Emulsifiers: Processing and Quality Control[1]

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Abstract

I. Characterization and Processing

Emulsifiers are surface-active agents (surfactants) which are added to an emulsion to increase its stability by interfacial action. They are divided into two broad categories, ionic or nonionic, according to the character of their colloidal solutions in water. As an eclectic guide to emulsifiers considered pertinent to the AOCS, greatest emphasis is placed on the description and processing of the nonionic type and only representative examples of the three classes of ionic surfactants, i.e., anionic, cationic, and amphoteric will be considered.

Nonionic types discussed in more detail include: polyol-fatty acid esters of glycol, glycerol, polyglycerol, tetritol and pentitol, hexitol, anhydro hexitols, and sugar, as well as the polyethanoxy and polylpropanoxy esters and ethers.

II. Controls

Common analytical procedures, i.e. acid number, saponification number, hydroxyl number, etc. and their significance are described.

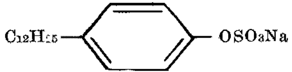
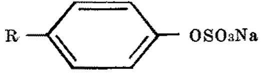
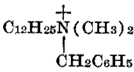
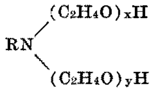
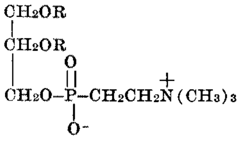
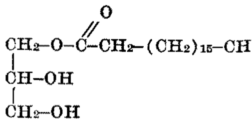
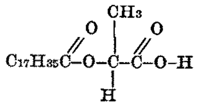
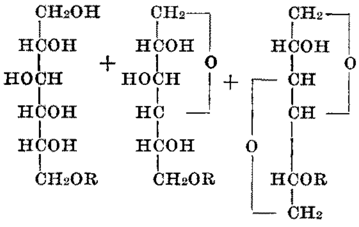
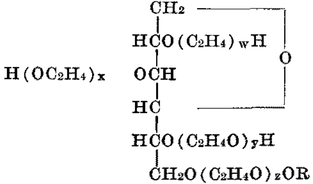
A combined statistical-chemical control program plays an important role in assuring batch to batch emulsifier uniformity. Consistent emulsifier performance is obtained by mating raw material acceptance plans, in-process control, and final product qualification. All of these elements are required for an effective program. Statistical Q.C. techniques maximize control benefits of chemical analysis. Newer analytical methods such as automated GLC increase the sensitivity of control decisions.

Introduction

Volume II of the monograph on surface-active agents by Schwartz, Perry, and Berch (1) states that the surfactant industry grew up in the years intervening between the first and second volumes (1947–1956). They also allege that the new name "surfactant," in their words, "a happy and convenient contraction of surface-active agents," suggests that this large group of substances has become well enough known to require a simple yet distinctive tag. The author would rather go along with Becher (2), who claims that this word serves no important purpose but, since it has become so widely entrenched in the literature, "there is no use in engaging in an altercation with the center of municipal authority."

Stirton (3) in Edition III of Bailey lists representative surface-active agents. Table I is derived from his list with some modification of the system of classification. Even this much-abridged list [McCutcheon (4) gives more than 3,000 surface-active agents] is more comprehensive than can be discussed herein. This paper must be an eclectic guide to those surface-active materials which would seem most pertinent to the membership of the AOCS; namely those used in foods.

TABLE I
Surfactants

I. Ionic	Formula
A. Anionic Compound	
"Sulfonated" oils	$RCH(OSO_3Na)R'$
Sodium alkyl sulfate	RCH_2OSO_3Na
Sulfated monoglyceride	$C_{11}H_{23}CO_2CH_2CHOHCH_2OSO_3Na$
Sodium dodecyl Sulfoacetate	$C_{12}H_{25}O_2CCH_2SO_3Na$
Dodecene-1-sulfonate (Las)	
Alkyl aryl sulfonate	
B. Cationic	
Dodecyl dimethylbenzylammonium chloride	 $C_{12}H_{25}\overset{+}{N}(CH_3)_2Cl$, $CH_2C_6H_5$
Oxyethylated amines	
C. Ampholytic	
N-dodecylaminoethanesulfonic acid	$C_{12}H_{25}\overset{+}{N}H_2CH_2CH_2J\overset{-}{O_3}$
Lecithin	
II. Nonionic	
Oxyethylated fatty acid (polyethylene glycol ester)	$C_{17}H_{35}CO_2(C_2H_4O)_nH$
Monoglyceride	
Stearoyl lactylic acid	
Sorbitan fatty acid	
(One mole R (fatty acid)/mol hexitan randomly attached to available OH groups)	
Polyoxyethylene sorbitol monoester	 $w+x+y+z=20$

(One mole R (fatty acid) randomly attached to available OH groups)

Surface-active or other agents added to an emulsion to increase its stability by interfacial action are known as emulsifiers, or emulsifying agents. Often

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[1] Presented at the 1966 AOCS Short Course, Michigan State University, Lansing, August 29–September 1, 1966, and the Primero Seminario, Monterrey Section, AOCS, I.T.E.S.M., January 23–25, 1967.

