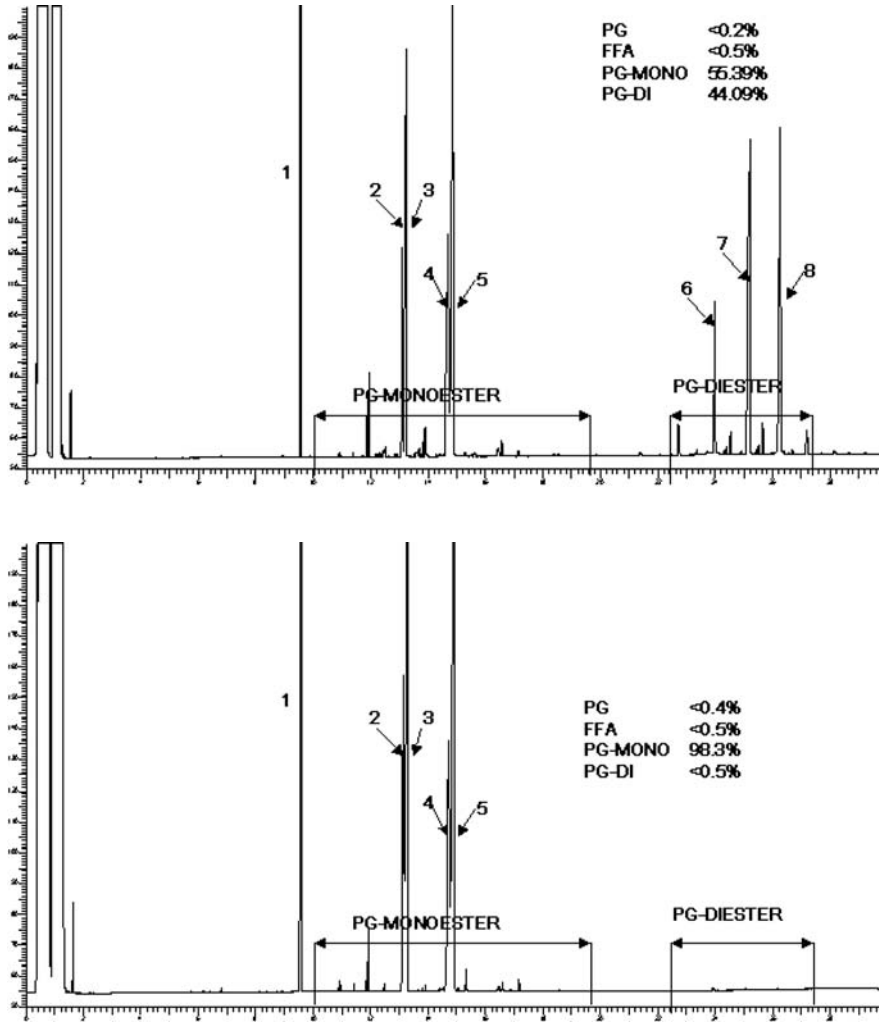

Fig. 8.2 Gas liquid chromatogram of (a) a typical commercial product of propylene glycol esters of fatty acids, 1: Internal standard – heptadecane, 2: 2-propyleneglycol monopalmitate, 3: 1-propyleneglycol monopalmitate, 4: 2-propyleneglycol monostearate, 5: 1-propyleneglycol monostearate, 6: propylene glycol dipalmitate, 7: propylene glycol diester with palmetic and stearic acid, 7: propylene glycerol distearate. The molar ratio between 1-propyleneglycol monoesters and 2-propyleneglycol monoesters is 2:1. Main fatty acids: palmitic and stearic acid, ratio 3:7. (b) Gas liquid chromatogram of commercial distilled propylene glycol monoester, 1: Internal standard – heptadecane, 2: 2-propyleneglycol monopalmitate, 3: 1-propyleneglycol monopalmitate, 4: 2-propyleneglycol monostearate, 5: 1-propyleneglycol monostearate. Main fatty acids: palmitic and stearic acids, ratio 1:1. The gas liquid chromatogram method is described in *JECFA*, 5th edn, paper 52 1997, p 135–140. (*Abbreviations*: PG: propylene glycol, FFA: free fatty acids, PG-mono: propylene glycol monoester, PG-DI: propylene glycol diester).

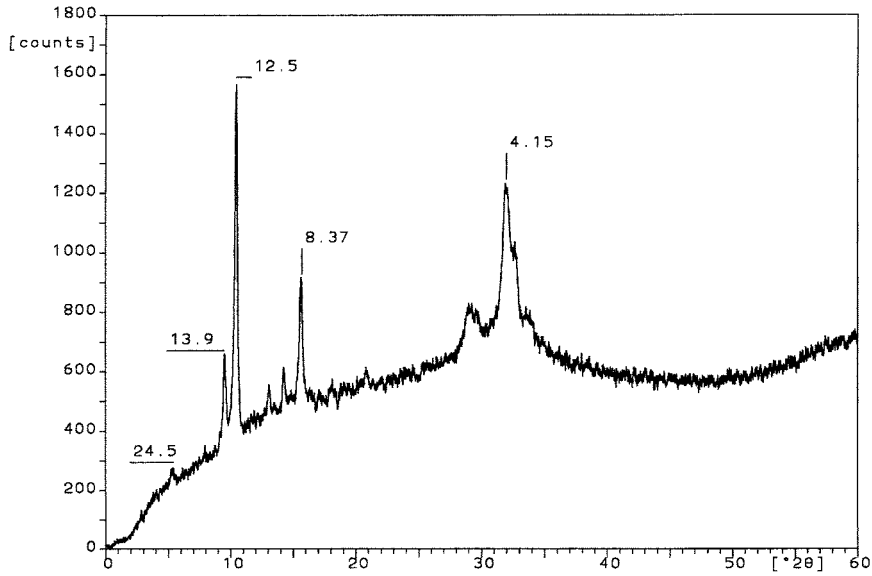

Fig. 8.3 X-ray diffraction spectra of distilled propylene glycol monostearate. Ratio of stearic acid to palmitic acid 1:1. Calculated first order long spacing: 49.7 Å. The main short spacing at 4.15 Å is indicative of the α-crystal form.

and active water dispersibility for a longer period. The most effective mixture found was an equal molar proportion of glycerol monostearate and propylene glycol monostearate. Both emulsifiers should have a minimum content of 90% monoester. A commercial emulsifier product referred to as 'Conjoined Crystals' was patented under US Patent Number 3,034,897 assigned to Eastman Kodak, Rochester, USA.

The commercial emulsifier combination of distilled saturated monoglycerides, usually made from hydrogenated lard, and distilled saturated propylene glycol monostearate was made by melting and co-crystallising them together into a fine powdered product. The active α-crystal form of the combination was claimed to be stable for a year, and the combination retained its cold-water dispersibility and aeration capacity for the same period.

The stability of the active α-crystal form was affected by both the molar proportion of the two emulsifiers and their fatty acid composition. When, for example, glycerol monopalmitate was mixed with equal molar proportions of propylene glycol monostearate, the glycerol monopalmitate shifted rapidly to its β-crystal form, and the mixture became water insoluble and lost the ability to foam. On the other hand, if the monoglycerides were made from hydrogenated soybean oil and contained a palmitic to stearic acid ratio of around 1:9, the blend retained its water dispersibility and aeration capacity for more than 18 months.

1, 3-Propanediol monostearate was ineffective in stabilising the α-crystalline form of glycerol monostearate based on hydrogenated lard. The fatty acid composition of the emulsifiers was of some importance with regard to the degree of unsaturation. Minor contents of unsaturated fatty acid esters reduced the stability of the active α-crystal form, and unsaturation in the propylene glycol ester part of the blend appeared to be more deleterious to stability than in the case when the unsaturation was in the glycerol monostearate part of the blend. In order to maintain the active crystal form for one year, the minimum content of propylene glycol ester in the combination was found to be about 50 molar percent.

When used in food formulations, propylene glycol esters being lipophilic, oil-soluble emulsifiers are usually added via the fat phase at a temperature above the melting point.

The effects of α-tending emulsifiers in liquid cake shortening products are related to a specific interfacial film formation, as described by Wootton *et al.* [7]. If the concentration at the oil/water interface exceeds the solubility limit, the adsorbed emulsifiers crystallise forming a multi-layered α-crystalline film with wax-like properties and encapsulating the liquid oil phase. It has been suggested that the encapsulation of liquid oil in cake shortenings prevents the detrimental effects of liquid oil on the foaming properties of flour proteins, resulting in better aeration and air incorporation in cake batters and improved volume and texture in the final product. This work paid no attention to any interactions between the water phase and the α-tending emulsifier film. However, such interactions are believed to take place during the aeration of whippable emulsions or powdered toppings [8, 9].

In the solid state, PGMS absorbs water in the crystalline lattice, causing the crystalline structure to swell and form an α-gel phase. The affinity of PGMS to water is due to the hydration of the OH groups and is probably similar to the hydration force described for monoglycerides, lecithin and other emulsifiers [10]. The interaction with water is dependent on temperature and occurs only in the solid state – contrasting with other emulsifiers (e.g. monoglycerides, stearoyl lactylates, polysorbates, etc.), which form liquid crystalline phases in water above their Krafft point [11].

The interaction between PGMS and water can be demonstrated by adding a solution of PGMS to liquid oil as a thin layer on a water phase, followed by cooling the mixture to approximately 5°C for several hours. Water penetration up through the PGMS/oil phase can then be observed, as demonstrated in Fig. 8.4.

The concentration of emulsifier in the oil phase in this model study should be considered as the concentration in the interfacial film formed at the surface of fat globules in an o/w emulsion. The corresponding bulk concentration of emulsifier in the oil phase may thus be much lower. All α-tending emulsifiers (PGMS, lactylated monoglycerides or acetylated monoglycerides) and glycerol monooleate show this absorption of water.

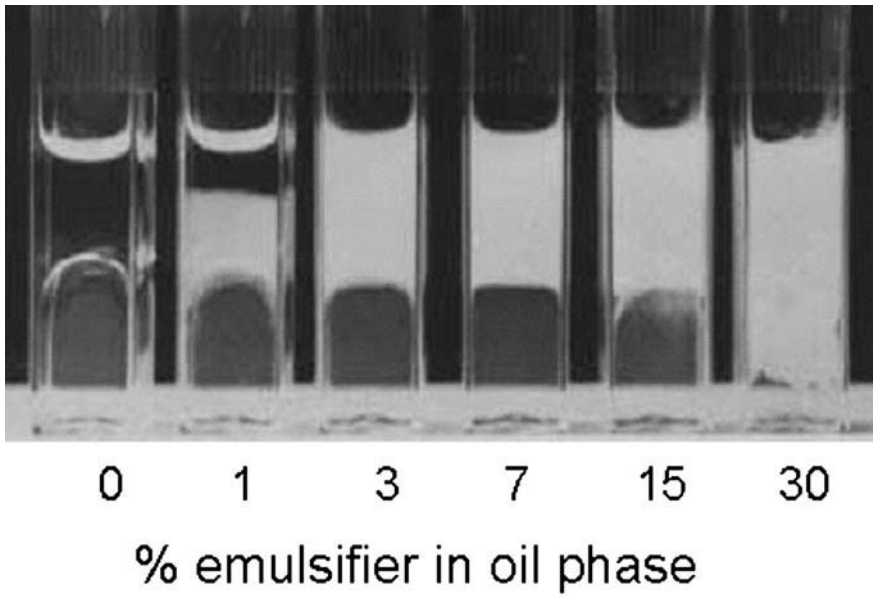

Fig. 8.4 Interaction of water and emulsifiers dissolved in soybean oil. The solution of emulsifiers in triglyceride oil is poured on top of a water layer and kept at 5°C for 24 hours. The concentration of emulsifier in the oil phase is from left: 0, 1%, 3%, 7%, 15% and 30%. The absorption of water through the polar groups of emulsifier crystals is seen as a white layer, penetrating into the oil phase. This interaction is typical for an α-tending emulsifiers (propylene glycol monostearate, acetylated monoglycerides and lactylated monoglycerides) and glycerol monooleate.

When the interfacial film is isolated and analysed by X-ray diffraction analysis, it is possible to follow the swelling of the interfacial film into a α-crystalline gel phase. High lauric fats such as hydrogenated coconut oil or palm kernel oil are often used in topping formulations and non-dairy whipping creams. X-ray data of bulk PGMS solutions in hydrogenated coconut fat is shown in Fig. 8.5.

Hydrogenated coconut oil crystallises in a stable β'-crystal form with long spacings of around 37 Å, short spacings of 4.18–3.83 Å and others. A mixture of PGMS and hydrogenated coconut oil shows two long spacings of 50 Å and 37.0 Å respectively, as illustrated in Fig. 5. This indicates that the emulsifier and fat phase do not co-crystallize forming a solid solution, but crystallise as two separate phases. When water is present, it will penetrate the PGMS crystals and 'swell' the fat phase, changing the globular structure of the fat phase to a matrix of crystal platelets. This process begins on the surface of fat globules in emulsions and, eventually, penetrates the total fat phase, depending on the emulsifier concentration, type of fat phase and temperature of the emulsion.

The X-ray data of an isolated interfacial fat–emulsifier–water layer shows a long spacing of 56–66 Å, which is 6–16 Å bigger than that of the fat–emulsifier

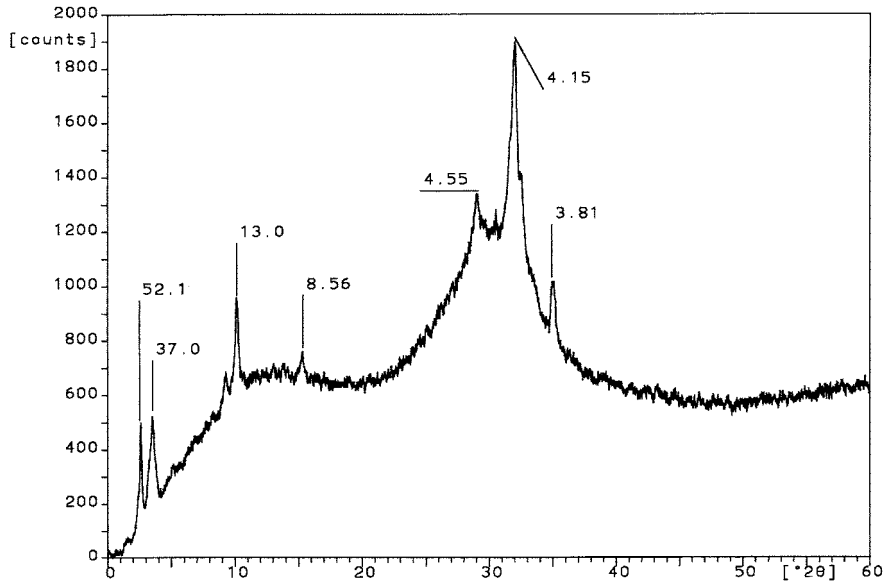

Fig. 8.5 X-ray diffraction spectra of a blend of hydrogenated coconut oil and distilled PGMS (1:1) after melt and cooled to room temperature. The appearance of two long spacings at 52 Å and 37 Å, corresponding to PGMS crystals and coconut crystals respectively, shows that the emulsifier and fat do not co-crystallise and form a solid solution, but crystallise in segregated crystals.

bulk phase [11]. This increase in interplanar spacing can only be due to a swelling of the emulsifier crystals, a mechanism that probably explains the function of PGMS in many aerated food applications, such as non-dairy whipping creams or toppings.

The α-crystalline property of PGMS is beneficial in many emulsifier combinations with monoglycerides in order to stabilise the monoglycerides in the active α-crystalline crystal form. This is especially utilised commercially in emulsifier combinations for whippable non-dairy creams, toppings, sponge cakes or other aerated foods.

