Fat-Based Food Emulsifiers

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ABSTRACT

Emulsifiers are widely used in foods in order to achieve the texture, taste, appearance and shelf life characteristics desired by today's consumers. A relatively limited number of fat-based emulsifiers is used alone and in various combinations to provide these characteristics. Bakery products is one of the more important food areas utilizing emulsifiers, and bread is the most important food within this class. The use of dough conditioners and softeners in bread represents one of the largest markets for fat-based emulsifiers. Therefore, the emphasis in this paper is on those fat-based emulsifiers used in the manufacture of bread. To a lesser extent, those emulsifiers used in other bakery products will also be covered.

INTRODUCTION

The food industry is the single largest industrial consumer of fat-based emulsifiers. Of an estimated 450 million pounds of fatty acid ester type emulsifiers produced in 1975, the food industry consumed almost 205 million pounds. This far exceeds the amount consumed by any other industrial segment.

If the food industry is further broken down by broad market segment, it will be found that the baking industry is not only one of the largest of the segments, it also easily accounts for the largest portion of all fat-based food emulsifiers used. It is, therefore, appropriate to concentrate on the baking industry in this discussion of the types of food emulsifiers and their function in the food industry. Although the baking industry in total consists of a vast number of plants producing everything from bread to cakes and icing-topped sweet rolls, the production of bread and rolls easily constitutes the largest volume of products. In 1972, the total bread produced in the United States was approximately 11 *billion* pounds. Additionally, approximately 3.5 *billion* pounds of rolls were produced.

In the years of our grandparents, almost all of the bread consumed was produced in small, local bakeries or at home. Now, however, almost all bread is produced in large, high speed manufacturing plants and then distributed over wide geographical areas. Thus the use of emulsifier type products in the baking industry has become increasingly important to assist in overcoming some of the problems generated by these changing manufacturing and distribution patterns. Dough conditioners and softeners are now used in the majority of the bread produced in this country, and this therefore constitutes one of the largest markets for fat-based food emulsifiers. This discussion therefore focuses on those emulsifiers used in the production of bread with a more limited discussion of emulsifiers used in other forms of bakery products.

HISTORY

Although "dough emulsifier" is now generally recognized to be a misnomer when used to describe the function of surfactants in bread, it is still widely used today. The term probably has its origins in the fact that mono- and diglycerides were, along with lecithin, the first fat-based surfactants to be used in bread. In the 1930s, it was discovered that incorporation of monoglycerides in shortening enabled the baker to produce cakes with higher ratios of sugar to flour than had been heretofore possible. These shortenings were therefore called high ratio shortenings. Because the monoglycerides functioned as emulsifiers in these systems, when the same products found their way into bread systems, it was natural that they be considered "dough emulsifiers." These "emulsifiers," when incorporated into bread systems, were found to produce a softer product with reduced staling tendencies. Initially of lesser importance, as the baking industry grew toward the larger wholesale bread-manufacturing plants, distribution times became significantly longer, and the softening and staling retarding functions of the monoglycerides became increasingly important. In addition to the longer distribution times, the consumer's taste was changing toward the softer white breads. Most of the bread produced today contains at least some monoglycerides.

At the same time that the importance of bread-softening emulsifiers was growing, changing manufacturing techniques were leading to the development of another type of fat-based surfacant, the dough conditioner or strengthener, as it is now known. High speed mixing equipment and automated production techniques were being introduced in order to produce the large volumes of bread required by the newest merchandising method, the supermarket. This equipment and techniques placed increasing demands on dough systems. Lot-to-lot variations in flour quality and increasing mechanical abuse led to a good deal of unsatisfactory bread being produced. Volume of the bread was inconsistent as were the internal and external appearances, thereby leading to consumer dissatisfaction and production difficulties. These factors led to the search for additives that would enable the large baker to manufacture the quality of bread demanded and to do so as rapidly and as consistently as possible. These research efforts led to the wide variety of surfactants currently in use by the baking industry.

