Functions of Emulsifiers in Food Systems

N. KROG, Grindsted Products, 38 Edwin Rahrs Vej, DK-8220 Brabrand, Denmark

ABSTRACT AND SUMMARY

The function of food grade emulsifiers in various food products (emulsions, starch based food, yeast raised bakery products, etc.) are reviewed. The stability of emulsions against coalescence of dispersed droplets is among other factors dependent on monoor multimolecular interfacial films with viscoelastic properties formed by adsorbed emulsifier molecules. Agglomeration of fat globules in whippable emulsion is needed to obtain desired foam stability and texture and can be controlled by lipophilic emulsifiers. Complex formation with starch components (amylose) is influenced both by the chemical structure of an emulsifier and by its physical behaviour in water. Interaction with proteins takes place primarily with anionic emulsifiers or very hydrophilic, nonionic types, which thereby improves the rheological properties of wheat gluten. Emulsifiers are also used as crystal modifying agents in fats where polymorphic changes during storage creates texture problems.



FIG. 1. Interfacial tension between soybean oil (SBO) and water at 50 C. Measured by the Du Nouy ring technique. Following emulsifiers are tested: Distilled propylene glycol monostearate (PGMS), Acetylated monoglycerides, acetylation degree: 0.7 (ACMG), Lactylated monoglycerides (GLP), Distilled monoglycerides from sunflower oil (GMO), Sodium stearoly-2-lactylate (SSL), Diacetyl tartaric acid ester of monoglycerides (DATEM), and Polysorbate 60 (PS).

INTRODUCTION

Many of our foods are complicated multiphase systems consisting of water, carbohydrates, proteins, fats, and oils, which are processed under highly automated conditions, distributed, and often stored for a considerable length of time before consumption takes place. Therefore special ingredients like surface active agents, also called emulsifiers or stabilizers, are needed to ensure uniform quality and shelf life stability.

Food grade emulsifiers are esters of edible fatty acids originating from animal or vegetable source, and polyvalent alcohols like glycerol, propylene glycol, sorbitol, and sucrose. Furthermore, these products can be modified by making derivatives with ethylene oxide or by esterification with organic acids like acetic acid, diacetyl tartaric acid, succinic acid, citric acid, or lactic acid, which makes it possible to tailor-make surface active materials with specific properties.

Molecular structure and chemical composition of some of the most commonly used emulsifiers have been published recently (1) and will, therefore, not be dealt with here.

Emulsifiers are amphiphilic substances which according to their chemical structure possess both hydrophilic and lipophilic properties. Generally speaking the function of such materials in food systems can be one or more of the following: (a) to promote emulsion stability, control agglomeration of fat globules, and stabilize aerated systems; (b) to improve texture and shelf life of starch containing products by complex formation with starch components; (c) to modify rheological properties of wheat doughs by interactions with gluten proteins; (d) to improve consistency and texture of fat-based products by controlling polymorphism and crystal structure of fats.

In the following text these functions are discussed and related to the chemical-physical properties of the specific type of emulsifiers used in each case.

EMULSIONS

Interfacial Tension

Due to the hydrophilic-lipophilic properties of emulsifier molecules they always orientate themselves at air-water or oil-water interfaces. This interfacial adsorption takes place independent of how the emulsifier is added to the system, and is energetically a more favorable situation than complete solution of the emulsifier in either the oil or the water phase. As a consequence of the adsorption of emulsifiers at the interface the interfacial tension is reduced. Figure 1 shows interfacial tension between water and soybean oil measured by a Du Nouy Tensiometer at 50 C.

Figure 2 shows interfacial tension measurements of soybean oil against a water phase containing 0.3% milk proteins (1 part skimmed milk + 10 parts distilled water). Addition of low polar emulsifiers like propylene glycol monostearate (PGMS) does not reduce the interfacial tension significantly even at concentrations of 5% of the oil phase. Lactylated monoglycerides (GLP) and distilled monoglycerides from sunflower oil (GMO) are slightly more active than PGMS. Anionic emulsifiers like sodium steroyl-2-lactylate (SSL) or especially diacetyl tartaric acid ester of monoglycerides (DATEM) are very active in reducing interfacial tension when the water phase contains proteins. Strongly polar, nonionic emulsifiers like Polysorbate 60 behave in a similar way.

