Fatty Interface Modifiers - Composition, Properties and Uses in the Food Industries*

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MANY foods, manufactured as well as naturally occurring, are dispersions of mutually insoluble phases, which are called either emulsions or suspensions, depending upon the character of the system. It is necessary that such food products meet certain requirements, the requirements varying with the nature of the product.

If we consider for a moment an emulsion consisting solely of, let us say, oil and water, everyone knows that the oil will quickly separate. It is also common knowledge that gum tragacanth, or for that matter, many other protective colloids, such as agar or various gums, gelatin, pectin, etc., stabilize such emulsions.

The use of protective colloids in the food industry is common. It is also a common practice, of particular importance in the manufacture of margarine and of ice cream, to stabilize emulsions by sudden chilling, which, among other things, increases the viscosity of the product.

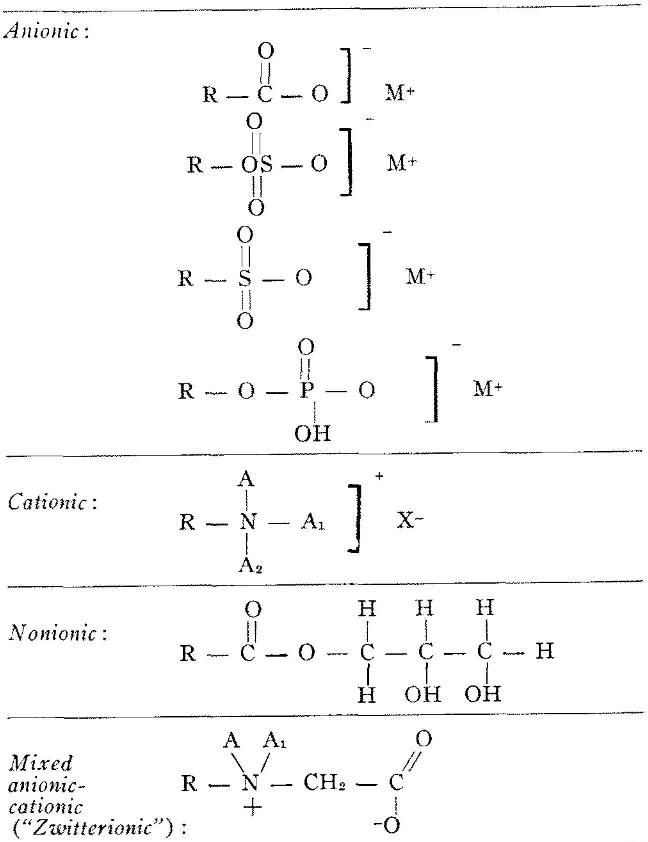
Referring again to the oil-water emulsion, the addition of a soap, as is well known, serves to stabilize the emulsion. The generally accepted Hardy-Langmuir-Harkins theory of the orientation of the emulsifying agent at the oil-water interface accounts for the increase in stability of the emulsion (1). According to that theory, the carboxyl ion end of the soap molecule is attracted to the aqueous side of the interface and the fatty part of the soap molecule is held by the oil phase; the soap thus acts to hold the oil and water phases in a dispersed form. By the same mechanism, soap facilitates the process of *dispersion* of the oil into discrete globules.

Soap is one of a large group of compounds which are operative in interface modification. An interface modifier is a substance that, by its presence, even in small quantities, changes the properties of the interface between immiscible phases, which may be solids, liquids, or gases.

Practically all interface modifiers consist of two component parts. One of these parts is hydrophilic, i.e., it tends to make the compound water soluble, and the other is lipophilic, i.e., it tends to impart fat solubility. As one of the authors (BRH) has shown (2), it is necessary that the hydrophilic and lipophilic properties of an interface modifier be properly balanced in order that the compound be effective (3). Furthermore, the necessary balance point, in terms of predominant hydrophile or lipophile character, of the compound will vary with the system in which it is to be used. In addition, it is also necessary that the hydrophile group be properly located in the molecule.

Interface modifiers may be classified as follows: An anionic agent is an interface modifier in which the lipophile group is part of a negative ion; in a cationic agent, the lipophile group is part of a positive ion; in a nonionic agent no ionization occurs; and finally, substances may be of mixed anionic-cationic type. Examples of the various types are shown in Table 1.

TABLE 1.
Types of Interface Modifiers.