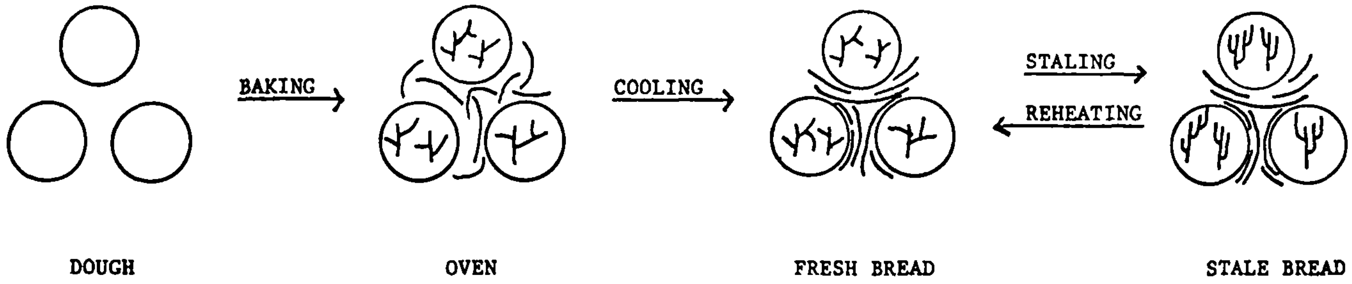
Those surfactants which are commonly used for their dough-strengthening properties in bread and other baked products include Polysorbate 60, calcium stearoyl-2-lactylate, lactylic stearate, sodium stearoyl fumarate, succinylated monoglyceride, sodium stearoyl-2-lactylate, and ethoxylated mono- and diglycerides. Other surfactants presently permitted by the Food and Drug Administration for use in bread include lecithin, hydroxylated lecithin, mono- and diglycerides, diacetyl tartaric acid esters of mono- and diglycerides, and propylene glycol mono- and diesters.

With the exception of mono- and diglycerides, these other surfactants are little used in bread in the United States at the present time. It is interesting to note that many of the surfactants used are direct derivatives of mono- and diglycerides. Others have closely related molecular structures. It should also be noted that, while the principal function of the products in dough systems is not that of emulsification, many of the products are in fact excellent emulsifiers and are used as such in other types of food systems.

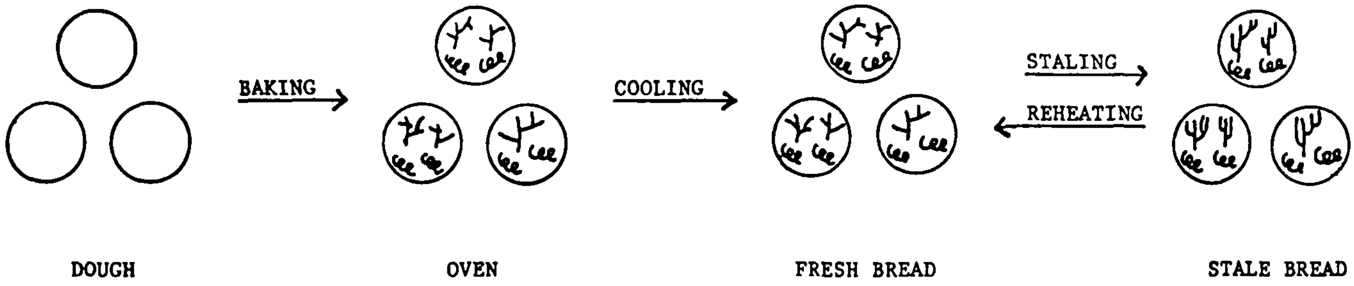
As previously mentioned, the surfactants used in the manufacture of bread are generally classified into two categories: dough strengtheners, and bread softeners. Most of the products will function to varying degrees as both softeners and strengtheners. However, certain emulsifiers such as monoglycerides function almost exclusively as softening agents while others, such as ethoxylated monoglycerides, have very effective strengthening properties and little softening effect.

Bread Softeners

Bread softeners are added to dough systems for two



(A) CONTAINING NO SURFACTANT



(B) CONTAINING A MONOGLYCERIDE SURFACTANT

FIG. 1. Graphic illustration of the role of starch fraction during the baking and aging of bread.

main reasons: to make the finished loaf of bread softer initially, and to retard the rate of staling. The staling of bread is a complex phenomenon generally characterized by a gradual loss of flavor, a toughening of the crust and a firming of the inside or crumb. Not much can be done about the flavor loss, but the firming of the crumb can be significantly retarded by the use of bread softeners. This firming phenomenon is generally regarded as being related to the crystallization rates of the starch fractions in the flour. Although the mechanism behind the effect of bread softeners is still not entirely known, it is generally thought that certain molecular configurations complex with the linear or amylose fraction of starch to form helical complexes called clathrates. Formation of this complex then affects the mobility of the amylose and prevents it from leaving the swollen starch granules and acting as a crystalline type of "glue."