INTERFACIAL TENSION SBO:WATER+PROTEINS



FIG. 2. Interfacial tension of soybean oil (SBO) against a water phase containing 0.3% milk proteins. For comparison and key to abbreviations see Fig. 1.

Interfacial Film Formation in Pure Oil/Water (O/W) Emulsions

An emulsion is thermodynamically an unstable system, which with storage will separate into two liquid phases. The dispersed oil droplets in an o/w emulsion may first flocculate into clusters of oil droplets, which then concentrate at the top of the emulsion like a creaming off process in milk. The individual oil droplets will then after approaching each other coalesce into bigger droplets, which eventually will form an oily layer on top of the water phase. The flocculation process in itself is not a sign of decreased emulsion stability, and the clusters of oil droplets can be redispersed by simple mechanical treatment. In several food emulsions, like whippable creams or ice cream mixes, a certain degree of flocculation is desired in order to obtain optimum foam stability and stiffness in the aerated product.

The crucial point in emulsion stability is to avoid coalescence of the dispersed droplets. The formation of a mechanically strong film by adsorbed emulsifying agents on the surface of the oil droplets is therefore an important factor against coalescence.

Figure 3 illustrates schematically the situation at an o/w interface with a monomolecular layer of emulsifiers having low, medium, and high hydrophilic properties. It should be emphasized that the conditions described here apply only to pure o/w emulsions, and not to emulsions containing proteins.

The lipophilic emulsifiers (monoglycerides, propylene glycol esters etc.) will at low concentration levels be partitioned between the oil phase and the interface (Fig. 3a). Very hydrophilic emulsifiers, like ethoxylated monoglycerides and polysorbates, will tend to form micelles in the water phase, and the degree to which they absorb at the interface will allow only for the formation of expanded monolayers (Fig. 3c).







FIG. 4. Photomicrograph of an oil/water (o/w) emulsion, 300x magnification, polarized light. Birefringent layers around oil droplets show liquid crystals oriented at the o/w interface.

The optimum stability of pure o/w emulsions is obtained by emulsifiers or blends hereof with medium hydrophiliclipophilic properties (HLB 8-12, see Fig. 3b), because they form condensed monolayers at the interface. Hydrophobic interaction between the closely packed fatty acid hydrocarbon chains in condensed monolayers is an important factor for obtaining surface films with viscoelastic properties which provide maximum stability against coalescence (2). If the concentration of the emulsifiers is high enough to form multilayered surface films, several other factors become important. The ability of many emulsifiers, even with low hydrophilic properties (monoglycerides), to form lyotropic, mesomorphic phases in aqueous bulk solutions (3) must be considered. Formation of liquid crystalline surface films built up by association of the emulsifier, oil, and water has been reported for many nonfood emulsions (4). Similar conditions may exist in food systems, but the



FIG. 5. Schematic model of proteins (the hatched area) adsorbed at oil/water interfaces of (a) fat globule without emulsifier and (b) fat globule containing an emulsifier with low HLB.



FIG. 6. Influence of lactylated monoglycerides (GLP) on % overrun (\circ - \circ) and foam stiffness (\blacksquare - \blacksquare) of whipped toppings. The foam stiffness is measured on a Bloom gelometer.

complex nature of most food emulsions makes it difficult to establish whether such films are present or not. In model o/w emulsions of soybean oil in water containing SSL strong birefringent layers around the dispersed oil droplets can be seen under a polarizing microscope as shown in Figure 4. The birefringent layers are liquid crystalline structures formed at the oil-water interface.

The structure of emulsifier-water mesophases has been related to rheological properties of surface films and emulsion stability (5,6). This shows that emulsifiers or blends hereof which can form lamellar mesophases in water with stable close packing conditions within the bimolecular layers of hydrocarbon chains also give viscoelastic surface films and optimum emulsion stability.