Anionic:	$\left[R-\overset{\overset{O}{\|}}{C}-O\right]^{-} M^{+}$ $\left[R-O\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O\right]^{-} M^{+}$ $\left[R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O\right]^{-} M^{+}$ $\left[R-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\vert}}{P}}-O\right]^{-} M^{+}$
Cationic:	$\left[R-\overset{\overset{A}{\vert}}{\underset{\underset{A_2}{\vert}}{N}}-A_1\right]^{+} X^{-}$
Nonionic:	$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\overset{\overset{H}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-\overset{\overset{H}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-H$
Mixed anionic-cationic ("Zwitterionic"):	$R-\overset{A\ \ A_1}{\overset{\backslash\,/}{\underset{+}{N}}}-CH_2-\overset{\overset{O}{/\!/}}{\underset{\underset{-O}{\vert}}{C}}$

R represents a lipophile group such as long chain alkyl, polycyclic, e.g. cholesteryl, aryl-alkyl, etc., and includes derivatives of those groups.
M^+ represents a positive ion such as Na^+, K^+, NH_4^+, etc. The groups to which R is attached are the "hydrophile" groups.
x^- represents a negative ion such as Cl^-, Br^-, I^-, other monovalent ions, or ½ a bivalent negative ion, etc.
A, A_1, A_2, represent H, alkyl, aryl, or heterocyclic groups or residues.

Many tests have been devised for the evaluation of the effectiveness of interface modifiers. Some half dozen or more are in common use; it appears, though, that in each of these tests a different complex of interface modifying function comes into play. For this reason, it will be understood that if a compound is shown to be effective by one test, it may well be of little or no value for another purpose. For example, it has been shown that there is no strict correlation between the lowering of surface tension and wetting power (4). It is also common knowledge that good detergents may or may not be good wetting agents. Substances which are potent antispattering agents in margarine may be either good or poor wetting agents, e.g. sodium monolaurin sulfate and cholesteryl betaine chloride are excellent antispattering agents, but the former is a good wetting agent and the latter is a poor wetting agent. The bactericidal activity of alkyl dimethyl benzyl ammonium chlorides varies with the nature of the alkyl group and the type of microorganism; against some bacteria the C_{12} derivative is most effective, and against others the C_8 derivative is most effec-

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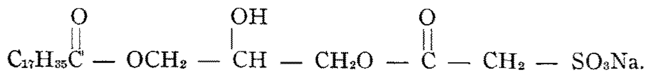
[*] This paper was presented at the May meeting of the American Oil Chemists' Society.

tive, although the C_{12} derivative has a greater effect on lowering the surface tension of water than any other member of the series (5).

Another case in point is monostearine sodium sulphoacetate,



$$C_{17}H_{35}\overset{\overset{O}{\|}}{C} - OCH_2 - \overset{\overset{OH}{|}}{CH} - CH_2O - \overset{\overset{O}{\|}}{C} - CH_2 - SO_3Na.$$

In the frying of oleomargarine (as an anti-spatterer), and in the lowering of the surface tension of water, this substance can be rated high, in a class with the best, but in the so-called "wetting-out" of textile fibers, as measured by the Draves test (6), monostearine sodium sulphoacetate is far from being equal to the best. Among the naturally occurring interface modifiers, cephaline is an interesting example. In anti-spattering it gives a good account of itself, but in "wetting-out" it is of practically no value whatever. Sodium butyl sulphate (C_4H_9—O—SO_3Na), in a proportion of one percent of the weight of the margarine, reduces spattering to such an extent that the margarine fries substantially like butter; yet, for general emulsifying purposes, sodium butyl sulphate is of but little value, if any.

Instances of lack of correlation of properties and functions of interface modifiers can be multiplied indefinitely. Furthermore, there are many striking cases in which this lack of correlation is manifested by an apparent specificity of reagent and function that is dramatic. Sodium octyl sulfate can effect a practically quantitative separation of sodium chloride and potassium chloride by froth flotation; substitution of longer alkyl groups for the octyl group may greatly increase the detergent, wetting, or other properties of the molecule, but such substances will not separate sodium chloride from potassium chloride anywhere nearly as effectively as sodium octyl sulfate (7). Fatty acid esters of glycerol, polyglycerols or sugars, have not been successfully replaced by other types of interface modifiers of comparable surface-active properties (as measured by the common methods), in cakes, in which a so-called "high-ratio" effect is produced.* The viscosity-lowering action in chocolate is highly specific to certain agents.*

It follows, therefore, that an interface modifier should preferably be tested in the system and for the purpose for which it is intended.

Among the food products in which interface modifiers are of great importance is oleomargarine. Oleomargarine is a water-in-oil emulsion containing about 80 percent oil and about 15 percent water in the form of milk, together with small amounts of other ingredients.