8.3 Production

Industrial production of propylene glycol fatty acid esters can take place via the esterification of propylene glycol with fatty acids, typically in the form of commercial stearic acid blends. The esterification is performed at temperatures of 170–210°C with or without the presence of an alkaline catalyst. During the reaction, water is separated from the reaction mixture by distillation. It is

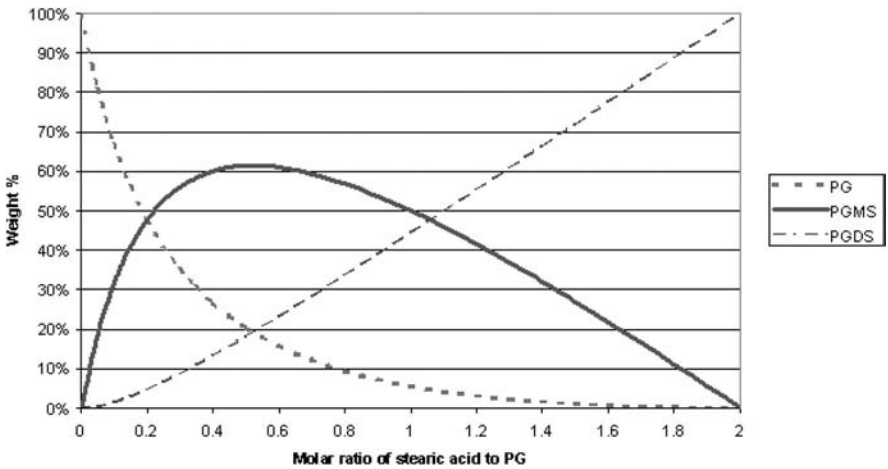

Fig. 8.6 Composition of the reaction mixture of the reaction between propylene glycol (PG) and stearic acid, depending on the molar ratio of stearic acid to PG.

possible to control the composition of the reaction mixture by changing the ratio between fatty acid and propylene glycol, Fig. 8.6 shows the theoretical composition of the reaction mixture after esterification of the fatty acid. After concentration of the reaction mixture by distillation of excess propylene glycol, the typical product consists of a mixture of about 50–70% monoesters and 30–50% diesters. Concentration of the monoester can be achieved by fractional crystallisation from hexane or via a molecular distillation process, which is part of an industrial production process. The final product has a monoester content of about 95% propylene glycol monoesters.

Figures 8.2a and 8.2b show the composition of a typical reaction mixture (a) after removal of the excess propylene glycol and (b) after molecular distillation of the propylene glycol monoester. The isomers of the individual fatty acid monoesters are seen on the chromatogram.

Propylene glycol esters can be prepared by a different method based on interesterification of fats (triglycerides) with propylene glycol in the presence of an alkaline catalyst. The reaction takes place at temperatures between 200°C and 300°C and pressures of up to 15 bar. The reaction mixture is quite complex, containing propylene glycol mono- and diesters together with monoglycerides, diglycerides and triglycerides and some free propylene glycol fatty acids and glycerol, Fig. 8.7 illustrates the complex nature of this equilibrium.

The concentration of monoesters can be achieved by molecular distillation, depending on the application, as in cake shortenings where the reaction mixture from the interesterification may be used directly.

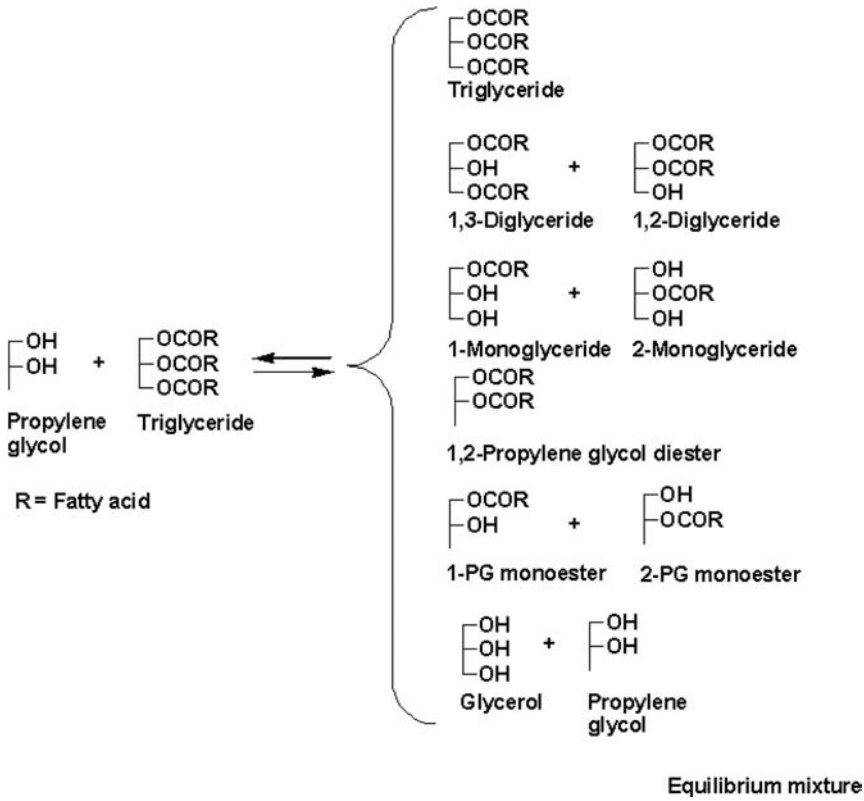

Fig. 8.7 Constituents of the equilibrium mixture formed by interesterification of propylene glycol and triglycerides.

The enzymatic esterification of propylene glycol with fatty acids has been described, but this technology is not used on a commercial scale as yet [12].

8.3.1 Regulatory status

The use of propylene glycol esters of fatty acids in foods, like for all other food emulsifiers, is controlled by health authorities. International organisations such as the FAO/WHO Codex Alimentarius Commission and the European Union (EU) are working on establishing compatible regulations for emulsifiers in food products. However, various differences in the regulation from country to country still exist. In the EU, propylene glycol esters of fatty acids are listed under reference number E477. The FAO/WHO Expert Committee on Food Additives has established an acceptable daily intake (ADI) value of 0–25 mg/kg body weight (calculated as propylene glycol).

The US/FDA reference number for propylene glycol mono- and diesters of fatty acids is §172.856.

Specifications for propylene glycol esters of fatty acids are listed in Table 8.2 together with analytical methods recommended by the European Food Emulsifier Manufacturers' Association (EFEMA).The purity criteria in the EU apply to the additive free from sodium, potassium and calcium salts of fatty acids. However, these substances may be present up to a maximum level of 6% (expressed as sodium oleate).

8.4 Food applications

8.4.1 Aerated bakery products and cake mixes

A cake batter prepared by single-stage mixing can be regarded as an emulsion as well as a foam, as the air bubbles are entrapped in the aqueous phase and, initially, stabilised by egg proteins. During mixing, the fat crystals are adsorbed to the surface of the air bubbles. This stabilises the large number of small air bubbles, which have to expand without rupturing during baking. It is essential that the fat crystals are β'-polymorph, since this crystal form performs better than the β-crystal form. The size, shape and number of adsorbed fat crystals determine the area of the interface that can be made available to air bubble surfaces per unit of fat. Small crystals, such as β'-crystals, have a large surface area to volume ratio and, therefore, are more efficient at stabilising bubbles during baking than the same weight of the larger β-crystals [13].

The introduction of emulsifiers, initially in the form of mono- and diglycerides, into cake shortenings enhances the emulsification of the shortening. The cake batter gains in viscosity and stability, and the incorporated air becomes more finely distributed, resulting in a larger cake volume and increased moistness and shelf life [14, 15].

When liquid shortenings became popular in the baking industry due to easy handling, PGMS was found to be a functional emulsifier in liquid cake shortenings [16].

Cake mixes contain all the dry ingredients for a cake recipe, the consumer adding water, eggs and, if required, oil or fat to the mix and thus producing the batter by mixing. This type of cake requires a high degree of tolerance due to variations in mix handling. The fat/emulsifier blend is, thus, required to ensure that the cake mix performs optimally under varying handling and mixing conditions.

The production of cake mixes involves a thorough mixing of the flour, sugar and fats/emulsifiers, where the fat phase is finely distributed as a thin film over the sugar particles and the flour/starch granules [17].

The cake mix industry has used emulsifiers in shortenings since the 1930s, when mono- and diglycerides became available. Later, after the Second World War, the development of organic acid ester derivatives of monoglycerides

Table 8.2 Specifications for propylene glycol esters of fatty acids (specifications: E 477; propane-1, 2-diol esters of fatty acids)

	EU (1)	FAO/WHO (2)	FCC (3)	Recommended analytical methods
Total fatty acid ester content	Min 85%	Min 85%	–	Composition of Food Additive Specifications. FAO Food and Nutrition Paper 52, Addendum 5, 1997, pp. 135–140
Total propane-1, 2-diol	11–31%	Min 11%	–	*Ibid.*
Free propane-1, 2-diol	Max. 5%	Max. 1.5%	Max. 1.5%	*Ibid.*
Dimer and trimer of propylene glycol	Max. 0.5%	Max. 0.5%	–	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 201–202
Free fatty acids (as oleic acid)	Max. 6%	–	–	AOCS Official Method Ca 5a-40
Sulphated ash	Max. 0.5%	Max. 0.5%	–	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 53–54
Acid value	–	Max. 4	Max. 4	FAO Food and Nutrition (1991) Paper 5, Rev. 2, p. 189
Soap (as potassium stearate)	–	Max. 7%	Max. 7.0%	Comp. of Food Additive Specifications. FAO Food and Nutrition Paper 52, Addendum 5, 1997, pp. 135–140
Residue on ignition	–	–	Max. 0.5%	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 53–54
Arsenic	Max. 3 mg/kg	–	–	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 69–73
Heavy metals (as Pb)	Max. 10 mg/kg	–	Max. 10 mg/kg	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 73–75
Lead	Max. 5 mg/kg	Max. 2 mg/kg	–	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 76–77
Mercury	Max. 1 mg/kg	–	–	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 77–79
Cadmium	Max. 1 mg/kg	–	–	FAO Food and Nutrition (1991) Paper 5, Rev. 2, pp. 59–68

(1): Composition Directive 98/86/EC of 11 November 1998.
(2): Compendium of Food Additive Specifications. FAO Food and Nutrition Paper 52, Addendum 5, 1997, pp. 135–140 + Addendum 8, 2000, p. 204.
(3): Food Chemical Codex, Fourth Edition, 1996, pp. 332–333.

(e.g. lactylated or acetylated monoglycerides) and propylene glycol monostearate represented an improvement on mono- and diglyceride use.

PGMS is an ideal emulsifier for this purpose due to its high solubility in fats and its ability to interact with water, forming films with α-gel structures and enhancing aeration and foam stability.

Painter [17] reported a comparison of different emulsifiers (monoglycerides, polyglycerol esters, PGMS and lactylated monoglycerides) in cake mixes containing hydrogenated animal fat as the shortening. Using a one-stage mixing method, PGMS produced 'the largest volume cake with a fine grain, moist eating quality, but slightly flat crown', followed by lactylated monoglycerides. The use of polyglycerol esters required pre-hydration of the emulsifier, which is not appropriate for the cake mix system.

8.4.2 Sponge cakes, fat-free cakes

Historically, cakes have been made using a two-stage mixing procedure. In the case of sponge cakes, the eggs and sugar were first aerated to a light foam before the flour was carefully blended in. The introduction of emulsifiers to the baking industry made it possible to use a single-stage mixing procedure that allowed all ingredients to be added in one step and aerated by high-speed mixers thus saving working time. Furthermore, the use of emulsifiers made it possible to produce cakes with a larger volume, a finer crumb structure and longer shelf life.

Aqueous gels, comprising a blend of distilled PGMS in combination with distilled, saturated monoglycerides, were very popular as aerating agents in the production of fat-free sponge cakes. In these products, the distilled PGMS was an essential part of the emulsifier blend in order to retain the active α-crystalline form of the hydrated emulsifier mixture [18].

The physical form of α-crystalline gels is a lamellar structure with bimolecular emulsifier layers separated by water layers [19, 20]. The thickness of the interspersed water layers can be up to several hundred Ångstrøm, and the stability of the water layer thickness is essential to the aeration capacity of the gel. Re-crystallisation of the monoglyceride part in the emulsifier blend from the meta-stable α-crystal form to the more stable β-crystal form reduces the water layer thickness and functionality as an aerating agent.

The use of α-gels containing about 30% active emulsifier facilitates mixing of all ingredients in one procedure and also in a reduction of the egg content. Furthermore, the α-gels produce high-volume cakes with a fine texture and appearance. The application of such gels as aerating agents in sponge cakes became especially popular among Europe's small bakeries in the 1960s. Later, the development of powdered emulsifier products based on PGMS and monoglycerides gradually replaced some of the aqueous gels. However, aqueous gels containing PGMS are important ingredients that are still used in many bakery products and confectionery industry [21].

8.4.3 Dessert products, toppings and non-dairy whipping creams

Many dessert products, in the form of aerated emulsions (vegetable fat-based whipping creams, powdered toppings etc.) contain α-tending emulsifiers to enhance whippability and foam stability.

The structure of topping powders and foams was compared with the microstructure of liquid non-dairy creams by Buchheim *et al*. [9] and Krog *et al*. [22].

The fat phase in a spray-dried emulsion, such as a topping base, is present as fine fat particles embedded in a matrix of protein and maltodextrin or other carriers. The particle size distribution of the fat phase within the dry powder particles is mainly determined by the manufacturing process and, to some extent, by the type of emulsifiers used.

After reconstituting the emulsion by mixing the powder with milk or water, usually in the ratio of 1:3, the fat phase undergoes a strong destabilisation process, which is primarily influenced by the type and concentration of the emulsifier used. The main feature of the destabilisation is a total change in physical structure from a globular fat phase to a matrix of crystal platelets. This transition of the fat structure increases the viscosity of the re-constituted mix and enhances aeration and foam formation. It is assumed that the driving force behind this destabilisation is the absorption of water into the fat particles, causing the fat particles to swell and disintegrate into crystalline platelets, which then aggregate to form a tri-dimensional network. When aerated, the fat crystals adsorb to the surface of the air cells thus stabilising the foam structure.

Figure 8.8 shows the relationship between the concentration of PGMS in topping powders, the viscosity of re-constituted topping emulsion and the foam texture index as measured by Stevens Texture Analyser. The crystallisation rate shown is related to the formation of crystal platelets [23].

The α-tending emulsifiers, in the form of PGMS or lactylated monoglycerides and glycerol monooleate, are highly functional in such aerated dessert products. The microstructure of the foams of toppings and liquid creams are however, quite different.

In contrast to liquid cream, the destabilisation of re-constituted topping powders is much stronger, resulting in a transformation of the fat phase from a globular state to a suspension of crystal platelets. The microstructure of a whipped topping is, thus, characterised by the presence of lipid crystals surrounding the air cells, in contrast to the structure of a non-dairy whipped cream where the air cells are covered with agglomerated fat globules. Figures 8.9a and 8.9b show the microstructure of (a) a re-constituted topping emulsion and (b) a whipped topping foam. The formation of crystal platelets is clearly seen in Fig. 8.9a, and very few globular fat particles are present. After whipping into a foam, Fig. 8.9b shows the adsorption of crystal platelets at the air/serum interface, stabilising the foam structure.