Figure 1 is an illustration of this proposed staling mechanism. As can be seen in example "A," water solubilizes and then extracts the amylose starch fraction from the swollen starch granules. After cooling, the amylose fraction crystallizes between the starch granules to give a rigid structure. In example "B," the monoglyceride surfactant causes the amylose to form a helical complex which is then less capable of being solubilized and extracted during cooking.

In addition to the starch-complexing properties of bread softeners, they can also have an effect on the moisture distribution between the protein and starch fractions of a food system. A decrease in the amount of water imbibed by the starch makes more water available for hydration of the gluten, and this too is thought to contribute to staling retarding.

Dough Strengtheners

Dough strengtheners, on the other hand, are added to perform a different type of function. These products are generally thought to bind principally to the protein fraction in flour, the gluten. The gluten fraction is responsible for providing the initial elasticity and gas-holding capabilities of the bread prior to the actual baking. This elasticity is a function of the quality and quantity of protein in the bread and is affected by such things as mixing time, speed, and the mechanical abuse to which the dough is subjected. Dough strengtheners are added to assist in evening out the above variables to enable the baker to provide a consistently high quality loaf of bread.

Strengtheners apparently function by forming a loose type of hydrogen bonded complex with the various protein fractions of the gluten. These complexes then apparently affect the interaction between the naturally occurring flour lipids and the other constituents of flour. In the case of certain dough strengtheners, they may also function to somehow provide a "coupling" action between the starch and protein flour fractions.

Figure 2 is an illustration of the possible way that one type of dough strengthener, the acyl lactylates, may complex with protein fractions. It can be seen that because of the particular molecular configurations of the surfactant and the protein fractions, the possibility exists for strong hydrogen bonding. Other dough strengtheners may complex in a similar fashion. Although a number of studies have been made which demonstrate that complexing takes place, little work has been done at present to identify the structure of the complex itself. In any event, the interaction of a surfactant with gluten serves to make the resulting dough drier, more pliable and extensible, and with increased gas retention properties. This then tends to give a bread with increased volume and a more finely grained crumb. Variations in bread quality due to lot-to-lot differences in ingredients are evened out. In addition, potentially adverse effects because of mechanical processing are reduced.

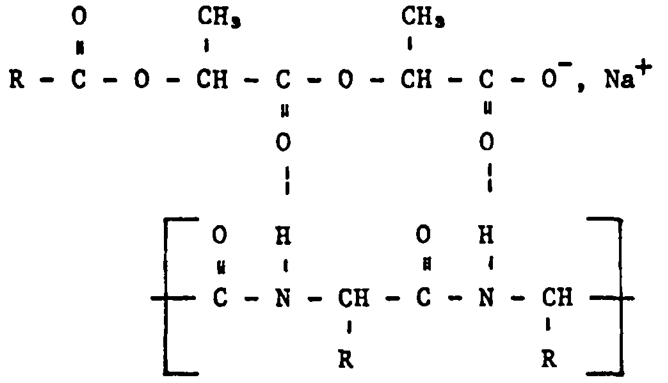


FIG. 2. Acyl lactylate complex with protein.

THE SURFACTANTS

Mono- and Diglycerides

The most widely used of the fat-based emulsifiers in bread, as in other food systems, are the monoglycerides. These are commonly referred to as mono- and diglycerides because they are usually sold in various combinations. However, the actual functional emulsifier is only the monoglyceride portion of the mixture. In addition, the one or α-monoglyceride is significantly more functional than the two or β-monoglyceride.

In general, monoglycerides comprise a group of three types, the 40, 60, and 90% α-monoglycerides. The balance in each case represents di- and triglycerides. These products are used in bread principally to impart initial softness and to retard staling. They have little dough-strengthening effect.

Monoglyceride can be prepared by the direct esterification of a selected fatty acid with glycerol. Depending on the proportions of glycerol and fatty acid used, various concentrations of monoglycerides are obtained. Because of inherent reactant solubilities under the esterification conditions used, maximum monoglyceride concentrations of ca. 65% are feasible with existing commercial processes. To obtain higher concentrations, the mono- and diglyceride mixture is subjected to distillation under high vacuum in centrifugal molecular stills. The resulting distilled monoglyceride consists of ca. 92-95% total monoglyceride with the remainder being principally diglyceride.