Given a sufficiently dispersed emulsion, a high degree of stability can be attained by chilling. It will be recalled that margarine is kept cold and has a high viscosity. However, on standing, some "leakage" of milk, or separation, may occur. This can be prevented by the incorporation, among other interface modifiers, of high molecular weight fatty acid monoglycerides, which are non-ionic interface modifiers.

Compared with butter, margarine, under the usual frying conditions, crackles louder and spatters more violently; in addition, the margarine milk curd bakes onto the frying pan, making cleaning laborious. These undesirable phenomena are due to the fact that frying breaks the emulsion and causes separation and coalescence of the aqueous phase. The water droplets, being heavier than the oil, collect under the oil and are superheated; this causes explosions into steam and is responsible for the crackling and spattering.

It has been found that certain interface modifiers are capable of eliminating these undesirable properties completely (2). The water phase is dispersed in the oil phase even at 100° C., and the fine water droplets evaporate quietly, without undue superheating, and with the formation of a characteristic froth. The milk curd is maintained in the form of well-dispersed small particles, which may be carried into the froth, and consequently do not bake on to the bottom of the pan.

A large number of antispattering agents was investigated to establish the necessary characteristics of such agents (2). Aside from edibility, freedom from objectionable color, odor, or taste, and low cost, a successful antispattering agent must have a proper balance between hydrophile and lipophile groups, proper orientation of the hydrophile groups at or near an extremity of the molecule, and must be non-volatile at frying temperatures.

Table 2 shows the comparative antispattering values of a few of the great number of compounds which have been investigated, the examples selected serving to illustrate the requirements just mentioned.

TABLE 2.
Comparative Antispattering Values.

Compound	Antispattering Value
1. Cholesteryl betaine chloride	Excellent
2. Cetyl betaine chloride	Excellent
3. Melissyl betaine chloride	Fair
4. Sodium propyl sulfate	None
5. Sodium butyl sulfate	Fair
6. 9, or 10-sulfostearic acid	Very poor
7. 2-sulfostearic acid	Excellent
8. Monostearine sulfoacetate (sodium salt)	Excellent

It should be noted that melissyl betaine chloride is too lipophilic and that sodium propyl sulfate is too hydrophilic; in both cases there is an improper hydrophile-lipophile balance. Numbers 6 and 7 illustrate the necessity for proper location of the hydrophile groups in the molecule. Numbers 1, 2, 7 and 8 have both proper balance and proper orientation. The last substance shown in Table 2 is used commercially.

Interface modifiers are present in, or added to, the ingredients of many other food products, e.g. mayonnaise, salad dressing, ice cream, chocolate products, vitamin preparations, and bakery products. They are also used in removal of fruit spray residues. These residues may become imbedded in or covered by the waxy outer covering of the fruit and consequently are not easily washed out by water or dilute acid. Addition of an interface modifier to the washing medium materially facilitates removal of the spray residues.

Food products in which interface modifiers play an important role are mayonnaise and salad dressings. Egg yolk, which is a remarkably stable natural emulsion itself, is one of the ingredients. It contains a lecithin-protein complex which acts as a potent interface modifier in the emulsification of the other mayonnaise and salad dressing constituents. It is a remarkable fact that addition of as little as 0.5 percent additional lecithin, e.g. soya bean lecithin, to the mayonnaise ruins the emulsion. Neither pure egg lecithin nor lecithin-free egg yolk will yield a satisfactory emulsion. Both constituents of the egg yolk are necessary.

Ice creams are emulsions of butter fat, non-fat milk solids, sugar, water and air, which are stabilized by freezing. Addition of a protective colloid is necessary to prevent the formation of large ice crystals. It is claimed that the addition of monoglycerides and diglycerides serves two purposes (8). It gives a finer texture and produces the desired overrun more quickly, effecting

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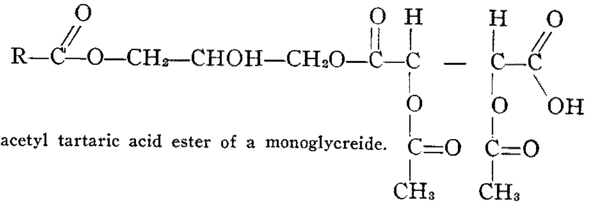
* These examples are discussed below.

a saving in power. (Overrun refers primarily to the amount of air emulsified in the ice cream.) Egg yolk is also used for the same purposes. Presumably the action of egg yolk in this case is due to the function of the lecithin complex as an interface modifier. Judging by representations made in the patent, monoglycerides and egg yolk are at least in part interchangeable in this case.