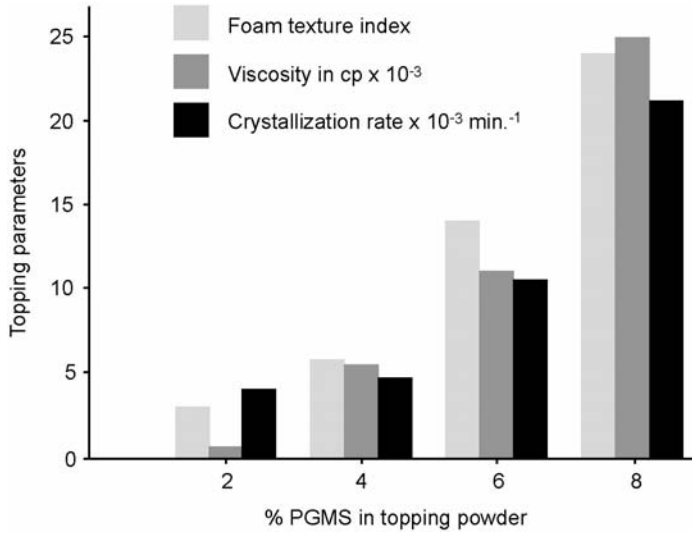

Fig. 8.8 The effect of the concentration of propylene glycol monostearate in topping fats on the viscosity of re-constituted topping emulsion and foam stiffness (measured by a Stevens Texture Analyser). The crystallisation rate is calculated from solid fat measurements by pulsed NMR analysis. (Adapted from [23]).

Table 8.3 Specific volume and foam stiffness of whipped creams and toppings

Sample	Overrun%	Foam stiffness* G^*, Pa
Dairy cream, 38% fat	144	4140
Dairy cream, 20% fat	43	843
Topping (PGMS), 15% fat	430	4700
Topping (PGMS), 20% fat	195	13800
Topping (GMU)**, 15% fat	135	9140

*Oscillatory test: Amplitude 6×10^{-4} radian, frequency: 0.1 Hz.
**Distilled, unsaturated monoglycerides (Dimodan® OT, Danisco A/S).

Due to the larger specific surface area of the crystal platelets compared to the globular fat particles with the same weight unit, a topping foam will have greater foam stiffness than whipped dairy cream, although the fat content is lower, as demonstrated in Table 8.3. The rheological data of topping foams with different fat contents shows that a whipped topping with 15% fat gives a higher volume (% overrun) than a dairy cream with 38% fat, but similar foam stiffness. Increasing the fat content in the topping to 20% gives a reduction in volume and a strong increase in foam stiffness.

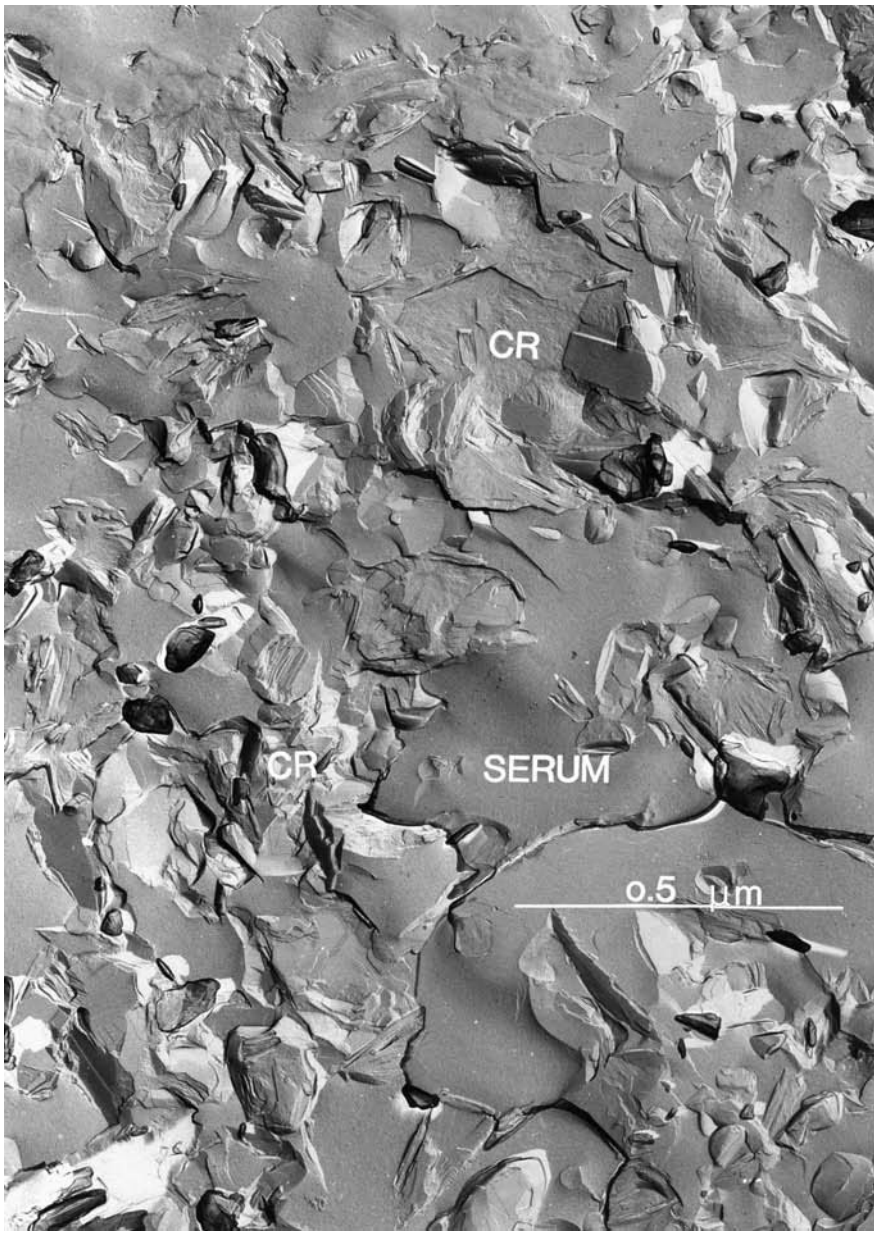

Fig. 8.9a Microstructure of (a) re-constituted topping mix containing 10% propylene glycol monostearate in the fat phase and (b) whipped topping foam, by freeze-fracture, transmission electron microscopy. (a) Shows the appearance of crystalline platelets (CR) in the mix before aerating and (b) shows the adsorption of the crystalline platelets around the air cells. No globular fat particles are visible here, but some may be present in the serum phase. The volume ratio between globular fat particles and crystal platelets depends on the concentration of emulsifiers in the topping fat phase. (Adapted from [22]).

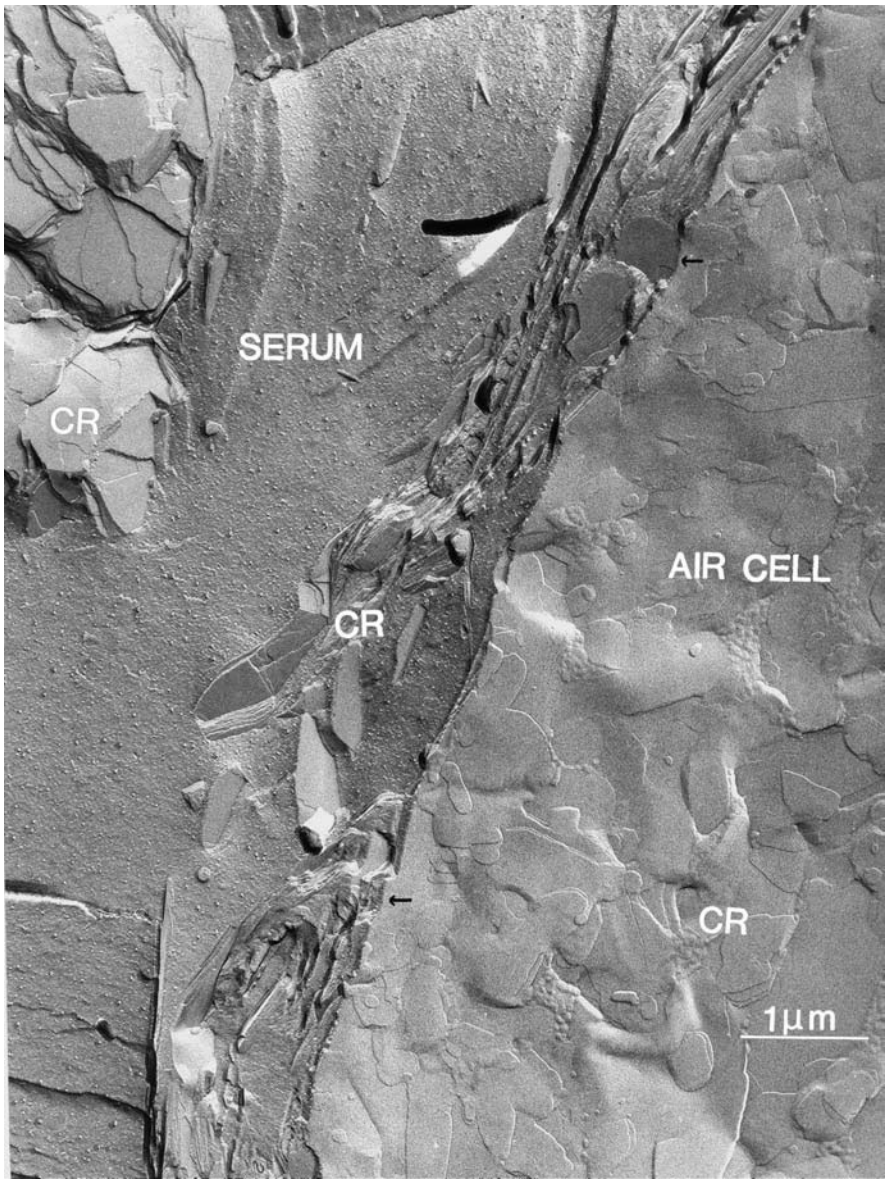

Fig. 8.9b

Replacing PGMS as emulsifier with distilled 90% glycerol monooleate (DIMODAN® OT, Danisco A/S) results in a similar foam volume, but the foams are stiffer than whipped dairy cream.

In the spray-dried topping products, the concentration of the emulsifiers in the fat phase is typically between 8% and 12%, and the emulsifiers used are mainly PGMS or lactylated monoglycerides. The liquid non-dairy cream products contain 2–4% milk proteins, 25–35% fat, usually hydrogenated coconut or palm kernel oil, together with a mixture of emulsifiers consisting of 0.2–0.5% polar emulsifiers (e.g. lecithin, diacetyl tartaric acid esters of monoglycerides, stearoyl lactylates or polysorbates) for obtaining emulsion stability during storage and 0.5–1.0% α-tending emulsifiers for enhancing shear-induced destabilisation during the whipping process.

The microstructure of a whipped liquid, non-dairy cream is shown in Fig. 8.10, which demonstrates the adsorption of fat globules around the air cells. Some of the fat globules are protruding into the air cell, forming a solid fat 'shell' around the air cell.

The destabilisation of liquid cream must not take place during transportation and storage, but only during the whipping process, when the fat globules are exposed to strong shear and colliding forces. The destabilisation of liquid creams mainly affects the surface layer of the fat globules, inducing agglomeration and

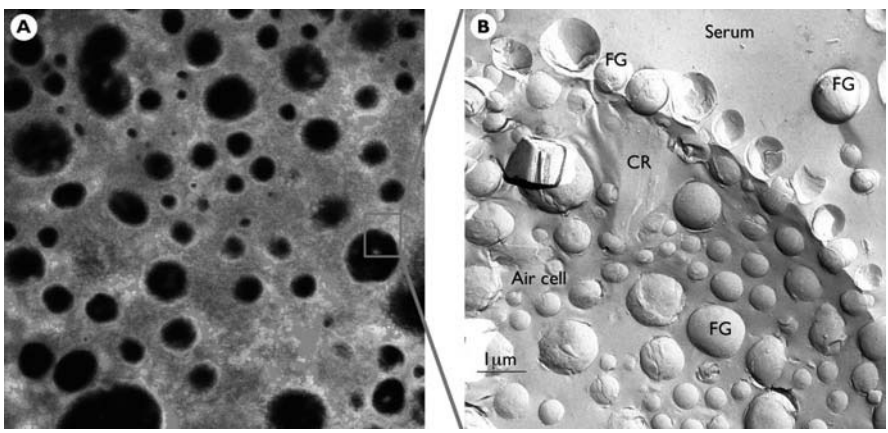

Fig. 8.10 Microstructure of whipped non-dairy cream at different magnifications demonstrating the foam structure of aerated emulsions. (A) Confocal laser scanning micrograph of whipped cream, image size 1.5 mm × 1.5 mm. The fat globules are stained with Nile Red and appear as red particles. The fat globules are agglomerated and adsorbed around the air cells, clusters of fat globules form bridges between air cells in the serum phase, stabilising the foam structure. The protein is stained with flourescein-S-isothiocyanate (FITC-I) and appears as a light grey background. The average air cell diameter is 30 μm. (B) Transmission electron micrograph showing a section of an air cell, demonstrating the adsorption of fat globules at the air–serum interface. The solid fat globules protrude into the air cell. Bar = 1 μm. (Courtesy of Danisco A/S, Brabrand).

partial coalescence of the fat phase, forming a network of fat globule aggregates, stabilising the air cell structure and providing a stable foam with good volume and texture.

The crystallisation of the fat phase in whippable emulsions is an important parameter in the destabilisation process [24], and may vary considerably according to the fat source used, affecting the whipping properties of the cream.

8.4.4 Other applications

In some countries, local soft ice cream producers use aqueous α-gels or powdered topping bases containing PGMS and monoglycerides as emulsifiers. Indeed, the use of PGMS in industrially produced ice cream has recently been patented [25]. The presumed function of PGMS in ice cream is to provide a finer ice crystal distribution and, thus, contribute to a smoother texture and better mouthfeel.

Outside the food industry, PGMS is found in many cosmetic applications, including creams and lotions.

Dedication

Flemming Vang Sparsø would like to dedicate this chapter to the memory of Niels Krog, 1929–2003.

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9 Stearoyl-2-lactylates and oleoyl lactylates

Troy Boutte and Larry Skogerson

9.1 Introduction

In the 1940s, one of the most prevalent emulsifiers used in bread baking in the United States was polyoxyethylene monostearate (POEMS). The use of POEMS eventually became unfavorable from a consumer point of view, providing an opportunity for other emulsifiers. At that point, the C.J. Patterson Company, where the lactylates were first developed, was embarking on a prolific research and product development effort.

In the 1950s when sodium stearoyl lactylate (SSL) research was initiated, the commercial bread market was already well established and fewer people made bread at home, resulting in a growing market. An obvious place to begin a new product development program was therefore in bread improvers. Initially, one of the main goals of this research was to develop a replacement for POEMS in bread baking. POEMS, due to the polyoxyethylene chain, acted as a protein aggregating agent and provided strength during the baking process. Due to the stearic acid moiety, POEMS provided a significant degree of crumb softening. Therefore, a replacement for POEMS would need similar characteristics to be commercially acceptable.

In the 1940s, several researchers [1–3] reported that anionic surfactants affected tolerance of dough to over-mixing and this provided part of the inspiration for the development of lactylates. A few years into the research program, in the early 1950s, stearoyl lactylic acid esters were tested and showed immediate promise as a POEMS replacer. The ability of lactic acid to polymerize was known at the time, and evidently it was believed that the lactic acid polymer would mimic the effects of the polyoxyethylene chain of POEMS. The stearic acid portion would of course provide the crumb softening as was the case with POEMS. The lactylic anion would hopefully improve bread volume and tolerance to over-mixing. In 1954, Thompson and Buddemeyer [4] published the first paper showing that calcium stearoyl lactylate (CSL) improved mix tolerance, bread volume and overall quality.

The early work on lactylates, while promising, was relatively slow since the acid form of the molecule is not readily dispersible. The stearoyl lactylic acid salts, however, were found to be much more dispersible in water and therefore more readily functional. In addition, the salt forms were easier to handle in a production environment.