Although monoglycerides can be prepared by direct esterification, most monoglycerides are prepared by the base-catalyzed interesterification reaction of excess glycerol directly with a fat. Again, up to ca. 65% α-monoglyceride can be obtained by using a reasonable excess of glycerol and carefully controlling the reaction conditions. At the conclusion of the ester interchange, the catalyst is neutralized and the excess glycerol removed by vacuum stripping.

The largest volume of monoglycerides used in baked products in general are of the 60% "soft" variety. These are prepared from partially hydrogenated animal or vegetable oils such as lard, and have a soft, plastic character similar to lard itself.

A considerable quantity of 60% "hard" monoglycerides prepared from fully hydrogenated oils is also used as are 90% distilled "hard" monoglycerides. These are sold either as powdered products to be added to the shortening or, in the case of the hard 90% monoglycerides, as microdispersions in water known as monoglyceride "hydrates."

Monoglyceride derivatives

While the monoglycerides have excellent softening and staling retardant properties and little dough-strengthening effect, many derivatives of monoglycerides function both as bread softeners and as dough strengtheners. This change in the functional properties of the monoglyceride may be due to an alteration in the hydrophilic-lipophilic balance of the molecule, or may possibly be due to the introduction of ionic species into the nonionic molecule, thereby affecting its polarity and bonding capabilities.

Figure 3 shows the structure of a succinylated monoglyceride. This product is manufactured by reacting a distilled monoglyceride with succinic anhydride at temperatures ranging from ca. 80 C-180 C. At the higher temperatures no catalyst is required, but at temperature below 95 C, it is desirable to accelerate the reaction by using a small amount of an alkaline catalyst.

Succinylation of the monoglyceride thus changes the properties of the product from one with essentially just softening properties to one with both softening and dough-strengthening properties. While the product retains starch-complexing abilities, it now also has protein-complexing properties. These changes may be due in part to the molecule now being anionic instead of nonionic, but is probably more related to the change in water solubility or the hydrophilic-lipophilic balance of the structure. For example, ethoxylated monoglycerides have even different complexing properties.

Ethoxylated mono- and diglycerides are the products formed when 20 moles of ethylene oxide are reacted with a mono- and diglyceride mixture. The reaction is carried out under 40-80 psi ethylene oxide pressure at ca. 150 C in the presence of a small quantity of a base such as sodium hydroxide.

It has been found that, while the ethoxylated mono- and diglyceride now have excellent dough-strengthening properties, the softening properties are now only marginal. This is generally interpreted to mean that it has only limited starch-complexing properties. While it is uncertain whether the strength of the protein complex formed is any different than that with succinylated monoglycerides, it has been postulated that the resulting functional effects on dough systems are from two different types of mechanisms.

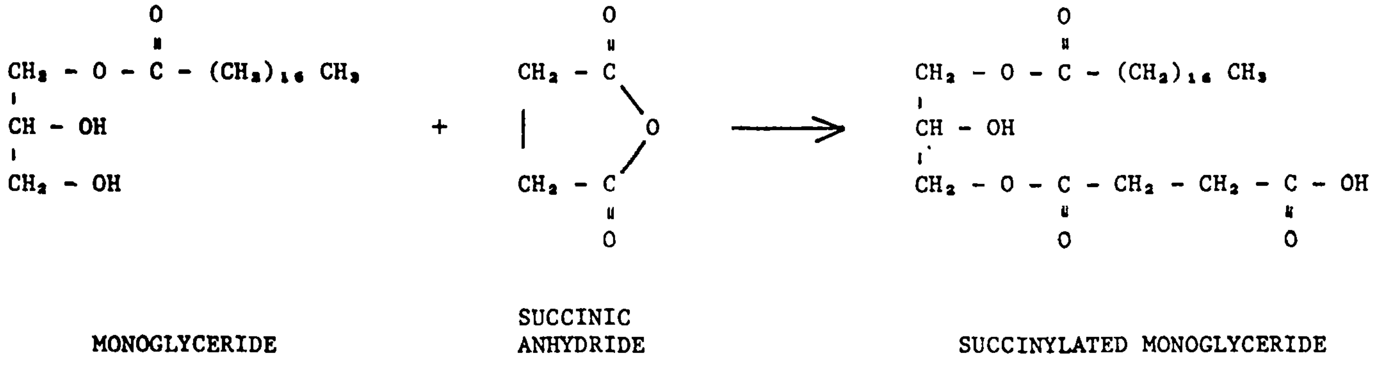


FIG. 3.