Agglomeration of Fat Globules

Whippable emulsions (imitation creams or spray dried toppings) normally contain proteins which provide a great deal of the stability needed by such products in their liquid form. In these emulsions the function of emulsifiers is to give the whipped cream a good volume, foam texture, and stability against synereses. The building structure of an aerated emulsion consists of agglomerated fat globules

TABLE I

Recipe for Whippable Imitation Cream

Fat (hardened coconut oil) Emulsifiers:	22.0%
SSL ^a Bolucostoto (0	0.3%
GLP ^b	0.1%
Sucrose	6.0%
Sodium caseinate	2.0%
Sodium phosphate	0.1%
Salt	0.1%
Stabilizer (Na-CMC)	0.4%
Water, flavor, color	68.4%
	100.0%

^aSodium steoryl-2-lactylate, Artodan SP50, Grindsted Prod. Inc., Kansas City, MO.

^bLactylated monoglycerides, Lactodan F15, Grindsted Prod. Inc., Kansas City, MO.

forming a network within the foam lamellae.

Lipophilic, so-called α -tending, emulsifiers like propylene glycol monostearate, acetylated monoglycerides, or lactylated monoglycerides are especially effective in promoting agglomeration of fat globules.

These emulsifiers are nonpolymorphic and can exist only in the α -crystalline form below their melting point. They are easily soluble in fats and form a rigid α -crystalline film on the surface of the fat globules. Unlike monoglycerides, neither propylene glycol esters nor the acetylated or lactylated derivatives of monoglycerides can associate with water into mesomorphic phases, but when dispersed in water they form o/w emulsions.

The exact mechanism of how α -tending emulsifiers promote agglomeration in fat droplets is not known, but the following hypothesis may be considered. As shown in Figure 5 the interface between the triglycerides of fats and water is covered with the carbonyl-groups ${}^{R}_{R}$ Co of the outer layer of triglycerides (7) giving the surface a negative charge.

Adsorbed proteins like globular casein subunits may be bound by hydrophobic interactions with the outer layers of triglycerides, forming a colloidal type of interface, which prevents agglomeration.

When the α -tending emulsifiers are present at the fatwater interface, they will be oriented with the OH-groups facing towards the water phase. The slightly more polar surface of the fat globules may prevent hydrophobic interactions between the adsorbed protein and the fat globule surface. Instead the adsorbed proteins may be losely bound by hydrogen bonds, which are much weaker than hydrophobic interactions. The protecting protein film is, therefore, more easily swept off during the whipping process, resulting in increased agglomeration of the fat globules.

A similar mechanism has been proposed for the functionality of monoglycerides or more polar emulsifiers in ice cream mix (8). Here the destabilization and agglomeration of fat globules take place during the freezing process. The structure of ice cream has been studied by electron microscopy using freeze-fractured preparations (8,9), and this shows clearly a network of agglomerated fat globules around the air bubbles.

Figure 6 shows the effect of lactylated monoglycerides on the overrun and foam stiffness of a whipped topping.

The basic recipe used is given in Table I. The toppings without GLP give too high overrun resulting in a whipped product with too little stability and no body. The best topping product is obtained with 0.5-1.0% GLP giving overrun from 220-250% and a foam stiffness index which corresponds to ideal stand-up properties and good body and texture.

Aeration and Foam Stability

A fat-containing cake batter is a complex emulsion/foam system containing suspended flour particles, dissolved sugar, and proteins (egg white globulin and ovomucin). The egg proteins play a vital role in stabilizing the aerated cake batter, but are counteracted by liquid fat which destabilizes the foam structure.

When liquid shortenings are used in cakes, the addition of α -tending emulsifiers [propylene glycol esters, GLP, acetylated monoglycerides (ACMG)] forms a protective α -crystalline membrane on the surface of the droplets of liquid shortenings preventing the oil from coming into contact with the dissolved proteins in a cake batter. More hydrophilic emulsifiers like polyglycerol esters, SSL, and polysorbates are used in cakes to increase the distribution of fat and increase viscosity of the water phase, which then promotes incorporation of air by reducing the occurence of film thinning in the foam lamellae.