The original patent was filed for calcium stearoyl lactylate (CSL) and sodium stearoyl lactylate (SSL) in 1951 [5]. CSL was first used as a bakery additive in the United States around 1962. Due to regulatory issues, SSL was first allowed for use in bakery additives in 1968.

During the patent application and food additive petition process, much work was done in all areas in respect to the lactylates. The synthesis procedures were optimized, animal feeding studies were conducted, and application testing was continued. This process was very active until the approval for SSL was granted. Starting in the late 1960s, many fundamental studies involving the chemistry and application of the lactylates were carried out both by industrial and academic laboratories. Many of the studies involved baking, but the lactylates were also tested in virtually every major food category, pet foods and also in cosmetics.

9.2 Lactylate regulations

Lactylate esters are permitted for use as food additives in essentially all countries around the world. Tables 9.1 through 9.4 list the applicable regulations for the United States and Europe. In many countries outside of the EU and the United States, *Codex Alimentarius* regulations are followed, sometimes with country-specific modifications. Comparison of lactylate regulations between different regulatory agencies shows a high degree of complexity and inconsistency. These tables illustrate the differences between the United States and the EU with respect to specifications and permitted uses.

In the United States (Table 9.1) there are three separate regulations:

1. Calcium stearoyl lactylate (CSL): Stearic acid, calcium counter ion, and composition specified (21CFR 172.844).
2. Sodium stearoyl lactylate (SSL): Stearic acid, sodium counter ion, and composition specified (21CFR 172.846).
3. Lactylic esters of fatty acids (LEFA): Nothing specified for either fatty acid, counter ion or composition (21CFR 172.848).

Table 9.1 Food lactylate regulations and specifications in the United States

	Calcium stearoyl lactylate (CSL)	Sodium stearoyl lactylate (SSL)	Lactylic esters of fatty acids
US regulation	21 CFR 172.844	21 CFR 172.846	21 CFR 172.848
Specifications			
Sodium	–	3.5–5.0%	None
Calcium	4.2–5.2%	–	None
Lactic acid	32–38%	31–34%	None
Ester value	125–164	150–190	None
Acid value	50–86	60–80	None

Table 9.2 Lactylate uses permitted in the United States

CSL	
Yeast leavened bakery products	0.5% of flour
Liquid and frozen egg whites	0.05%
Dried egg whites	0.5%
Whipped vegetable oil topping	0.3%
Dehydrated potatoes	0.5%
SSL	
Baked goods, pancakes, waffles	0.5% of flour
Icings, fillings, puddings, toppings	0.2%
Beverage creamers	0.3%
Dehydrated potatoes	0.5%
Snack dips	0.2%
Sauces and gravies	0.25%
Prepared mixes of above	As indicated above
Cream liqueurs	0.5%
LEFA	
Bakery mixes	To achieve the intended physical or technical effect
Baked products	"
Cake icings, fillings, and toppings	"
Dehydrated fruits and vegetables	"
Dehydrated fruit and vegetable juices	"
Vegetable-fat coffee whiteners	"
Frozen desserts	"
Liquid shortening for household use	"
Pancake mixes	"
Precooked instant rice	"
Pudding mixes	"

In addition to the specified compositional differences, the approved uses and use levels are also different between the three materials (Table 9.2). Presumably these differences arose because the initial petitions were submitted and reviewed at different times and by different parties. Considering the chemical similarities in composition among the three different species, the regulatory distinctions are difficult to rationalize at this time.

In the EU there are only two regulations, one for the sodium salt and the other for the calcium salt (Table 9.3.). There is no regulation comparable to that for lactylic esters of fatty acids in the United States. Curiously, though the compositional specifications for the two are somewhat dissimilar, the permitted uses and use levels are the same (Table 9.4.).

9.3 Lactylate manufacturing

Lactylate esters are synthesized from food grade fatty acids and lactic acid. Because of the high esterification temperatures that are used, the raw materials

Table 9.3 Food lactylate regulations and specifications in the EU

European regulation	E 481	E 482
Specifications		
Sodium	–	2.5–5.0%
Calcium	1.0–5.2%	–
Lactic acid	15–40%	15–40%
Ester value	125–190	90–190
Acid value	50–130	60–130

Table 9.4 Lactylate uses permitted in the EU

Fine baked goods	5 g/kg
Quick cook rice	4 g/kg
Breakfast cereals	5 g/kg
Emulsified liqueur	8 g/l
Spirits <15% alcohol	8 g/l
Cereal-based snacks	2 g/kg
Chewing gum	2 g/kg
Fat emulsions	9 g/kg
Desserts	5 g/kg
Sugar confectionery	5 g/kg
Beverage whiteners	3 g/kg
Cereal- and potato-based snacks	5 g/kg
Minced and diced canned meats	4 g/kg
Powders for preparation of hot beverages	2 g/l
Dietetic foods for special medical purposes	2 g/l
Bread	3 g/kg
Mostarda di fruitta	2 g/kg Individually or in combination

should not contain significant levels of heat sensitive materials. Heat stable lactic acid should be specified to avoid the generation of unacceptable levels of colored degradation products. The fatty acids should be free from the chick edema factor in order to be food grade. Current production of fatty acids involves a molecular distillation step so that non-food grade contaminants are not normally a problem.

A generalized structure of sodium stearoyl lactylate with stearic acid esterified to lactic acid is given in Fig. 9.1. Since lactic acid contains a hydroxyl as well as a carboxyl group, the fatty acid can be esterified to a single lactic acid or to a lactic acid polymer. In commercial preparations of SSL and other lactylate esters the number of lactic acids, n, ranges from 1 to 4. On a total product basis typical distributions are about 50% stearoyl-1-lactylate, 20% stearoyl-2-lactylate, 5% stearoyl-3-lactylate and trace amounts of stearoyl-4-lactylate. In addition to the presence of multiple species of lactylate esters, there is also some unreacted fatty acid and polylactic acid. The approximate breakdown is 60–70% lactylate esters, 15–20% unreacted fatty acid, and the remainder polylactic acid and sodium (or calcium).

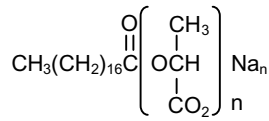

Fig. 9.1 Sodium stearoyl lactylate.

The reaction that occurs during manufacturing is a base catalyzed esterification. Tsen and Hoover [6] described a process for preparing lactylate esters by this method. Raw materials used in the manufacturing process are fatty acid, 88% lactic acid, and an alkaline catalyst. The carbonates or hydroxides of either sodium or calcium are used depending on the product to be manufactured. Usually, the carbonates are preferred because of their lower cost. The esterification reaction is carried out in a chemical reactor that is resistant to corrosion by the lactic acid. Molten fatty acid and 88% lactic acid are charged into the reactor forming a two-phase mixture and the catalyst is added slowly with agitation. Because lactic acid is a stronger acid than stearic or other fatty acids the lactic acid is neutralized first. An alternative sequence for charging the reactor is to use a lactic acid salt rather than adding lactic acid and base separately. The exact order of addition has no effect on the final product as long as equivalent reactants are used.

Nitrogen gas is sparged into the reactor throughout the entire process for two important reasons. First, to prevent oxidation of reactants and products, and second to remove water because any amount of water present in the system would drive the reaction toward hydrolysis rather than toward esterification. A significant amount of water is included with the 88% lactic acid and each ester bond formed generates an additional water molecule.

After neutralization, the reaction temperature is increased to about 200°C. During the heating process water is continually driven off and carried away by the nitrogen sparge. As the system becomes more anhydrous, lactic acid and its salts continue to polymerize (88% lactic acid contains about 30% lactic polymers). At some point the system becomes hydrophobic enough for the lactic polymers and fatty acid to become mutually soluble. The series of reactions that lead to formation of fatty acid–lactylate esters is outlined in Fig. 9.2. First, a fatty acid carboxylate attacks a lactic acid polymer to form a mixed anhydride.

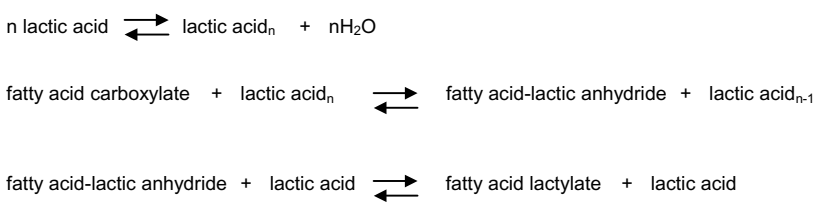

Fig. 9.2 Reaction sequence in formation of lactylate esters.

The mixed anhydride then reacts with the hydroxyl of a lactic acid to form the lactylate ester. Since the anhydride can be hydrolyzed by water, it is important that the water formed during lactic acid polymerization be effectively removed by the nitrogen sparge. The sequence shown in Fig. 9.2 is repeated with a buildup of lactylate esters until the specified acid value is reached and a decision is made to terminate the reaction.

After the reaction has reached the specified end point the product is converted to the final form. The most convenient form for SSL and CSL is as a free-flowing powder. Normally these products are flaked and then ground into a fine powder. A less frequent process for SSL is spray chilling. Apparently, molten CSL has too high a viscosity to be easily spray chilled. The physical characteristics of lactylate esters are strongly dependent on the composition. For example, lactylic esters of stearic acid (low sodium content) crystallise into a rather soft and pliable material that is unsuitable for flaking and grinding. Consequently, the low sodium version is normally sold in blocks that must be melted for use.

When oleic acid is used as the fatty acid, the final product is a liquid with a melting point below 0°C. Even in this case, however, the physical characteristics depend on the exact composition since the viscosity of the liquid can range from very thin to very thick. Presumably, the viscosity is strongly affected by the amount of lactic acid polymers and possibly by interactions between the different lactylate esters.

An alternative synthetic process involves the reaction of acid halides of fatty acids with lactic acid or its polymers [7, 8]. In this method lactic acid oligomers were synthesized and dehydrated by azeotropic distillation with benzene. When oligomers with specific degrees of polymerization were used, the corresponding lactylate species were obtained. Obviously, the acid halide approach leads to a number of environmental and toxicity issues for food products because of the organic solvents that were used. On the other hand, lactylic esters with a much better definition of composition were synthesized. No data were presented to suggest that the more pure lactylates were more functional than those prepared by base-catalyzed esterification.

9.4 Lactylate chemistry

Commercial preparations of lactylate esters are relatively low melting materials with a broad melting point of about 50°C. Because of their high degree of hydrophilicity, lactylate salts hydrate readily in water at ambient temperature. The less neutralized these materials are, the more soluble they are in fat and the slower they are to hydrate. In addition, the calcium salts hydrate more slowly than do the sodium salts. This may explain why CSL and SSL appear to have somewhat different functionalities in short baking processes. In general, minimal, if any, difference is seen with the hydrated forms.

Table 9.5 Effect of hard fat addition on flow characteristics of SSL

Sample	Resistance to		Melting point range (°C)
	Hygroscopicity	Caking 43°C	
SSL	Extreme	Poor	48.0–50.4
SSL + 2.5% hard fat	Slight to moderate	Good	59.2–66.0
SSL + 9% hard fat	Slight	Very good	58.3–65.3
SSL + 30% hard fat	Very slight	Very good	58.6–64.8

When lactylates are manufactured to specification and then handled properly during distribution, the free flowing characteristic is maintained. However, the products are hygroscopic and have a relatively low melting point, therefore storage at high temperatures and/or in high humidity can cause the product to lump. The problems tend to be more pronounced with SSL because its rate of hydration is faster. Because of these handling issues, a number of attempts have been made to improve the handling characteristics of lactylates.

One approach was to generate lactylate hydrates [9]. In this study it was shown that hydrated gels containing 40% SSL could be prepared and would remain functional for periods of at least two to three months. Observations made with the gels are contrary to the widely held belief that lactylates are readily hydrolyzed. In fact, lactylates in water have a half-life of 2 to 3 months (unpublished observations).

A second approach was to incorporate a small amount of hard fat (soybean stearine) into the molten lactylate prior to flaking and grinding [10]. Three criteria were used to determine the improvement of handling characteristics. These were hygroscopicity, resistance to caking at 43°C (110°F), and melting point. Results are shown in Table 9.5. Handling characteristics clearly improved with the addition of hard fat up to about 10%.

9.5 Lactylate applications

In spite of the earlier approval of CSL, SSL is sold today in the United States in far greater quantities than CSL or the lactylic acid form. Therefore, the majority of applications data generated involves application of SSL.

One of the fundamental properties of an emulsifier is the presence of both polar and non-polar moieties in its molecular structure. The lactylates certainly meet those criteria with the fatty acid representing the non-polar portion and the ionic lactic acid polymer representing the polar portion. Another property of an emulsifier, implied by the name itself, is the ability to form a stable emulsion between water and oil or fat. Yet another property of emulsifiers in some food systems is the ability to form complexes with starch and protein. Still other emulsifiers are ionic in nature, which imparts special functionality in

some applications. Several commercial emulsifiers are capable of forming an emulsion and perhaps complexing with starch. However, the lactylates are one of the few, if not the only emulsifiers to combine all of these attributes into one product. The ionic nature of the lactylates, combined with their ability to form very stable emulsions and strong complexes with both protein and starch, makes them virtually indispensable in some applications. In addition, the ease of use, particularly of SSL, due to its rapid aqueous dispersion further sets it apart as a multi-functional, convenient, and economical ingredient.

9.6 Interactions between lactylates and starch

The stearic acid moiety of the lactylates participates in starch complexing in a manner believed to be similar to that of glycerol monostearate (GMS). The commonly accepted theory is that the stearic acid moiety is intercalated into the slightly non-polar helical starch structure resulting in an insoluble complex. The insoluble starch/lactylate complex resists retrogradation, resulting in improved starch function and reduced staling in bakery goods. However, if GMS and lactylates worked in exactly the same manner, a combination of these two ingredients would not be expected to be semi-additive with regard to preventing bread crumb staling. It is possible therefore that the ionic nature of the lactylates creates ionic repulsion between starch/lactylate complexes, which could partly explain the improved bread crumb softening with SSL and GMS combinations. Also, since bread crumb structure is essentially starch granules embedded in a protein matrix, it is possible that the modification of the protein matrix by the lactylates modifies intergranular interaction, thereby retarding staling.

It is known that glycerol monooleate is far inferior to glycerol monostearate with regard to bread crumb softening. The commonly accepted explanation for this is that for starch interaction, the fatty acid portion of an emulsifier should be of a linear nature. However, Riisom *et al.* [11] reported that glycerol monooleate (GMO), when delivered as an emulsion with sodium deoxycholate, complexes starch as well as glycerol monostearate. Presumably, the physical orientation of GMO as a result of micelle formation with sodium deoxycholate is favorable for interaction with starch. The interaction of glycerol monostearate with starch is also known to depend on its physical orientation in an aqueous system [12]. In comparison, oleoyl lactylic acid (OLA), a liquid lactylate, is known to be very similar to SSL concerning bread crumb softening. It is also known that OLA is not a very good in situ starch complexing agent (unpublished results) supporting the theory that at least some of the crumb softening effects of the lactylates are due to both starch and protein interactions.

Tenney *et al.* [13] studied the effects of 0.5% SSL on the hot paste viscosity of corn, rice, wheat, potato, and tapioca starches from pH 3.0 to 9.0. The effects of SSL were quite variable, depending greatly on the type of starch and the pH

of the solution. In general, SSL usually increased the transition temperature, which is the onset of gelatinization, especially in the higher pH range. At all pH levels, the effect of SSL on final viscosity was always greater for tapioca and corn starch with maximum increases of about 50%. Viscosity of potato starch was always less when SSL was added ranging from a 40% reduction at pH 3 to a 50% reduction at pH 5.0. The maximum change in transition temperature was 16°C for corn starch at pH 9.0 and 4.5°C for potato starch at pH 6.0.