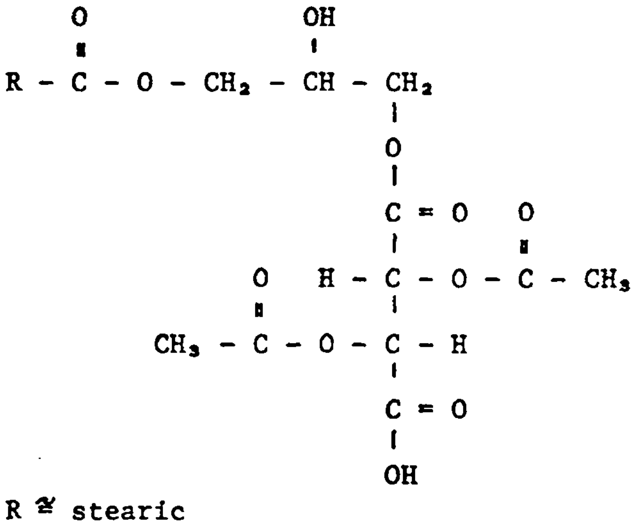


FIG. 4. Diacetyl tartaric acid esters of monoglycerides.

In the case of charged molecules such as SMG, the effects are probably due to a reduction in electrostatic repulsion of protein molecules. In the case of nonionic molecules such as EMG, the effects are probably due to increased capabilities of the complex to hydrogen bond.

Another derivative of monoglycerides that has been used for years in European countries, but that is little used in the United States, is the diacetyl tartaric acid esters of mono- and diglycerides (Figure 4). These are made by reacting acetic anhydride with tartaric acid at ca. 120 C to form diacetyl tartaric anhydride. The byproduct, acetic anhydride, is removed by vacuum stripping. The diacetyl tartaric anhydride is then reacted at ca. 120 C with the mono- and diglycerides to form the desired product.

The introduction of the diacetyl tartaric acid ester group into the mono- and diglyceride raises the HLB of the product and increases its water dispersibility. The resulting product has both softening and dough-strengthing properties. At the present time, the DATA esters, as they are called, are not widely used in the United States, probably because of function-cost relationships as compared to other available products.

Non-Monoglyceride Derivatives

Sorbitan monostearate (Fig. 5) is prepared by reacting sorbitol with stearic acid at 225-250 C in the presence of an acid catalyst. Anhydrization of the sorbitol occurs at the same time as the esterification proceeds, and the resulting product is the sorbitan ester. Note the similarities of the structure to that of a monoglyceride.

Although sorbitan monostearate is not approved for use in bread, it is widely used as a lipophilic emulsifier in chemically leavened baked products such as cakes. A derivative, however, of sorbitan monostearate, the 20 mole ethylene oxide adduct known as polysorbate 60, is approved for use in bread. The polyoxyethylene sorbitan monostearate is prepared by incrementally adding ethylene oxide at 40-80 psig to sorbitan monostearate at 140-160 C containing a small amount of base as catalyst. The reaction is continued until the desired amount of ethoxylation is attained.

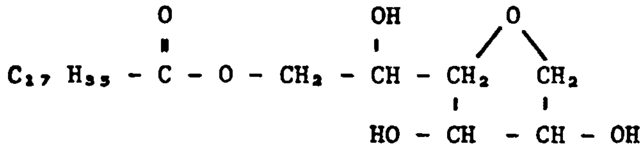


FIG. 5. Sorbitan monostearate.

Like the ethoxylated mono- and diglycerides, which structure it resembles, the polysorbate 60 also functions mainly as a dough strengthener with only marginal dough-softening properties. It is, therefore, generally used in conjunction with mono- and diglycerides to give the optimum softening and strengthening properties.

Calcium stearoyl-2-lactylate (Fig. 6), along with its sodium counterpart, is probably the most widely used surfactant in bread next to the mono- and diglycerides. Both products combine both softening and dough-strengthening properties with the sodium salt giving a slightly greater crumb-softening effect. As is the case with other products exhibiting both effects, it has been demonstrated that the lactylates form complexes with both the starch and the protein fractions of the flour system.