In the chocolate industry, particularly in chocolate coatings, interface modifiers are of great importance. The two agents which are commonly employed are sodium diglyceride phosphate and lecithin (9).

Chocolate coatings are a suspension of solids in fat, the properties of which are particularly and adversely affected by the presence of traces of free moisture as distinguished from bound moisture. The incorporation of the interface modifiers in chocolate results in the following extremely important improvements: The dispersion of the dried powdered ingredients within the fat medium is enhanced, the viscosity is lowered, and the flow characteristics improved. To the extent that moisture is present or enters the chocolate from one source or another, it is maintained by the interface modifier in an emulsified or bound state, thus mitigating the markedly objectionable effects of free moisture. This is particularly important under conditions where ice cream bars or other moist materials are being dipped or enrobed, or where fresh surfaces of the chocolate coating batch are repeatedly being exposed to atmospheric moisture; under such conditions, in the absence of an interface modifier, there is a progressive absorption of moisture, with a progressive increase in viscosity and a concomitant progressive change in other physical characteristics which render the coating progressively less suitable. Moreover, the interface modifier stabilizes the viscosity of the chocolate coating in relation to aging, storage, remelting and agitation. The tendency to fat staining of wrappers at high temperatures is reduced. The finish and gloss of the coating are improved. The practical temperature range for coating is extended. Finally, insofar as interfacial tension between fat and water is diminished, adhesion of the coating to a more or less aqueous center is appreciably augmented.

Leaving chocolate and turning to vitamins—it is sometimes desired to emulsify a fat-soluble vitamin in an aqueous medium as, for example, in the case of enriching milk with vitamin D. A very convenient method is to dissolve the vitamin in an oil containing an interface modifier, such as polyglycerol esters of fatty acids, or a diacetyl tartaric acid ester of a monoglyceride (10):



Diacetyl tartaric acid ester of a monoglycreide.

The oil phase then is easily and stably dispersed in the aqueous phase.

The baking industry, also, has made good use of interface modifiers (11).

Most cakes are emulsions containing fat, water, and gas phases, together with flour, sugar and egg material. The desirable properties, in such cakes, are: sweetness, moisture, tenderness, good volume, good texture and good keeping qualities. In general practice with ordinary shortenings, the amount of sugar is usually limited to less than the weight of flour present, or in any event, not exceeding it.

TABLE 3.

Extracts from Cake Formulas.

		Ordinary Formula %	Enriched Formula %
Sugar		28.6	28.6
Flour		28.6	20.4
Moisture	Skim milk	17.1	22.5
	Egg white	11.5	15.4

It is a fact that an increase in the ratio of sugar to flour, together with an increase in the water content, results in a sweeter, moister, more tender cake. However, an increase in the sugar content, with the accompanying increase of moisture content, yields a cake which shrinks or falls objectionably after being removed from the oven.

When interface modifiers of the proper type, such as mono- or diglycerides or fatty acid esters of polyglycerols, are incorporated in the batter, the ratio of sugar to flour and the water content may be increased.*,† A better cake is produced in all respects, particularly with regard to keeping quality and volume.

The interface modifiers may be incorporated in the shortening, in the egg constituent, in prepared cake flours or in the baking powder. The use of these nonionic reagents in baking powders, in addition to the value just described, represents a convenient method of preparing a slow-acting baking powder.

Angel food cakes differ from the ordinary cake in that they contain no fatty shortening. They are merely a foam of sugar, flour, egg white and air or CO_2. Such cakes do not keep as well as cakes which contain shortening and they have the undesirable property of "tackiness"; when the air is expelled from the "crumb" in chewing, the cake solids have a tough, rubbery consistency. It has been found that the addition of small proportions of certain fatty esters of polyphosphoric acids to the cake formula produces the following improvements: about 20 percent increase in volume; more uniform and smaller air cells and, therefore, better texture; more desirable chewing properties because the air is not expelled from the cake as rapidly; and improved keeping qualities (12).

Since the use of interface modifiers in the food industries is a comparatively new field, a great deal of knowledge still remains to be acquired. As we learn more about the colloidal properties and metabolism of foods, we may expect a far greater and more general application of interface modifiers in foods than has been the case up to the present time.

Acknowledgment

The authors wish to express their indebtedness for the contributions of Dr. M. M. Gladstone to the organization of this paper and for presenting it at the May, 1941, meeting of the A.O.C.S.