Tenney and van Vactor [14] studied the effects of SSL on the hot paste viscosity of modified waxy corn starch and modified tapioca starches in the amylograph at pH 4.5 and 6.5. In contrast to the results with native starches, there was little effect on the modified starches at either pH on either transition temperature or the viscosity with levels of SSL up to 1.0%. One modified tapioca (Purity D), however, did show a 20°C increase in transition temperature and a significant decrease in 25°C viscosity in a pH dependent manner.

Krog [15] also studied the effects of SSL and CSL on starch as compared to diacetyl tartaric acid esters of mono- and diglycerides (DATEM) and GMS. GMS caused the greatest increase in the pasting temperature of wheat and tapioca starch followed in order by SSL, CSL, and DATEM. Krog also found that pH was very important in determining the pasting temperature and peak viscosity of starch in the presence of emulsifiers. Ionic concentration also had an effect on results. Krog reported that DATEM made from unsaturated fatty acids has similar effects on starch to DATEM made with saturated fatty acids, and hypothesized that the effects of DATEM on starch may also be related to the polar group.

Ghiasi *et al.* [16] studied the effects of SSL and palm oil based monoglycerides on the swelling and solubility of wheat starch at various temperatures. Monoglycerides were found to be effective at delaying swelling of starch granules up to 120°C (Table 9.6). SSL delayed swelling up to about 85°C after which there was a rapid increase in swelling, similar to the control by 95°C. Ghiasi concluded that material leached from the starch granule was similar, whether from

Table 9.6 Effect of temperature and added surfactant – sodium stearoyl lactylate (SSL) or monoglycerides (MG) – on starch solubility and iodine affinities of leached solubles

Pasting temperature (°C)	Solubility (%)			Iodine affinity of leached solubles (%)		
	Control	MG	SSL	Control	MG	SSL
75	5.9	1.4	1.1	18.5	4.4	3.9
85	9.1	1.7	1.7	17.8	7.3	9.2
95	34.5	4.8	34.3	15.5	11.7	15.7
120	80.0	20.1	79.0	7.4	6.3	7.0

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the control or in the presence of an emulsifier. Further, Ghiasi *et al.* [17] also showed using X-ray diffraction that the starch–SSL complex was present at up to 80°C, but disappeared at 95°C. The SSL–starch complex rapidly reformed as the temperature decreased. Since the SSL–starch complex dissociates at 95°C, Ghiasi *et al.* hypothesized that if iodine were added at this point, then the iodine and SSL would compete for binding sites in the starch helix. The results were supportive of his hypothesis and leave little doubt that SSL enters the starch helix.

9.7 Interactions between lactylates and proteins

In addition to starch interactions, the lactylates also interact strongly with proteins. Lactylates are believed to interact with protein in at least two ways. The stearic acid moiety is believed to form hydrophobic bonds with non-polar regions on the protein [5]. Also, ion pairing is believed to occur between the carboxylic portion of the lactylate and charged amino acid residues on the protein. Neutralization of charges on the protein can result in protein aggregation, which is sometimes desirable. In the case of bread dough, this results in increased dough viscosity, better gas retention, and ultimately greater bread volume.

DeStefanis *et al.* [18] showed that SSL is associated with the protein fraction of bread dough during the mixing, proofing, and early baking stage. At approximately 60°C, as the gluten denatures and starch begins to gelatinize, SSL transfers to the starch fraction and forms a complex. DATEM, however, remained bound to the protein fraction through the entire baking process. Therefore, even though DATEM is known to partially complex with starch in a simple starch solution, it does not interact substantially with wheat starch during bread baking. Instead, DATEM remains bound to the protein fraction. This largely explains the poor bread crumb softening by DATEM in comparison to SSL, even though DATEM complexes starch in situ. It may also explain why DATEM sometimes produces slightly more dough strength and volume than SSL.

9.8 Lactylates in yeast-raised bakery products and crumb softening

In the United States, the current estimated sales of lactylates is approximately 50 million lbs/year putting it second only to monoglycerides in total sales. By far, the largest percentage of lactylate sales in the United States is in the market segment of yeast-raised bakery products. Within the yeast-raised product market, the largest percentage of sales is in the pan bread segment. The vast majority of the lactylate used is SSL.

There are several reasons behind the success of lactylates in yeast-raised goods. SSL is readily soluble in dough with no pre-hydration, it is relatively stabile with regard to shipping, storage, and flour premixes. It is also relatively

inexpensive to manufacture and provides excellent dough machining properties, bread volume, and crumb softness. Probably, the main reason behind the success of lactylates in yeast-raised goods is dual functionality with regard to strengthening and crumb softening. These advantages make SSL one of, if not the most, useful yeast-raised bakery additives.

Crumb softening effects similar to that of the lactylates can be achieved by a few other emulsifiers, namely GMS, and in particular pre-hydrated GMS. It is interesting to note that the relative effectiveness of SSL and pre-hydrated GMS depends, to some extent, on the flour being used, further indicating that they achieve crumb softening in slightly different ways.

With regard to crumb softening, SSL is superior to CSL and therefore CSL will not be considered here. Although the crumb softening effects of SSL varies to some extent from flour to flour, there is generally a dramatic improvement. Many bakeries in the United States tend to use SSL at 0.375% based on flour. This is the point of diminishing returns with many flours when trying to simultaneously maximize strength, volume, and softness.

With the advent of bacterial amylase enzymatic crumb softeners in the United States starting in the 1970s, and especially the introduction of maltogenic amylases in the 1980s, the importance of emulsifiers as crumb softeners was diminished. However, the use of SSL and other emulsifiers in conjunction with enzymatic softeners is still practiced by a majority of bakeries. There are several reasons for this, including the improved handling of doughs containing SSL, improved crumb structure, and the continuing need for improved volume and resistance to abuse and mechanical shock. In addition, in spite of the popularity of extended bread shelf life in the United States, a considerable amount of bread is produced for markets that require less than three days of shelf life. Emulsifiers provide adequate softness for these products at a cost similar to many enzymatic softeners and in addition provide dough conditioning.

The initial introduction of bacterial amylase was not met with general acceptance. The quality of the bread made with bacterial amylase was unpredictable, sometimes resulting in unacceptably gummy bread. Bacterial amylase is not inactivated by the baking process and can continue to degrade starch during bread storage, sometimes resulting in bread that literally collapses. The effects of bacterial amylase are unpredictable, partly because it is inactivated by cold temperatures and exacerbated by warm temperatures. Therefore, for best results the amount of bacterial amylase would have to be tailored to the particular temperature profile the bread experiences throughout the distribution network. The effects are also heavily dependent on the source of flour.

The introduction of maltogenic amylase greatly improved options for bakers. Maltogenic amylases produce very soft bread with a dry mouthfeel in a very predictable manner. The degree of crumb moistness, or adhesive value, in terms texture analysis, can be controlled to some extent by combining bacterial and maltogenic amylase, which basically have opposite effects on crumb adhesive

value. However, the effects of bacterial amylase are still unpredictable. We have found that the use of SSL and monoglycerides reduces the need for bacterial amylase, producing bread with similar softness and adhesive values (unpublished results). This provides some insurance against excessively gummy bread, while maintaining maximum softness and overall food quality.

9.9 Dough strengthening

Due to their protein aggregating qualities the lactylates also provide very good volume enhancement and resistance to mechanical abuse and shock. A distinction is made between volume enhancement and shock resistance. Although monoglyceride and fungal amylase, for example, provide some volume enhancement, virtually no resistance to mechanical shock is provided. Both CSL and SSL, as well as the stearoyl lactylic acid form (SLA), provide very good yeast-raised dough strengthening effects. CSL was studied more extensively in the early C.J. Patterson research program and was commercialized first. Early results indicated that CSL was preferred in lean formulas with SSL being developed later for richer formulations. Today, very little CSL is sold in the United States, but much of what is sold does go into lean hearth bread type formulations. The lesser degree of crumb softening can actually be advantageous in hearth-type breads where a soft crumb is not always desirable.

The strengthening effect of the lactylates relates to their ability to aggregate proteins, which helps in the formation of the gluten matrix. The effect is to produce a dough that is more viscous yet not overly elastic, as in the case of a dough that is overly oxidized. The dough is also softer than the unemulsified dough and that allows more abusive mechanical working without causing irreversible damage to the protein structure.

The maximum legal limit of SSL in the United States is 0.5% based on flour in yeast-raised dough. However, in relatively mild processing conditions, it is often not necessary to use over 0.375%. In fact, in breads, where symmetry is very important such as hamburger buns and white pan bread, it is sometimes advisable to use 0.25% SSL to maximize symmetry. The effect of SSL is also known to vary somewhat from flour to flour. Pan bread and buns made from certain flours that respond strongly to SSL can suffer from excessive break and shred and may have poor symmetry in general. This same effect, however, can be quite desirable in hearth loaves where a lot of break and shred is sometimes desirable and where perfect symmetry is sometimes undesirable.

The effect of lactylates on dough handling properties and proof volume are related to protein complexing. However, the effect of lactylates on starch becomes equally important during the late baking stage and during cooling of the final baked product. As proofed dough is heated in the early baking phase, the lactylates begin transferring from the protein to the starch. The coating of

Table 9.7 The effects of SSL and CSL on donut volume

		Volume, width of four donuts (cm)		
Formula	Dough type	Control	0.5% SSL	0.5% CSL
Lean	Straight	33.7	38.1	37.5
Medium	Straight	33.0	38.1	36.2
Rich	Straight	34.9	38.1	34.9
Lean	Sponge	34.3	34.9	33.0
Medium	Sponge	34.3	37.5	34.9
Rich	Sponge	34.6	38.1	34.9

the starch significantly delays starch gelatinization, which keeps viscosity low and allows additional expansion in the oven. Once the starch gelatinizes, however, the resulting lactylate–starch complex is considerably more viscous than dough with no lactylate. As the starch cools after leaving the oven, the increased viscosity provides support, and in addition sets faster. These phenomena taken together are believed to reduce shrinkage and wrinkling of the final product. Indeed, yeast-raised products made without emulsifiers may achieve similar volumes to emulsified doughs during the baking phase, only to shrink and wrinkle excessively during cooling. The crust of unemulsified loaves will often have a leathery and unappealing texture. This is particularly evident in hearth loaves where a crisp crust is usually desired. Since both DATEM and SSL are known to produce crisp bread crust, it is likely that this phenomenon relates more to their effect on the starch–protein relationship rather than the starch itself, since DATEM does not complex starch in bread dough.

Many of the same benefits conferred by lactylates on baked yeast-raised goods are apparent in fried and steamed yeast-raised products as well. As an example, fried donuts made with SSL in a medium rich formulation are compared to a control with no SSL in Table 9.7 [19]. It should be noted that the improvement due to the lactylates was dependent on formulation. Although SSL significantly improved performance over the control at all levels of shortening and sugar, the overall effect was greater at higher levels of shortening and sugar.

9.10 Cakes and chemically leavened baked goods

In yeast-raised bakery goods, emulsifiers are typically not acting as emulsifiers in the truest sense, but as protein and starch complexing agents. In contrast, chemically leavened baked goods require true emulsification to produce the types of products many consumers prefer.

Before the introduction of modern shortenings, and particularly before the introduction of shortenings containing monoglycerides in the 1920s, cakes were made with less shortening and sugar than is customary today. The fats available

did not aerate well because of their β-crystalline configuration and relatively firm consistency at the temperature of a cake batter.

The introduction of partially hydrogenated shortening in a β'-crystalline configuration was of great benefit to the cake baker. The small β'-crystals allowed much greater air incorporation. The addition of nitrogen during the processing of these shortenings also allowed an increase in the solids content of the shortening while maintaining a soft texture. The addition of mono- and diglycerides to these shortenings did not increase air incorporation, but helped to produce smaller air cells that were more resistant to coalescence. The improved aeration and stability allowed the baker to use more sugar and shortening without emulsion breakdown. As a result, the cakes made with emulsified shortening were referred to as high ratio due to the high ratio of sugar to flour. The cakes produced with the emulsified shortening possessed a softer texture, finer cell structure, and had better shelf life.

As other emulsifiers, such as glycerol lactopalmitate and propylene glycol fatty acid esters were developed it was discovered that combinations of emulsifiers tend to produce even more stabile batter emulsions. In addition, many of the new emulsifiers, due to the disruptive effect of the various polar groups on crystal structure, have a tendency to crystallise in small α-crystals and came to be known as alpha-tending emulsifiers. The small α-crystals have tremendous surface area compared to β-crystals and can pack together closely forming a stabile, solid emulsifier film around an oil micelle. The film segregates the oil from proteins allowing the proteinaceous aqueous phase to be aerated without being destabilized by the oil. Therefore, these emulsifiers allowed the use of high levels of fluid shortenings or even oil in cake batters, but also improved the function of solid shortenings that contain high percentages of oil.

Before the introduction of the lactylates, the only ionic emulsifier available for food use was egg lecithin. Due to the amphoteric nature of lecithin, its effectiveness as an ionic emulsifier is limited. Also, the predominance of unsaturated fatty acids reduces effectiveness in cake baking. The lactylates, however, can be prepared from saturated fatty acids and are strictly anionic in nature. In addition, the lactylates are also alpha tending. The higher melting point of saturated emulsifiers, which is related to their ability to pack closely together in a rigid structure around micelles, tends to create more stable emulsions. The anionic nature of the lactylates is believed to create a negative charge around micelles. Micelles with like charges repel one another, which minimizes coalescence, resulting in high volume and fine crumb structure. Due presumably to the anionic nature, SSL is also known to affect the continuity of egg albumen and wheat protein structure [20].

In addition, the heterogeneous nature of the lactylates is also thought to contribute to general functionality, but especially in the case of a chemically leavened batter. Lactic acid polymerizes during lactylate synthesis creating appreciable amounts of lactic acid monomer, dimer, trimer, and tetramer. These

polymers, when esterified to stearic acid and partially neutralized, result in a wide range of polarities and molecular weights. An appreciable amount of sodium soaps of fatty acid are formed and an appreciable amount of free stearic acid remains in the final product. All of these factors combine to make the lactylates an excellent emulsifier in chemically leavened batters.

Buddemeyer and Moneymaker [21], two of the original researchers involved in lactylate development, proposed that part of the effectiveness of lactylates in chemically leavened batters was due to the production of carbon dioxide in the fat phase of the batter by neutralization of the lactylic acid with sodium bicarbonate. This was thought to be particularly effective if the lactylate was present in the shortening. This would provide additional nuclei for air cells in cakes made with shortening, but presumably would provide little benefit in cakes made with liquid shortening or oil.

In the United States, SSL is commonly used in cake formulas, but due to FDA usage-level restrictions it is typically used in conjunction with larger amounts of other emulsifiers, such as propylene glycol monostearate and monoglycerides. Stearoyl lactylic acid (SLA) is also sometimes used in cake formulations, but due to difficulty in dispersing the acid form it is usually sold pre-hydrated. There is no usage limit on SLA in the United States, but it is still typically combined with other emulsifiers for greater effect.

Trimbo and Miller [22] studied the effects of several emulsifiers, as well as basic ingredients such as egg whites, on tunneling in yellow cakes. Tunneling was found to be more prevalent when batter moisture was low, when batter density was substantially below 1.0, when baking temperatures were higher and when smaller baking pans were used. These factors lead to the theory that tunnels are caused by formation of large pockets of steam after at least some of the crust and crumb have begun to set. It was found that the most effective way to reduce or eliminate tunnels, without causing other faults, was to include up to 0.18% of SSL or sodium stearoyl fumarate (SSF). The addition of approximately 3% egg yolk also eliminated tunnels. Thomas *et al.* [23] reported on the ability of SSF to affect pasting curves of various starches. SSF was shown to be extremely effective at preventing starch gelatinization, implying that a major reason for tunneling is an early onset of gelatinization.