Distilled saturated monoglycerides are very effective aerating agents in low fat cake recipes when used in the form of a liquid-crystalline dispersion or the corresponding α -crystalline "gel" form. The monoglycerides can be prepared in the active dispersion form by mixing with water at a temperature of 60-65 C. Precautions should be taken to avoid overheating of the mixture which causes phase changes and separation of a highly viscous, isotropic phase according to the binary phase diagram of monoglyceridewater, shown in Figure 7. A concentration of 5-10% distilled GMS in water is normally used. Addition of an equivalent amount of sodium hydroxide to the water phase to neutralize the free fatty acids present in the GMS (normally 0.3-0.5%) will ensure optimum swelling condi-



FIG. 7. Phase diagram of distilled saturated monoglycerides from hydrogenated lard (commercial product: Dimodan P, made by Grindsted Products and water. Abbreviations used: Fluid is = Fluid isotropic, Visc. is = Viscous isotropic (= cubic phase).

tions for the lamellar mesophase formed at 60-65 C. The sodium salts of the free fatty acids will also stabilize the α -crystalline gel structure formed when the GMS-water dispersion is cooled to room temperature.

Figure 8 shows air distribution in fat-free cake batters where (a) an emulsion of mono-diglycerides and (b) a dispersion of distilled monoglycerides in water have been



FIG. 8. Cake Batters. Photomicrographs of cake batters man on an Oakes mixer with (a) mono-diglyceride emulsion added, and (b) with a dispersion of distilled monoglycerides. Magnification 250 x.



FIG. 9. Molecular model of a glucose ring (6 units) illustrating the inside diameter of an amylose helix compared to the molecular dimensions of a glycol monostearate molecule.

added. In spite of the actual monoglyceride content in each batter being the same, the liquid crystalline dispersion form of the monoglycerides gives a much more uniform air distribution than does the mono-diglyceride emulsion.

The finer air distribution gives a greater viscosity of the batter and better volume and texture of the final cake. Monoglycerides will also decrease starch gelatinization during the baking process resulting in a better cake structure.

STARCH COMPLEXING

Emulsifiers are commonly used in starch-containing foods like macaroni and other pasta foods, processed potato products, or desserts based on pregelatinized starch, in order to improve texture. The function of emulsifiers in bread as crumb softening agents is also closely related to interaction between the emulsifiers and the starch components, especially the linear amylose fraction hereof.

The complex formation between surface active agents and the amylose fraction of starch is a well-known



FIG. 10. Schematic model of the orientation of monoglyceride molecules in crystals obtained (a) from melt or organic solvents and (b) from an aqueous dispersion (hydrate form).

phenomena, which has been described in details in the literature several years ago. The first observations of that nature were in fact made over 30 yr ago, when complex formation between corn starch and fatty acids was reported (10).

It is generally accepted that the linear amylose fraction of starch forms a helical structure in the presence of a complexing agent (iodine, butanol, fatty acids, or emulsifiers). In the helical form the interior surface is build up by C-H groups and glycosidic oxygen atoms forming a lipophilic core, while all the polar OH groups are positioned on the outer surface of the helix (11). The helical form is thus stabilized by the presence of long hydrocarbon chains which meet the hydrophobic solvation requirements of the helix. The complex is insoluble in water, and the process is irreversible.

The inside diameter of the amylose helix is 4.5-6.0 Å depending on the number of glucose units per helical turn, which vary from 6 to 8. Straight hydrocarbon chains, such as saturated monoglycerides possess, can very easily be enclosed in the helical core, but the presence of a double bond in the fatty acid chain (*cis*-configuration) makes it impossible for such fatty acids to fit into the helix. A molecular model of GMS and of the amylose helix illustrating the inside diameter is shown in Figure 9.

Raman spectroscopy studies on wet amylose complexes with monoglycerides have shown that the structure of the fatty acid chain in the helix core is in a liquid-like state. When the complex is dried, the structure of the fatty acid chain changes to a more extended form similar to the crystalline state (K. Larsson, private communication).