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* It is commonly and erroneously accepted by many in the industry that the amount of water which can be emulsified in a shortening is a measure of the efficiency of the shortening in the production of cakes with increased proportions of sugar and moisture. Although it is true that a shortening containing the above-mentioned interface modifiers retains more water than a plain shortening, it is also true that fatty acid esters of polyglycerols are more efficient than monoglycerides in the so-called "high-ratio" effects, in spite of the fact that shortenings containing the latter can retain more water than those containing the former.

† Furthermore, the proportions of sugar and moisture may be increased to a certain extent if additional egg yolk is incorporated in the cake batter.

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Studies on the Chemistry of the Fatty Acids VIII The Reaction of Thiocyanogen with Linoleic and Linolenic Acids

The Application of the Thiocyanogen Reaction to the Determination of these Acids in Fatty Acids Mixtures[*]

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THE reaction of thiocyanogen with the unsaturated fatty acids and their glycerides was proposed by Kaufmann (1, 2, 3, 4) and by Kaufmann and Keller (5) as the basis for the analysis of fatty acid mixtures containing oleic, linoleic and linolenic acids. Simultaneous equations were set up, based on iodine and thiocyanogen numbers, for the calculation of the composition of such mixtures. These equations were derived from the fundamental assumptions that the iodine numbers of the unsaturated acids were equal to the theoretical values and that the thiocyanogen numbers of oleic, linoleic and linolenic acids were values equivalent to reaction with one, one, and two double bonds respectively.

In his study of the reaction of thiocyanogen with linoleic acid, Kaufmann (2) employed a specimen of trilinolein, the iodine number of which was 169.1 (theory 173.3). The thiocyanogen number was 79.5 and 82.5 at 5 and 17 hours reaction time respectively (theory for one double bond, 86.7). In evaluating the reaction of thiocyanogen with linolenic acid Kaufmann and Keller (5) avoided the use of acid prepared by debromination because they were not sure that it was identical with the natural acid. They based their conclusions, therefore, on thiocyanogen values obtained on a mixture of linoleic and linolenic acids obtained from linseed oil acids by a procedure whereby most of the saturated acids and oleic were removed by crystallization of the lithium soaps. The composition of the mixture was the same whether calculated directly from the iodine number as a binary mixture or from simultaneous equations, based on the assumption that the reaction of thiocyanogen was the theoretical for one and two double bonds with linoleic and linolenic acids respectively.

Since Kaufmann's original proposals several investigators, working with debromination linoleic and linolenic acids, have observed variations from the assumed theoretical thiocyanogen numbers. Waterman, Bertram and van Westen (6) reported a thiocyanogen number of 92.5 for linoleic acid (theory 90.6). Riemenschneider and Wheeler (*7*) in a study of the reaction curve of methyl linoleate reported a value of 89.0 (theory 86.3) for a 24 hour reaction period, and Wheeler, Riemenschneider and Sando (8) in a similar study of trilinolein observed a value of 90.5 (theory 86.7). They advocated a four-hour reaction period for analysis of glyceride mixtures, since the reaction with triolein and trilinolein was almost exactly the theoretical in that period. Kass, Lundberg and Burr (9) found 96.3, and Hilditch and Murti (10) 95.9 for linoleic acid.

Kimura (11) observed that thiocyanogen reacted with debromination linolenic acid to a value between one and two double bonds. Shinowara and Brown (12) found a thiocyanogen number of 161.0 for linolenic acid (theory for two double bonds, 182.5). Very recently Kass, Loeb, Norris and Burr (13) reported 167.3 and Hilditch and Murti, 162.5, for debromination linolenic acid. In these reports in which actual reaction curves were described (7, 8, 13), either with the acids or their esters, it was found that the thiocyanogen reaction was continuous up to and beyond 24 hours with the two and three bond acids and that the reaction did not entirely cease at any point of partial saturation.

In 1936 a committee of The American Chemical Society drew up a procedure of analysis (14). The reagent in this procedure was 0.2 N. with respect to thiocyanogen instead of 0.1 N as proposed by Kaufmann. This procedure was employed by Kass et al (8, 13).

In the more recent reports cited above the possibilities that the debromination acids which were used might contain appreciable amounts of isomeric acids and that these conceivably might react at a different rate from that of the natural acid have been overlooked. Both Kaufmann and Keller (5) and Kimura (11) suggested that the acids might be heterogeneous without, however, the confirmation of experimental evidence. Some light is thrown on this angle of the question by the data of Shinowara and Brown (12) who reported thiocyanogen values of 152.6 and 154.1 on two specimens of linolenic acid of iodine numbers 260 and 262 respectively; these specimens were pre-

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[*] Presented in part at the Cincinnati meeting of the American Chemical Society, 1940.

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