9.11 Lactylate use in cookies and crackers

As is the case with many food products, perfectly acceptable cookies can be made on a small scale without using emulsifiers. However, even for small-scale production, the use of an emulsifier improves the handling properties of cookie dough and the food quality of the final cookie. When cookies are processed on a larger scale, the benefits of an emulsifier become much more apparent. An appropriately selected emulsifier will reduce dough viscosity, reduce sticking

to machinery surfaces, reduce variability in cookie spread, maintain definition of the stamped cookie surface, and improve crumb uniformity and food quality. Emulsifiers can also reduce the need for shortening while maintaining or even improving food quality.

The basic principle of cookie dough mixing is the thorough coating of flour with shortening, resulting in a small but reproducible amount of gluten development. Excessive working of the dough results in too much gluten development and poor machining, baking, and food qualities. Therefore, cookie flours are generally made from soft wheat with low to medium protein content to reduce gluten development. Excessive protein results in tough and hard cookies while deficient protein results in excessive spread and loss of stamp definition. High protein flour will require more shortening, sugar, and leavening and the opposite is true for low protein flours.

Therefore, proper selection of flour, proper mixing, and formula balancing will eliminate many problems associated with cookies. However, even with proper flour selection, an excess of gluten development can occur before ingredients are properly mixed. Therefore, sufficient shortening should be included in the mix to thoroughly coat the flour surface, and this 'shortens' or minimizes gluten formation. The shortening coating also reduces the need for water in the formula, which would lead to more starch gelatinization. The shortening should be soft enough to mix quickly and completely at the relatively cool temperature of a cookie dough, but still contain sufficient solids to prevent oiling out in the final cookie.

Lactylates are used in cookie and cracker formulations primarily to achieve a more uniform distribution of shortening in the dough. This results in decreased dough viscosity, improved machining, increased and more uniform spread, and improved food qualities. In addition, lactylates can reduce the amount of shortening required, thereby reducing formula cost while maintaining other characteristics.

Figure 9.3 [24] shows the effects of SSL (Emplex) on the force required to break rotary cut cookies on a shear press. Cookies baked with 75% of normal shortening content plus 0.5% SSL were as tender as control cookies. Cookies with 50% shortening reduction and 0.6% SSL were also as tender as the control cookies. Similarly, rotary molded cookies with 75% or 50% of the control shortening were as tender as the control cookies when SSL was used at 0.5% and 1.0%, respectively. The appearance of the reduced shortening cookies was equal to the control cookies. A semi-skilled taste panel rated cookies made with SSL and various shortening reductions (Table 9.8.). A 25% reduction of shortening with 0.5% SSL produces a cookie that is quite acceptable.

In addition, Tsen *et al.* [25] compared the effects of several emulsifiers to increase the width to height ratio, or spread, of cookies supplemented with various percentages of soy flour (Table 9.9). They concluded that 0.5% SSL could reduce shortening requirements by up to 33% while maintaining similar spread ratios to

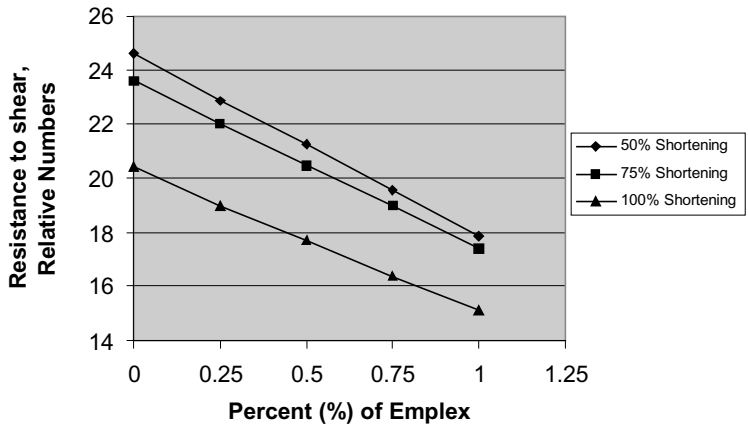

Fig. 9.3 The effect of Emplex on resistance to shear of rotary cut cookies at various shortening levels.

Table 9.8 Taste preferences of cookies made with Emplex and reduced shortening

% of SSL	Shortening (%)	Appearance	Taste preference
No add control	90	Good	5
0.5	90	Good	2
0.5	88	Good	3
0.5	75	Good	4
0.5	50	Good	1

Table 9.9 Effect of various additives on the spread ratio of cookies made from flour II and 28% shortening in the formula

0.5% Additive	Spread ratio
No additive	8.8
Monoglyceride	8.3
Ethoxylated monoglyceride	8.8
Sodium stearoyl fumarate	10.4
Sodium stearoyl lactylate	10.0
Sucrose monopalmitate	9.8
Sucrose mono and distearate	9.6
Sucrose distearate	9.7
Sorbitan monostearate	9.2
Sorbitan monostearate	9.3
Succinylated monoglyceride	9.2

a control cookies. Tsen also theorized that the improving effect of the emulsifier was related to the coating of the starch. The emulsifier coating on the starch delays gelatinization and allows extra time for spreading before the starch sets. That theory does not explain why GMS, an excellent starch complexing agent, is far less effective than SSL at increasing cookie spread. In a low water and high fat system such as a cookie, the monoglyceride may be distributed primarily in the fat phase, especially at elevated temperature, resulting in poor starch complexing. SSL, being much more polar than monoglyceride, may still be in the aqueous phase where it must be to interact with the starch.

9.12 Application of lactylates in pastas

The most basic pasta formulations are very simple, and obviously pasta can be manufactured with only semolina and water. However, there are specific situations where addition of an emulsifier or dough conditioner can provide significant benefit. Even though emulsifiers could provide a general insurance against overcooking and excessive stickiness, most pasta manufacturers in the United States do not use emulsifiers except in specific cases. The most notable case is the use of emulsifier to maintain firmness in canned pasta or for pasta destined for use in soups.

Pasta doughs are very similar to the bread doughs already discussed. The dough must be developed enough to be cohesive and allow mechanical manipulation without falling apart. Excessive development can create an over elastic dough that is difficult to process. The proper use of emulsifiers can produce pasta that has more cohesiveness, while maintaining good machining properties.

Semolina, like wheat, contains a significant percentage of protein and a high percentage of starch. Therefore, there is an opportunity for forming complexes with emulsifiers. In the case of pasta, since it will ultimately be boiled rather than baked, the problems encountered are slightly different from those of bread dough. In bread dough, starch is not fully gelatinized due to limited water. Indeed, bread made with fully gelatinized starch is not very appealing. The starch on the surface of pasta, however, is boiled in excess water. This can cause the surface of overcooked pasta to look dull and off colored and may create a rough edge. This will also lead to greater cooking losses as starch is leached into the cooking water. From a culinary point of view, the fully hydrated starch reduces the ability of the pasta to ‘take up sauce’ since the starch on the surface is already ruptured, resulting in reduced food quality.

The inclusion of SSL into pasta reduces many of the problems associated with pasta production. The primary benefit of adding SSL is to increase the firmness of the pasta after cooking and canning. SSL at 0.5% of formula weight also resulted in the lowest cooking loss, least stickiness, and shiniest appearance

[26]. Pasta made with 0.5% SSL was judged firmer than pasta made with 0.5% glycerol monostearate.

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10 Ammonium phosphatides

Viggo Norn

10.1 Introduction

Ammonium phosphatide is a food emulsifier in the form of ammonia-neutralized phosphoric esters of mono- and diglycerides. The emulsifier is therefore a mixture of ammonium salts of various phosphatides. The original development of ammonium phosphatide goes back more than 50 years and was carried out by the British chocolate manufacturer, Cadbury [1]. The aim of the work was to find an alternative to soy lecithin and avoid the problems of off-flavours connected with lecithin. Primarily, ammonium phosphatide has been closely connected with the production of chocolate, and even today it has limited use and legalized only for application in chocolate. Within the EU the ammonium phosphatides are listed, together with analytical parameters under the reference number E 422, and European legislation allows up to 1% addition of ammonium phosphatide.

Ammonium phosphatides consist of a mixture of phosphatidic acids compounds, where the fatty acid composition is dependent on the source of vegetable fats or oil used. Another parameter for the final ammonium phosphatide is the relation between mono- and diglyceride. This relation will also be reflected in the final composition of the emulsifier. The mono- and diglycerides used for the ammonium phosphatide also include some triglycerides, which will normally be present in the commercial ammonium phosphatides as neutral oil or fat. The emulsifier appears as a yellowish to light brown semi-solid material with a melting point in the range of 20–50°C, or in the case of lower melting point as an oil. The ammonium phosphatides are characterized by a bland smell and taste, and the mouthfeel is smooth, like oil or fat.

10.2 Production of ammonium phosphatides

Production of ammnonium phosphatides takes place in several individual stages. In the first stage basic mono- and diglycerides are produced. Normally, the mono- and diglycerides are manufactured in a high temperature glycerolysis, i.e. a reaction between glycerol and triglyceride yielding a product composition where the content of monoglyceride and/or diglyceride is controlled from the initial relation between glycerol and triglyceride. In general, the major fraction from

the glycerolysis will be the diglyceride, e.g. a composition of 12% monoglyceride, 48% diglyceride and 40% triglyceride is reported by Bradford [2]. The glycerides from the high temperature reaction will, in addition to the abovementioned constituents, contain a small amount of unreacted glycerol as well as some off-flavour chemicals formed at high temperature. To remove the excess glycerol and obtain a neutral tasting and smelling mono- and diglyceride the product is deodorized, a refining which can be carried out very efficiently on a thin film distilling column. The succeeding step in the process to ammonium phosphatide is the formation of the phosphoric acid ester, which takes place by adding phosphorus pentoxide to the glycerides under carefully controlled conditions, i.e. temperature, pressure etc. and under vigorous stirring. The reaction is exothermic and, due to the nature of the pentoxide, requires a low humidity. When the phosphorylation has taken place, the phosphatide is neutralized by adding ammonia to the reactor. The ammonia is fed to the reactor as a gas, which is absorbed in the reaction mixture and reacts with the acid moieties of the phosphatides. A surplus of gas is normally added and this will react with any free phosphoric acid formed from the pentoxide. Only small amounts of unreacted ammonia will be present in the liquid emulsifier after the reaction has ended. The pressure of the reactor is reduced to remove any unreacted ammonia and remove the gas from the product. During the reaction some solid residues in the form of phosphates will be formed. The latter are not required for the final product and can be removed by filtration, leaving the final ammonium phosphatides as a clear oily liquid of neutral taste and smell. The process diagram is shown in Fig. 10.1.

It is thus clear that ammonium phosphatide is a mixture of several substances originating from the starting material that consists of two principal glycerides, i.e. monoglyceride and diglyceride, and these glycerides exist in two positional isomeric forms, which allow phosphorylation of the 1 or 2 position of the glycerol backbone. In addition, the phosphorylation will result in monophosphate esters as well as diesters [3]. Bradford [2] reports the separation of some of the major fractions from the phosphatides before neutralization with ammonia using chromatography. He isolated six fractions from the chromatography; five are diglyceride esters of phosphoric acid, in some cases the compounds are identified as double ester between diglycerides or diglyceride and monoglyceride, and only one is assigned the diester between monoglyceride structures. In addition to the orthophosphate esters, there are some diphosphate esters and again this type is identified as a diphosphate esterified with one or two diglyceride moieties. Figure 10.2 shows some of the compounds isolated from phosphatidic acid.

Analytical and mechanistic studies using chromatography and NMR to monitor the course of phosphorylation have shown that the order of reactivity is monoglycerides 1,2-diglyceride followed by the 1,3-isomer, a sequence reflecting the steric hindrance of the esters [4]. Further, it can be expected that the

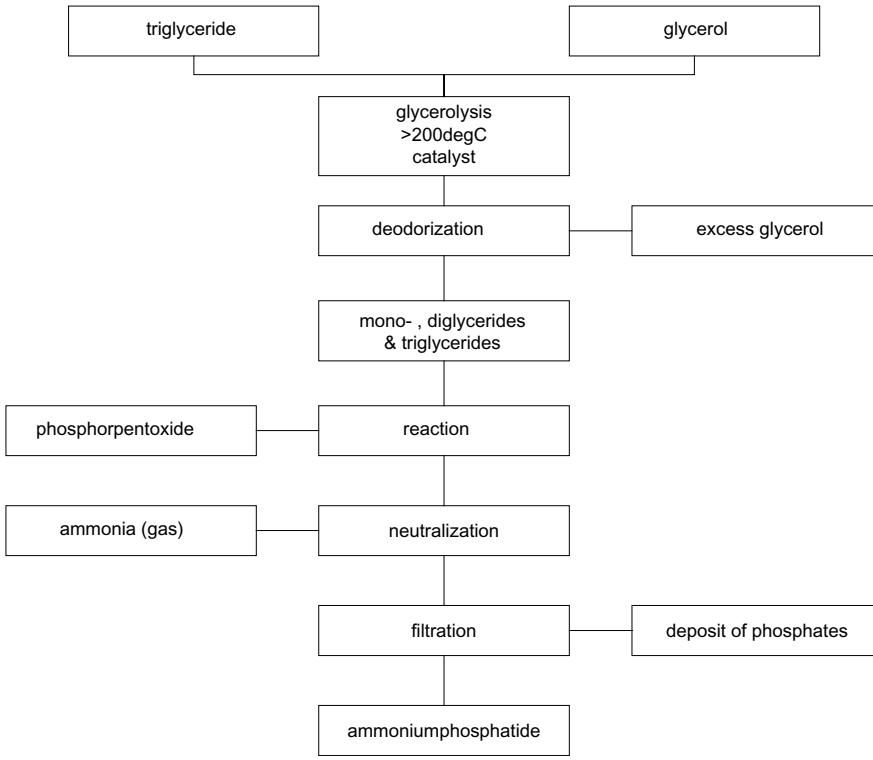

Fig. 10.1 Ammonium phosphatide process diagram.

phosphorus pentoxide, which exists as a tricyclic dimer, at the start of the phosphorylation will form polyphosphates, and the latter will progressively cleave to mono- and diphosphates as the process progresses, a series of reactions for phosphorylation of simple alcohols by phosphorus pentoxide reported by Cherbuliez and Weniger [5].