TABLE II

Type of emulsifie r		Amylose complexing index
Distilled monoglycerides:		
1.	from hydrogenated lard	
	(65% monostearin, 30% monopalmitin)	92
2.	from hydrogenated soybean oil	
	(85% monostearin)	87
3.	from unhydrogenated lard	
	(45% monoolein)	35
4.	from unhydrogenated soybean oil	
	(55% monolinolein)	28
Acetvlated monoglycerides		0
Mono-	diglycerides (saturated)	Ť
	(50% mono-ester)	42
Organi	c acid esters of monoglycerides:	
1.	Lactylated monoglycerides	22
2.	Succinylated monoglycerides	63
3.	Diacetyl tartaric acid esters	49
Propyle	ene glycol monostearate	
	(90% monoester)	15
Sorbitan monostearate		18
Polysorbate 60		32
Sodium stearoyl-2-lactylate		72
Calciur	n stearoyl-2-lactylate	65
Lecithin (from soybean oil)		16

Amylose Complexing Effect of Emulsifiers

Amylose Complexing Index

The ability of food emulsifiers to form insoluble complexes with amylose is dependent on their chemical configuration and solubility in water. Various methods of evaluating the complexing effect of emulsifiers have been described. Measurements of the reduction in iodine affinity of amylose influenced by surface active agents have been used (12), but of more practical value to the food industry are methods giving information about quantity and type of emulsifier needed to inactivate amylose by precipitating it out of solution. We have used a method where the amount of insoluble complex is measured after reacting 5 mg emulsifier with 100 mg amylose in solution at 60 C for 1 hr (13). The amount of amylose precipitated in percentage of the amylose in solution is called the amylose complexing index (ACI).

Table II shows ACI values of various types of emulsifiers. Distilled, saturated monoglycerides are most effective followed by succinylated monoglycerides and sodium stearoyl-2-lactylates. Monoglycerides from unsaturated fats or emulsifiers with a rather complicated structure in their polar region like sucrose esters or sorbitan esters are poor amylose complexing agents. This may be explained by their steric configuration.

Lipophilic emulsifiers like acetylated monoglycerides or distilled propylene glycol esters are also poor amylose complexing agents. This is from a structural point of view surprising since these products with regard to molecular configuration and dimensions are not so different from saturated monoglycerides. The reason why acetylated monoglycerides or propylene glycol esters do not complex with amylose may therefore be due to their lipophilic character and consequently low dispersability in water. In order to complex with amylose the complexing agent must be dissolved in the aqueous phase on a molecular level.

The ability of distilled monoglycerides to be dispersed in water in the form of micellar aggregates with lamellar structure is no doubt very important for their amylose complexing effect. When monoglycerides in the β -crystalline form are added to a solution of amylose, no precipitation takes place. Not until the mixture is heated to a temperature of ca. 55 C, where the β -crystals transform to a lamellar dispersion, does the complex formation with amylose take place.

A good correlation between the amylose complex formation and crumb softening effect of monoglycerides in bread has been found (14,15). In such applications the monoglycerides are added in form of so-called hydrates, which is a suspension of monoglycerides in β -crystal form in water.

The monoglycerides are crystallized in an aqueous phase from a liquid crystalline state, and the surface of the β -crystals will therefore consist of the polar groups of the monoglycerides. Figure 10a shows the orientation of GMS molecules crystallized from melt forming a surface consisting of the nonpolar fatty acid CH₃-end groups. Figure 10b shows the proposed crystallization from an aqueous dispersion resulting in crystal surface consisting of the polar OH-groups of the monoglycerides (16).

By making such a product the specific surface of the monoglycerides is increased ca. 700 times compared to a normal powdered monoglyceride product. Figure 11 shows a photomicrograph taken by scanning electron microscopy of a freeze dried monoglyceride hydrate. The β -crystals are shaped like thin plates with a thickness of ca. 0.1 μ m corresponding to a specific surface of 20 m²/g. The greater specific surface gives a better distribution in the dough providing optimum effects. Furthermore the thin β -crystals adsorb on the surface of starch granules during dough mixing and delay gelatinization during the baking period, at which time the actual complex formation with free amylose also takes place.



FIG. 11. Scanning electron microscopy photomicrograph of a freeze dried distilled monoglyceride hydrate. Magnification 10.000 x.