The lactylates can be prepared in several ways but are generally prepared by reacting stearic acid with lactic acid at 180-200 C in the presence of the desired base. The water of reaction is removed continuously by inert gas sparge. Resulting products are solids and are either ground or spray-cooled to a powder form. Acid form of the lactylate, lactylic stearate, is also approved for use in bread but is little used because it is inherently more expensive to produce than the calcium or sodium salts and contributes no apparent functional advantages.

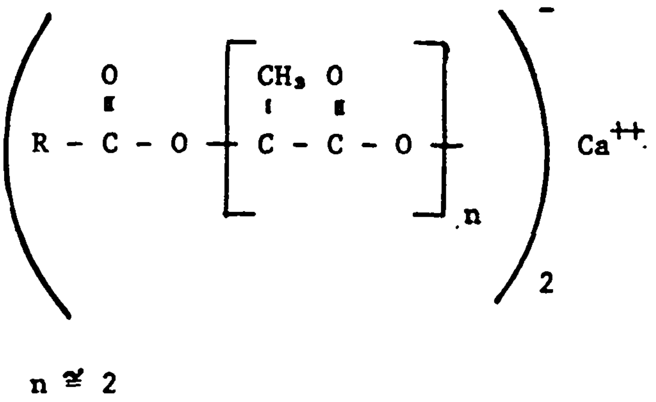


FIG. 6. Calcium stearoyl-2-lactylate.

Another product that is approved for use in bread but that is no longer used is sodium stearyl fumarate. This product was manufactured by reacting maleic anhydride with stearyl alcohol followed by isomerization to the fumarate ester and then conversion to the sodium salt. Although functionally effective as a softener and strengthener, the product was expensive to make and never gained significant acceptance by the commercial bakers.

Comparative functional effects in bread of the various fat-based surfactants are shown in Table I. Strengthening properties are manifested by loaf volume response and softening properties by the degree of staling inhibition.

OTHER BAKERY PRODUCTS

Bakery products other than bread also constitute a significant market for fat-based emulsifiers. These are products such as cakes, doughnuts, cookies, icings, fillings, etc. In these products, the surfactants function more as true emulsifiers. However, staleness retarding is also an important consideration. Many of the surfactants previously mentioned are used in these other bakery products. Again, the mono- and diglycerides are most widely used. Sorbitan monostearate and polyoxyethylene sorbitan monostearate are also widely used. In addition the following products are used: lactated mono- and diglycerides; propylene glycol monosteareate; polyglycerol esters of fatty acids. All of

TABLE I

Functional Improvements of Dough Strengtheners in Bread

Compound	Loaf volume	Firming inhibition	Relative bread quality
Polysorbate 60	Very good	Little effect	Good
Calcium stearoyl-2-lactylate	Very good	Good +	Very good
Lactylic stearate	Good +	Good +	Very good
Sodium stearyl fumarate	Fair	Very good	Good
Sodium stearoyl-2-lactylate	Very good	Very good	Very good
Succinylated monoglyceride	Very good	Good +	Very good
Ethoxylated mono- and diglycerides	Very good	Little effect	Fair

these products are manufactured by the reaction of fatty acids with the appropriate polyol using standard esterification techniques.

Generally, at least two and as many as five of the emulsifiers are used in various combinations to give the desired functional properties. The function of surfactants in these nonbread bakery products is principally to completely emulsify the fat with the water to give a system of optimum stability. Air entrapment is also an important function in whipped products and in chemically leavened systems such as cakes and doughnuts. In these systems, entrapped air in the fat serves as foci for gas expansion. Greater quantities of finely divided fat globules containing entrapped air lead to improved volume response on baking. Tenderness and grain structure are also enhanced.

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Polyglycerol Esters

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ABSTRACT

When glycerol is heated with an alkaline catalyst to over 230 C, water is evolved and polymerization occurs to form a whole family of polyglycerols ranging from diglycerol with 3 hydroxy groups, to triacontaglycerol with 32 hydroxy groups. The carboxylic acid esters of polyglycerols prepared by direct esterification or by interchange, may be solid or liquid; saturated or unsaturated; aliphatic or aromatic; mono, di- or polycarboxylic acid esters; mono-, di-, or polyesters of the polyglycerol; single or mixed acid esters; high or low molecular weight; water or oil soluble; and with an HLB from about 4 to about 13. Polyglycerol esters find utility in a wide variety of food products including beverages, desserts, toppings and baked goods. They are thermally stable and find application in several industrial systems.

Polyglycerol esters have been commercially available for about 20 years. At the present time, they are being offered