10.3 Physical and chemical properties of ammonium phosphatides

The physical appearance of ammonium phosphatides depends on the source of fatty acid, thus fully hardened fatty acids as palmitic and stearic acids result in an emulsifier with a melting point above 50°C, while unsaturated acids yield soft or liquid ammonium phosphatides with melting points below 40°C [6]. Ammonium phosphatides are found to be stable emulsifiers and for Palsgaard 4448 (an ammonium phosphatide emulsifier) it has been shown that this is stable in melted form. The properties of this emulsifier have been monitored as the

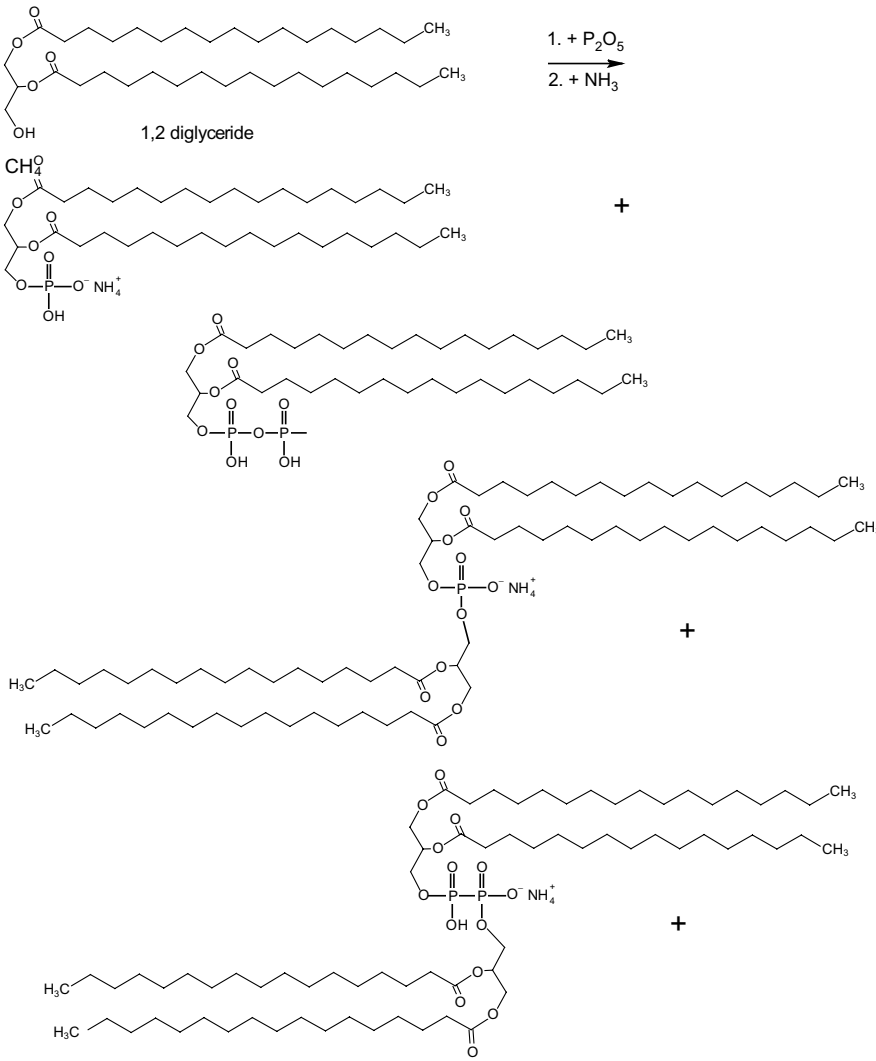

Fig. 10.2 Ammonium phophatides from 1, 2-diglyceride.

ability to reduce viscosity of chocolate, which remains unchanged even after 6 months of storage at 60°C [7]. The emulsifier is soluble in triglyceride above the melting point and can be dissolved in several non-polar organic solvents. The ammonium phosphatides are only slightly dispersible in water. There is no work reported in the literature concerning the relationship between the emulsifier and water, but a preliminary examination reveals that an ammonium phosphatide

emulsifier consisting of approximately 60% phosphatides and 40% triglycerides when mixed with water forms a stable dispersion of spherical bodies. When the dispersion was examined under a microscope in polarized light no bifringence was observed indicating that mesomorphic phases were not present [8]. A similar kind of observation is reported by Rydhag and Wilton [9] for lecithin with triglycerides present, and it is plausible that ammonium phosphatides to a certain extent will act with water like lecithin. In two-phase systems, such as rapeseed oil and water, a small addition of ammonium phosphatides is found to reduce the surface tension, thus 0.2% ammonium phosphatide will decrease the tension approximately by 50%, i.e. 10 dyn/cm. At higher concentrations of ammonium phosphatides, the system will exist as two separate phases where the organic part, i.e. the ammonium phosphatides, form an approximately 50% hydrate. The latter does not exhibit any bifringence in polarized light, and DSC analysis does not show any phase transition from 15 to 85°C [8].

10.4 Food applications of ammonium phosphatides

The idea behind the development of ammonium phosphatides was to obtain an alternative to soybean lecithin for use in chocolate products, an application where the properties of the lecithin reduce the viscosity of chocolate in melted form. The functionality of the ammonium phosphatides is similar to that of lecithin in reducing the viscosity controlling the rheology of chocolate systems. Thus, the addition to chocolate will reduce the plastic viscosity making a reduction of cocoa butter possible and making the chocolate easy to handle in operations such as moulding and coating.

Chocolate and its compounds are multiphase systems where the continuous phase is triglycerides, i.e. cocoa fat, in which solid materials in the form of finely grained sugar and cocoa are dispersed. Chocolate is mostly produced in processes similar to the one shown in Fig. 10.3. The first step is a mixing of all the major ingredients such as cocoa liquor, cocoa and sugar to a crumble mass with a fat content in the range of 25–40%. The next step is to get the right particle size of the solids. This refining is often done on roll refiners, which grind the solids to the specified particle size, i.e. for good qualities of chocolate maximum 35 μm. During the refining, agglomerates of solids will also be rubbed out and the triglycerides will be better distributed due to the forces exerted on the chocolate. Thus, the cocoa butter will cover the surface of the solid particles to a higher extent and a better lubrication of the system is obtained. The resulting chocolate mix is moved to the conching step, where the raw chocolate is mixed in heavy duty mixers under controlled temperature for several hours (4–72 hours) depending on the type and quality of the final chocolate. During the conching step moisture is reduced and, in addition, undesirable volatiles that affect the flavour of the chocolate are also removed. At the same time the mixing will help

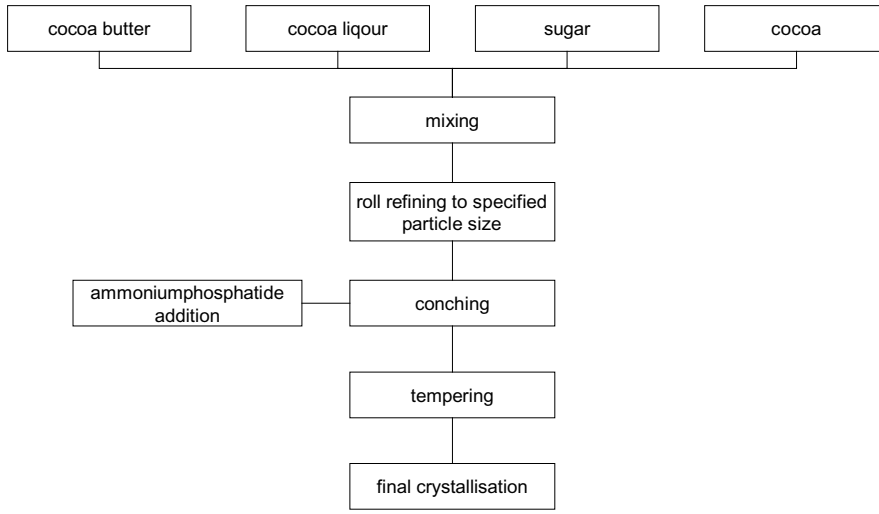

Fig. 10.3 Chocolate process.

to break any agglomerates and attain the optimal wetting of the solid particles with triglycerides, i.e. improve the lubrication of the chocolate. During the conching, the dispersion will change from a rather dry appearance to a viscous fluid. To get a product with uniform quality and shape from batch to batch, ammonium phosphatide is added to the chocolate at the start of the conching and second time added towards the end, the last one being done to get the final adjustment of the fluid properties of the melted chocolate. The emulsifier will reduce the viscosity of the chocolate dramatically (see below), which will help attain the optimal coating of the solid particles with cocoa butter. The reduction of the viscosity will also result in a chocolate with flow properties allowing degasification to fill out moulds without any defects, or to secure good covering properties [10]. The fluid dynamics of chocolate are an important and complex issue as chocolate is a dispersion with a very high content of solids and in molten form does not act as a simple Newtonian liquid, but exhibits a plastic flow that can be fitted to the Casson model. The effect of ammonium phosphatides on the viscosity of chocolate is shown in Fig. 10.4, where the rheograms of a 30% (fat) milk chocolate, where respectively 0.4% and 0.6% ammonium phosphatide (Palsgaard 4448) have been added and are recorded in the form of the shear stress versus the shear rates. This figure also shows the data for 0.4% and 0.6% additions of lecithin as references. In the 0.4% addition of emulsifier to the chocolate it is observed that the flow curves of ammonium phosphatide and lecithin added chocolates are nearly identical. In the case of the 0.6% addition the picture changes, the ammonium phosphatide provides a further significant

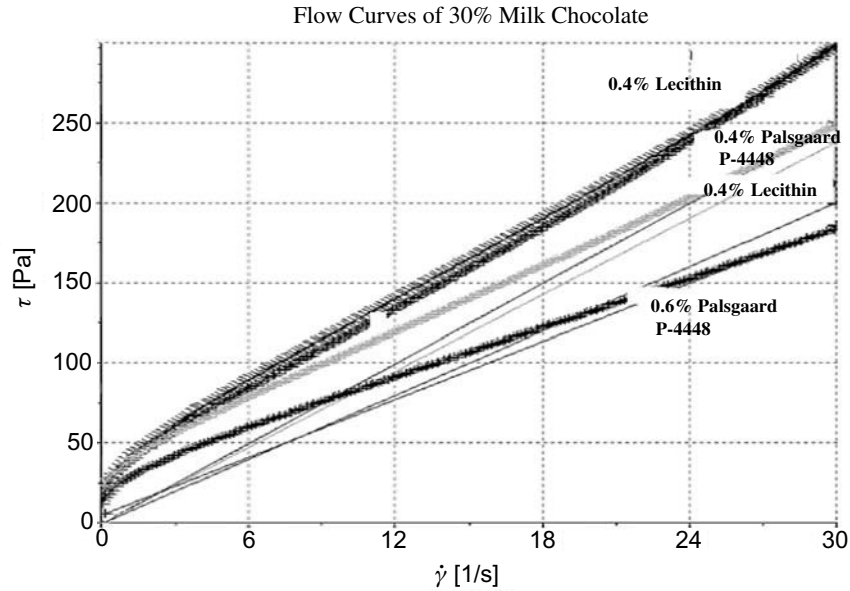

Fig. 10.4 Ammonium phosphatide effect on viscosity of milk chocolate.

reduction of the viscosity; and a comparison with the 0.6% lecithin curve shows that the effect from the emulsifier is much more pronounced. At the same time the ammonium phosphatide also results in a significant lower Casson yield value (Table 10.1), an important parameter for chocolate, when it comes to filling the moulds or when the product is used for coating.

In the case of dark or bitter chocolates a different picture than that of the milk chocolate is observed. For lecithin it is observed that increasing the addition from 0.4% to 0.6% does not give any further reduction in the viscosity of the dark chocolate (see Fig. 10.5). In the case of ammonium phosphatide (Palsgaard 4448), an increase in the addition to the chocolate is found to decrease the viscosity, but it is also found that the ammonium phosphatide in the dark chocolate

Table 10.1 Plastic viscosity and Casson yield value for 30% milk chocolate

	Plastic viscosity (Pa)	Casson yield value (Pa-s)
Milk chocolate added 0.40% lecitin	14.92	6.824
Milk chocolate 0.40% Palsgaard 4448	15.75	6.398
Milk chocolate 0,60% lecithin	17.59	4.956
Milk chocolate 0.60% Palsgaard 4448	10.85	3.612

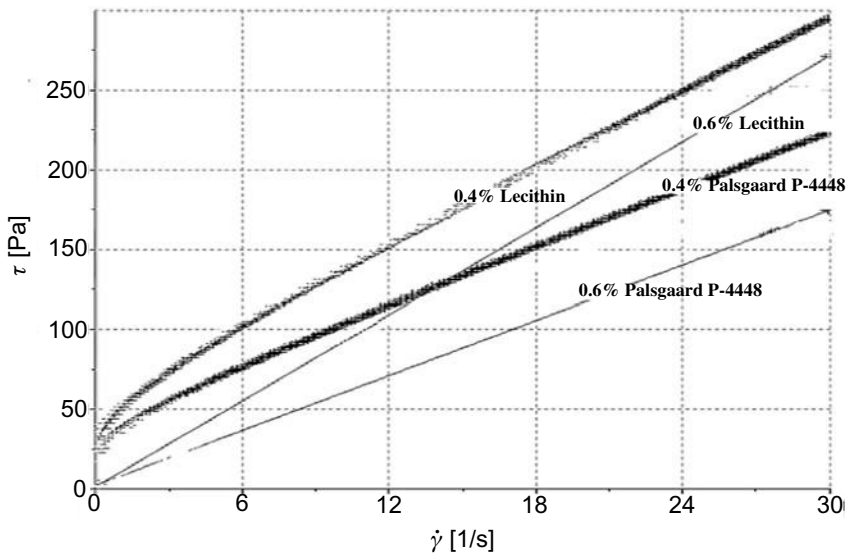

Fig. 10.5 Ammonium phosphatide effect on viscosity of dark chocolate.

Table 10.2 Plastic viscosity and Casson yield value for 30% dark chocolate

	Plastic viscosity (Pa)	Casson yield value (Pa·s)
Dark chocolate added 0.4% lecithin	25.22	5.295
Dark chocolate added 0.4% Palsgaard 4448	17.80	4.088
Dark chocolate added 0.6% lecithin	28.37	4.803
Dark chocolate added 0.6% Palsgaard 4448	18.02	3.553

is a much more efficient viscosity reducing agent in comparison to lecithin at both 0.4% and 0.6% levels. Here the ammonium phosphatide curves are below the corresponding lines for lecithin. Table 10.2 shows the figures recorded for the plastic viscosities and the yield values, and it is observed that the extra addition of ammonium phosphatide has a positive effect in reducing both values, while the extra addition of lecithin actually results in an increase in the plastic viscosity. The power of the ammonium phosphatides as a versatile viscosity-controlling additive is also evident with respect to the yield values. Results such as this can be found in application sheets describing the use of ammonium phosphatides in chocolate and also in the literature, e.g. Minifie [10] finds ammonium phosphatide more efficient than lecithin.

The exact mechanism behind the viscosity reduction effect of ammonium phosphatides is not known, but it is likely that they act in the same manner

as lecithin. The latter is thought to be associated to the hydrophilic surfaces of sugar and milk particles [11]. Recently, Coupland *et al*. [12] hypothesised that due to moisture sugar particles in chocolate are aggregated through liquid bridges and the phopholipids are absorbed on the moist carbohydrate surface forming a film and thus promote the de-agglomeration of the sugar particles. Further addition of the lecithin gets added to the existing lecithin film, which will build up as multilayers. The formation of the multilayers can be thought to expose hydrophilic groups to each other, creating forces like electrostatic attraction hydrogen bonding between separate multilayers, which results in an increase in the viscosity.

Ammonium phosphatides differ with respect to this viscosity response when the emulsifier is added in higher concentrations. It is likely that the ammonium phosphatides can pack more closely to the sugar surface due to their less bulky ammonium groups and in this manner do not form multilayers at practical concentrations of the emulsifier. It is also possible that the ammonium moiety of the phosphatide, due to a stronger basicity, exhibits a higher affinity to the carbohydrates than the corresponding nitrogen part of lecithin, and in this way the ammonium phosphatide will be absorbed to a higher degree on the sugar particles. The absorption of the nitrogen, i.e. the ammonium group to the sugar, can be explained from the weak acid nature of the carbohydrate and the basicity of the ammonium group forming an electrostatic attraction. More important can be the hetero-intermolecular hydrogen bonding in the form of strong N-H$\cdots$O bonding, which must be considered as a significant parameter when the ammonium phosphatides associate with the sugar particles, or rather with the water surrounding the carbohydrate. In relation to nitrogen containing phosphatides from lecithin, the $NH_{4.}^{+}$ group will be better dissolved because of the unsubstituted positive ammonium ion, while alkyl-substituted groups will have decreasing forces of hydrogen bonding with the increasing substitution [13]. As lecithin contains nitrogen moieties in the form of alkylamines of different types, the lecithin therefore cannot be so strongly associated to the sugar particles as ammonium phosphatide.