FIG. 12. Influence of diacetyl tartaric acid esters (DATEM), stearoyl-2-lactylates (SSL, CSL), and monoglycerides (GMS) on final proof time, dough elasticity, and dough volume measured on a Brabender Maturograph.

In pure starch products (processed potatoes, pasta foods) distilled monoglycerides will be most active when added in the form of an aqueous dispersion. The presence of nonpolar lipids like diglycerides or triglycerides (fats) may actually inactivate the monoglycerides with respect to complex formation. The nonpolar lipids will make emulsions where some of the monoglycerides will be adsorbed at the interface and thus be unable to react with amylose.

PROTEIN INTERACTIONS

The main application of emulsifiers, where the interaction with proteins is the major functions, is in bakery doughs (bread, buns, and rolls) as so-called dough conditioning agents. The types of emulsifiers used in this application are primarily anion-active compounds such as stearoyl-2-lactylates, organic acid derivatives of monoglycerides like diacetyl tartaric acid esters, and succinylated monoglycerides, or hydrophilic nonionic emulsifiers as ethoxylated derivatives of monoglycerides, or polysorbates. The effects obtained by using a dough conditioner are improved dough processing characteristics, together with increased volume, and finer texture of the baked goods. Although many questions still remain unanswered, it is well-known



FIG. 13. Amount of diacetyl tartaric acid ester of monomyristin (DATE-C14) extracted from freeze dried dough as (I) free lipids extracted with chloroform, (II) bound lipids extracted with water saturated butanol, and (III) strongly bound lipids extracted with ether after hydrolysis with hydrochloric acid. The percentage of DATE-C14 is calculated on basis of the flour content.

today that such dough conditioners primarily interact with the gluten proteins during dough mixing. Furthermore some of these emulsifiers do also give a considerable crumb softening effect in bread, depending on their ability to form complexes with amylose (see Table II).

The effect of emulsifiers on dough elasticity and gas retention during the fermentation period can be measured by Brabender Maturograph.

Figure 12 shows the influence of DATEM, SSL, calcium steroyl-2-lactylate (CSL), and GMS (hydrate-form) on final proof time, dough elasticity, and dough volume. The basic dough recipe for the maturograph experiments is: 300 g flour (Northern Spring 11.7% protein), 6 g salt, 15 g yeast, and 90 ppm ascorbic acid. The ingredients are mixed with water to 500 units on a Farinograph, and the emulsifiers tested have been added directly in the Farinograph mixing bowl. DATEM and SSL especially show a marked influence on the dough elasticity and volume.

Studies on lipid-binding during dough mixing have shown that emulsifiers along with many other lipids bind to the gluten fraction (17-20) and are able to replace flour



FIG. 14. Distribution of flour lipids. Influence of diacetyl tartaric acid ester of monomyristin (DATE-C14) on the distribution of flour lipids in dough. (I) Free lipids extracted by chloroform, (II) bound lipids extracted by water saturated butanol, and (III) strongly bound lipids extracted by ether after hydrolysis in hydrochloric acid. The percentage of lipids is calculated on basis of the flour content.

lipids. As an example the influence of DATEM on the distribution of flour lipids in dough is shown here. A diacetyl tartaric acid ester of pure glycerol monomyristin (DATA-C14) was used in this work. Due to the fact that flour lipids contain only traces of myristic acid, it was possible to determine the amount of DATE-C14 in various fractions of lipids extracted from dough by means of quantitative gas liquid chromatography (GLC) methods (20).

The degree of strength at which lipids are bound to dough components is normally characterized by their extractability with solvents of different polarity. Chloroform, water saturated butanol (WBS), and acid hydrolysis followed by ether extraction were used to determine free, bound, and strongly bound lipids. Figure 13 shows the content of DATE-C14 in free, bound, and strongly bound lipids from dough as a function of DATE-C14 added to the flour. The total recovery of DATE-C14 in each case was 95-100%. Figure 14 shows the amount of original flour lipids determined by subtracting the content of DATE-C14 from the total extracted lipid content. This shows that the amount of flour lipids in the CHCL₃ extract increases and that the amount in the WSB extract decreases with increasing amount of DATE-C14 added. This indicates that the DATE-C14 substitutes the flour lipids in association with gluten components. Similar results have been found with SSL, CSL, and ethoxylated GMS in principle, although more detailed studies (17) show the ability of these emulsifiers to replace flour lipids differs from one to another.