Often chocolate is used as a coating for different fillings and the latter will frequently be alcohol based in the form of liqueur or brandy, e.g. in filled pralines. With these types of products the industry faces the problem that, over time, the chocolate absorbs some of the water/alcohol, and in serious cases the chocolate can be more or less dissolved. In both cases the products will be defective and of less appeal to the consumer and becomes unsaleable. In a study Holdgaard and Wickman [14] tested two dark chocolates with an ethanol-based filling, one chocolate with soy lecithin as emulsifier and the other with ammonium phosphatide (Palsgaard 4448). After tempering, both chocolates were moulded to key and tongue shapes and then totally covered with an alcohol-syrup/sugar solutions for 7 days at 26°C in closed containers. Two different alcohol solutions were tested; one with 8.5% ethanol in glucose syrup and a second with 8.5%

Table 10.3 The effect of emulsifier on chocolate absorption of alcohol syrup

Emulsifier	Lecithin	Lecithin	Ammonium phosphatide (Palsgaard 4448)	Ammonium phosphatide (Palsgaard 4448)
Moulded shape	Tongue	Key	Tongue	Key
% Absorbed alcohol-glucose	261	182	95	98
% Absorbed alcohol-sucrose		310		164

ethanol in a sucrose solution. After 7 days of storage in the alcohol syrups the absorptions were recorded as the gain in the weight of the moulded pieces of chocolate. The results are shown in Table 10.3. The ammonium phosphatides were found to retard the absorption of the liqueur far better than the soy lecithin. The mechanism for this seems to be a stronger association of the ammonium phosphatide to the sugar of the chocolate than the lecithin, an association which makes a more tight barrier preventing the sugar in the chocolate from absorbing water from the alcohol syrups, and in this way establishing an equilibrium between the syrup and the sugar of the chocolate.

Another important parameter in chocolate production is the temper of the chocolate, i.e. the ability to get the cocoa butter to crystallize in the correct form. Addition of emulsifiers can have a negative effect on the tempering of chocolate. In the case of phospholipids, according to Savage and Dimick [15] those naturally present in cocoa butter can delay the onset of the crystallisation while the choline fraction will promote the nucleation and crystal growth. Minifie [10] mentions that only high lecithin addition ($>1\%$) will decrease the inflection temperature as low as 21°C. In the case of the liquid ammonium phosphatide (Palsgaard 4448) the negative effect is minor and comparable to or less than lecithin, and often the temperature of the tempering process does not need to be as low as with lecithin.

10.5 Other food applications

Besides the application of ammonium phosphatide in chocolate, only a few other applications have been reported. In a patent, Schneider [16] claims that ammonium phosphatides give better volumes and qualities in white bread. Addition of ammonium phosphatide in chewing gum is reported [17] to provide a good texture and flavour. The flavour of the gum is reported to be clean due to the bland taste and smell of the ammonium phosphatide. In a study testing the formation of rancidity in rapeseed oil, Kourimska *et al*. [18] find the ammonium phosphatides to be neutral and to inhibit the rancidification of the vegetable oil. The decay is monitored via sensory analysis as well as by peroxide value and formation of polar substances.

10.6 Summary

This chapter has presented a short review of the ammonium phosphatides and primarily the application of the emulsifier in chocolate production to control the properties of the fluid chocolate. When it comes to the molecular level, very little is known about emulsifier mechanism in chocolate, but it is likely that the macroscospic effect observed can be related to the affinity of the ammonium phosphatide emulsifier to the sugar and the water present in the chocolate. It is thought the ammonium phosphatide will interact with the water bound to the sugar and in this way will neutralize the drawback from the moisture present in the chocolate.

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Appendix 1 Hydrophile lipophyle balance

The hydrophilic–lipophilic balance (hydrophile lipophyle balance) system for the classification of emulsifiers was first used by the laboratory staff of the Atlas Powder Company in America and may be defined as

$$\text{HLB} = 20^{*}\ (M_0/M)$$

where M_0 is the molecular weight of the hydrophilic part of the emulsifier molecule and M is the total molecular weight. The scale is therefore from 0 to 20.

Emulsifiers with a highly hydrophilic nature have high HLB values, whereas those which are predominantly lipophilic (low hydrophilic nature) have a low HLB value. The HLB value of an emulsifier may be used as a guide to its most appropriate application. Generally, the phase for which the molecule has the greater affinity is the outer phase. Those emulsifiers with a high HLB value stabilise in oil-in-water emulsions and those with a low HLB value stabilise in water-in-oil systems.

HLB range use

0–3	antifoaming agents
4–6	w/o emulsifying agent
7–9	wetting agent
8–18	o/w emulsifying agent
13–15	detergents
10–18	solubilisers

Disadvantages of the HLB system
The inability to take into account:

(i) the effect of temperature
(ii) the presence of additives
(iii) the concentration of emulsifying agents.

A detailed description of the HLB system is discussed by Griffin and reviewed by Friberg.

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Appendix 2 E-numbers, names and synonyms of food emulsifiers

E 322 Lecithins
Phosphatides, phospholipids.

E 431 Polyoxyethylene (40) stearate
Polyoxyl (40) stearate; polyoxyethylene (40) monostearate; polyoxyethylene stearates.

E 432 Polyoxyethylene sorbitan monolaurate (Polysorbate 20)
Polysorbate; polyoxyethylene (20) sorbitan monolaurate; sorbitan monododecanoate; poly(oxy-1,2-ethanediyl) derivative. Tween 20.

E 433 Polyoxyethylene sorbitan monooleate (Polysorbate 80)
Polysorbate; polyoxyethylene (20) sorbitan monooleate; sorbitan mono 9-octadecenoate; poly(oxy-1,2-ethanediyl) derivative. Tween 80.

E 434 Polyoxyethylene sorbitan monopalmitate (Polysorbate 40)
Polysorbate; polyoxyethylene (20) sorbitan monopalmitate. Tween 40.

E 435 Polyoxyethylene sorbitan monostearate (Polysorbate 60)
Polysorbate; polyoxyethylene (20) sorbitan monostearate; sorbitan monooctadecanoate; poly(oxy-1,2-ethanediyl) derivative. Tween 60.

E 436 Polyoxyethylene sorbitan tristearate (Polysorbate 65)
Polysorbate; polyoxyethylene (20) sorbitan tristearate. Tween 65.

E 442 Ammonium phosphatides
Ammonium salts of phosphatidic acid; mixed ammonium salts of phosphorylated glycerides; EMULSIFIER YN.

E 471 Mono- and diglycerides of fatty acids
Glyceryl monostearate, glyceryl monopalmitate, glyceryl monooleate, etc.; monostearin, monopalmitin, monoolein, etc.; GMS (for glycerol monostearate).

E 472a Acetic acid esters of mono- and diglycerides of fatty acids
ACETEM; acetic acid esters of mono- and diglycerides; acetoglycerides; acetylated mono- and diglycerides; acetic and fatty acid esters of glycerol; acetylated monoglycerides.

E 472b Lactic acid esters of mono- and diglycerides of fatty acids
LACTEM; lactic acid esters of mono- and diglycerides; lactoglycerides; lactic and fatty acid esters of glycerol; mono- and diglycerides of fatty acids esterified with lactic acid; glyceryl-lacto esters of fatty acids; lactated mono-diglycerides; GLP.

E 472c Citric acid esters of mono- and diglycerides of fatty acids
CITREM; citric acid esters of mono- and diglycerides; citroglycerides; citric and fatty acid esters of glycerol; mono- and diglycerides of fatty acids esterified with citric acid.

E 472e Mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids
DATEM; diacetyltartaric acid esters of mono- and diglycerides; mono- and diglycerides of fatty acids esterified with mono- and diacetyltartaric acid; diacetyltartaric and fatty acid esters of glycerol. DATA Esters.

E 473 Sucrose esters of fatty acids
Sucroesters; sugar esters; sucrose fatty acid esters.

E 474 Sucroglycerides
Sugar glycerides.

E 475 Polyglycerol esters of fatty acids
Polyglycerol fatty acid esters; polyglycerin esters of fatty acid esters; PGE.

E 477 Propane-1,2-diol esters of fatty acids
Propylene glycol esters of fatty acids; propylene glycol mono- and diester; propylene glycol mono- and diesters of fatty acids; propylene glycol monostearate (or other appropriate ester); PGME.

E 481 Sodium stearoyl-2-lactylate
Sodium stearoyl lactylate; SSL.

E 482 Calcium stearoyl-2-lactylate
Calcium stearoyl lactylate; CSL.

E 491 Sorbitan monostearate
Sorbitan esters; SMS, Span 60.

E 492 Sorbitan tristearate
Sorbitan esters; STS, Span 65.

E 493 Sorbitan monolaurate
Sorbitan esters; SML, Span 20.

E 494 Sorbitan monooleate
Sorbitan esters; SMO, Span 80.

E 495 Sorbitan monopalmitate
Sorbitan esters; SMP, Span 40.

E 496 Sorbitan trioleate
Sorbitan esters; STO, Span 85.

Appendix 3

Summary of food emulsifier applications

	E322	E431	E432	E433	E434	E435	E436	E422	E471	E472a	E472b	E472c	E472e	E472f	E473	E474	E475	E476	E477	E481	E482	E491	E492	E493	E494	E495
Baked goods, e.g. bread, cakes, biscuits	■								■	■		■	■	■						■	■					
Fine bakery wares	■		■	■	■	■	■				■				■	■	■		■	■	■	■	■	■	■	■
Toppings and coatings for fine bakery wares															■							■	■	■	■	■
Yeast for baking																						■	■	■	■	■
Fat emulsions for baking purposes			■	■	■	■	■								■	■			■							
Confectionery	■		■	■	■	■	■		■						■	■	■		■	■	■	■	■	■	■	■
Chewing gum	■		■	■	■	■	■		■						■	■	■		■	■	■	■	■	■	■	■
Chocolate	■							■			■							■					■			
Dairy products, e.g. imitation creams, desserts, edible ices	■		■	■	■	■	■		■		■		■	■	■	■	■		■	■	■	■	■	■	■	■
Antispattering agent	■											■					■									
Carriers and solvents for colours, fat-soluble antioxidants and antifoaming agents			■	■	■	■	■						■	■	■	■	■					■	■	■	■	■
Synergists for antioxidants	■											■														
Fat emulsions																				■	■		■			■
Modification of fat crystallisation				■	■	■	■										■						■	■		■
Low fat spreads and emulsions												■						■								
Fats, e.g. margarines, spreads, shortenings	■								■		■	■										■				
Starch, e.g. mashed potatoes, pasta, quick cook rice	■								■											■						

(Continued)

	E322	E431	E432	E433	E434	E435	E436	E422	E471	E472a	E472b	E472c	E472e	E472f	E473	E474	E475	E476	E477	E481	E482	E491	E492	E493	E494	E495
Emulsified sauces	■		■	■	■	■	■						■	■	■	■						■	■	■	■	■
Emulsified liqueurs and spirits																				■						
Wine		■																								
Spirituous beverages (excluding wine and beer)													■	■	■	■					■	■				
Non-alcoholic aniseed-based drinks															■	■										
Canned liquid coffee													■	■	■	■				■						
Beverage whiteners															■	■	■		■	■	■		■		■	■
Liquid tea concentrates and liquid fruit and herbal infusion concentrates																							■		■	■
Dietary food supplements			■	■	■	■	■								■	■	■					■	■	■	■	■
Dietetic formulae for weight control			■	■	■	■	■												■	■		■	■	■	■	■
Dietetic foods intended for medical purposes			■	■	■	■	■								■	■	■		■			■	■	■	■	■
Instant drinks	■																								■	
Powders for the preparation of hot beverages																				■					■	
Soups and broths			■	■	■	■	■								■	■										
Cereal and potato-based snacks																				■					■	
Coatings										■																
Egg products																	■									
Sausages and comminuted meat products												■	■	■	■	■				■	■					
Topping powders										■	■															
Dressings																		■								
Breakfast cereals																	■			■	■					
Jelly marmalade																								■		
Fresh fruits, surface treatment															■											

With thanks to the EFEMA Index of Emulsifiers (3rd edn) for the base information used to construct this table.

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Appendix 4 Recommended analytical methods for food emulsifiers – list of references

No.	Title (Subject)	Reference
A 1	Limit test for heavy metals	FAO Food and Nutrition Paper 5, Rev. 2, pp. 73–75
A 2	Limit test for lead	FAO Food and Nutrition Paper 5, Rev. 2, pp. 76–77
A 3	Limit test for arsenic	FAO Food and Nutrition Paper 5, Rev. 2, pp. 69–73
A 4	Limit test for cadmium	FAO Food and Nutrition Paper 5, Rev. 2, pp. 59–68
A 5	Limit test for mercury	FAO Food and Nutrition Paper 5, Rev. 2, pp. 77–79
A 6	Sulphated ash/residue on ignition	FAO Food and Nutrition Paper 5, Rev. 2, pp. 53–54
A 7	Free alkali (sodium salts)	AOCS Official Method Da 4a–48
A 8	Free alkali (potassium salts)	AOCS Official Method Da 5–44
A 9	1,4-dioxane content	FAO Food and Nutrition Paper 5, Rev. 2, pp. 95–97
A 10	Water content	FAO Food and Nutrition Paper 5, Rev. 2, pp. 84–86
A 11	Loss on drying	FAO Food and Nutrition Paper 5, Rev. 2, pp. 58–59
A 12	Alcohol insoluble substances	AOCS Official Method Da 3–48
A 13	Petroleum ether insoluble substances	AOCS Official Method Ja 3–55
A 14	Unsaponifiable matter	Food Chemicals Codex IV, pp. 828–829
A 15	Free fatty acids	AOCS Official Method Ca 5a–40
A 16	Free glycerol	FAO Food and Nutrition Paper 5, Rev. 2, pp. 195–197
A 17	Free glycerol and polyglycerol	AOCS Official Method Cd 11b–91
A 18	Acid value	FAO Food and Nutrition Paper 5, Rev. 2, p. 189
A 19	Saponification value	FAO Food and Nutrition Paper 5, Rev. 2, pp. 203–204
A 20	Hydroxyl value	FAO Food and Nutrition Paper 5, Rev. 2, pp. 190–191
A 21	Total fatty acids	DGF Einheitsmethoden C-III 2 (97)
A 22	Total glycerol	Food Chemicals Codex IV, p. 120
A 23	Total acetic acid	Food Chemicals Codex IV, pp. 119–120
A 24	Total lactic acid	Food Chemicals Codex IV, p. 181
A 25	Total dimer and trimer of 1,2-propanediol	FAO Food and Nutrition Paper 5, Rev. 2, pp. 201–202
A 26	Total glycerol and polyglycerol	FAO Food and Nutrition Paper 5, Rev. 2, pp. 199–200
A 27	Total mono- and diglycerides	AOCS, 5th edition, Cd 11b–91
A 28	1-monoglycerides	FAO Food and Nutrition Paper 5, Rev. 2, pp. 195–196
A 29	Refractive index	FAO Food and Nutrition Paper 5, Rev. 2, p. 45
A 30	Potassium content as potassium oxide	AOCS Official Method Da 27–48
A 31	Sodium content as sodium oxide	AOCS Official Method Da 27–48
A 32	Reichert–Meissl value	Food Chemicals Codex IV, pp. 826–827
A 33	Melting range	FAO Food and Nutrition Paper 5, Rev. 2, p. 42
A 34	Oxyethylene content	FAO Food and Nutrition Paper 5, Rev. 2, pp. 197–199
A 35	Congealing range	FAO Food and Nutrition Paper 5, Rev. 2, p. 189

No.	Title (Subject)	Reference
A 36	Sorbitol, sorbitan and isosorbide esters content	FAO Food and Nutrition Paper 5, Rev. 2, pp. 204–205
A 37	Free ethylene oxide	DGF Einheitsmethoden H16a (94)
A 38	Ethylene glycols (mono- and diglycol)	DGF Einheitsmethoden H16a (94) (only monoethylene)

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