Despite the considerable research work concentrated on the subject very little is known about the molecular interactions involved. Surface active lipids may be bound to proteins both by hydrophobic interactions, hydrogen bonding, or ionic reactions, and it is still very unclear which mode of interaction is most important. The lipids which interact with gluten by hydrophobic associations only are often poor in effect as dough conditioners and sometimes even detrimental to a dough. It may be that the dual effect of both hydrophobic and hydrophilic interactions between lipids and gluten proteins as suggested by several research workers (17,20) is necessary in order to obtain the desired functionality of an emulsifier as dough conditioner.

FAT CRYSTALLIZATION

The polymorphism of fats causes problems like "blooming" in chocolate coatings or "sandiness" in margarine made from sunflower oil. Sorbitan esters of palmitic and stearic acids have found specific applications in such products as crystal modifying agents. The addition of sorbitan esters stabilize the intermediate β' -crystal form of fats and prevents the formation of the β -form, which is the most stable crystal form of many fats exhibiting polymorphism. Especially sorbitan esters containing more than one fatty acid radical per molecule (sorbitan tristearate) are effective as crystal modifiers. It is assumed that sorbitan tristearate can be accomodated by the β' -crystal lattice of triglycerides and by steric hindrance prevent formation of the more densely packed β -crystal form.

REFERENCES

- Lauridsen, J.B. JAOCS 53:400 (1976). 2. Boyd, J.V., C. Parkinson, and P. Sherman, J. Coll. Interface Sci.
- 41:359 (1972). 3. Krog, N., in "Water Relations of Foods," edited by R.B. Duckworth, Academic Press, London, New York, San Francisco, 1975.

- Friberg, S., JAOCS 48:578 (1971).
 Boyd, J.V., N. Krog, and P. Sherman. Paper No. 7 at symposium on Theory and Practice of Emulsion Technology, Brünel Univ., London, 1974.
- 6. Krog, N., Fette Seifen Anstr. 77:267 (1975).
- 7. Larsson, K., M. Lundquist, S. Ställberg-Stenhagens, and E. Stenhagen, J. Coll. Interface Sci. 29:268 (1969).
- 8. Berger, K.G., and G.W. White. Dairy Ind. Int. 41:199 (1976) and Ibid. 41:236 (1976).
- 9. Berger, K.G., B.K. Bullimore, G.W. White, and W.B. Wright, Dairy Ind. 37:419 (1972). 10. Schoch, T.J., and C.B. Williams, J. Am. Chem. Soc. 66:1232
- (1964).
- 11. Banks, W., and C.T. Greenwood, Biopolymers 11:315 (1972).
- Osman, E.M., S.J. Leith, M. Fles, Cereal Chem. 38:449 (1961).
 Krog, N., Die Stärke/Starch 23:206 (1971).
- Krog, N., and B. Nybo Jensen, J. Food Technol. 5:77 (1970).
 Lagendijk, J., and H.J. Pennings, Cereal Sci. Today 15:354
- (1970).
- 16. Larsson, K. in "Surface active lipids in foods," S.C.I. Monograph No. 32, Soc. Chem. Ind., Belgrave Square, London, 1968. 17.
- Chung, O.K., and C.C. Tsen, Cereal Chem. 52:533 and 549 (1975).
- 18. Mann, D.L., and W.R. Morrison, J. Sci. Food Agr. 25:1109 (1974).
- 19. De Stefanis, V.A., F.H. Chung, N.A. Ruzza, J.G. Ponte, and R.H. Cotton, Paper No. 95 at AACC Annual Meeting, Montreal, Can., 1974.
- 20. Krog, N., Paper No. 138 at AACC 60th Annual Meeting, Kansas City, Mo., 1975.
- 21. Hoseney, R.C., K.F. Finney, and Y. Pomeranz, Cereal Chem. 47:135 (1970).

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