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the surface-active material is used in a food product, not to emulsify and not primarily because of its effect on an interphase but because of some property which may be altered by its surface activity. For instance, we might consider the use of surfactants to inhibit the staling of bread and other dough systems. Some attribute the anti-staling activity to the ability of the long-chain saturated fatty acid portion to clatherate within the starch helix, thus inhibiting the coacervation of the amylopectin or crystallization of the starch granule, which is the principal manifestation of bread staling.

Fatty acids per se are ineffectual; to be effective they must be linked with a hydrophilic segment to enable them to permeate the starch granule. Long-chain saturated fatty acids were designated; oleic acid derivatives are not effective. One wonders whether it is the double bond or the *cis* configuration which detracts from the efficacy of this acid. It would be of interest to obtain glyceryl-mono-oleate or polyoxyethylene (POE) oleate in which the oleic is all of the *trans* configuration and compare its effectiveness with the stearate esters.

As shown in Table I, surfactants may be grouped into two general classes according to the character of their colloidal dispersion in water: a) ionic: form ions in solution; depending on the action of the ion-active group, these are designated anionic, cationic, and ampholytic (amphoteric). (These are not mutually compatible since they tend to neutralize each other.); b) nonionic: covalent, show no tendency to ionize, may be combined with other nonionics and either anionic or cationic agents. (These are quite immune to the action of electrolytes, i.e., acids, caustic, etc.).

Since ionic surfactants, with one or two minor exceptions, are little used as direct additives in foods, this paper will be devoted to a discussion of nonionic surface-active agents. The 1963 Short Course on "Advances in Soaps and Detergents" lists several papers that describe processing of ionic surfactants.

Nonionics

According to Becher (2), nonionics represent the largest and fastest growing group of emulsifying agents. Illustrative of their increasing importance is the fact that an entire book devoted to this subject is just out. In fact, information in this section is derived mainly from "Nonionic Surfactants," edited by M. J. Schick and published by Marcel Dekker Inc. Extracts are quoted by permission of Dekker. If it is assumed that the chapter on "Polyol Surfactants" by F. R. Benson is representative, this book provides a most complete bibliography to the voluminous literature pertaining to this one class of surfactants.

The nonionics are comprised of a hydrocarbon residue and a repetition of such weakly hydrophilic groups as ether linkages or hydroxyl groups. The chain of weak hydrophilic units has the same effect as one strong hydrophilic unit except that no ionization takes place. Thus nonionics may be utilized in conjunction with any one class of ionic surfactants.

Typical lipophilic groups used in the preparation of nonionics are fatty alcohols, partial esters of fatty alcohols, alkyl substituted phenols, fatty acids, rosin acids, and tall oil. Representative of the reaction used to produce the nonionics is that utilized by I. G. Farbenindustrie in making some of the earliest members of this class, the *Peregals* and *Igepals*. They are made by reacting fatty alcohols and substituted phenols with an excess of ethylene oxide and have formulas such as

$$RO(CH_2CH_2O)_nH$$

Since n can be varied at will, the molar proportions which control the properties can be selected. Also the hydrophobic groups available are sufficiently numerous so that a veritably endless variety of nonionic surfactants can be and are being made. In effect, the emulsifying agent can be tailor-made for each particular application. As implied above, the most important property of the nonionics is the relative size of the hydrophilic and lipophilic portions of the molecule or hydrophile-lipophile balance (HLB). Griffin (5) may not have been the first to recognize this important property, but his concept of classifying nonionics by HLB value has contributed more to the systematic selection of such emulsifiers than anything else in the literature. The HLB of a representative group of nonionic emulsifiers is shown in Table II.

A detailed discussion of HLB and list of references are given in the section on emulsions by Griffin in "Encyclopedia of Chemical Technology" (Vol. 8, Second Edition, pages 117–154, John Wiley and Sons Inc., 1965). Becher (2) also discusses this and covers the various methods of determining HLB (Table II).

Nonionics are best described in terms of the linkage between the lipophilic group and the solubilizing (hydrophilic) one. We have mentioned examples of the ether linkage formed by the reaction of hydroxyl-containing compounds with ethylene oxide. Propylene oxide may also be used.

Esters formed by the reaction of polyhydric alcohols with fatty acids are probably most familiar to this industry and are the type most extensively approved for food use. Hydrophilic properties of these polyol surfactants are derived from oxygen linkages such as ether groups formed by dehydration of the starting polyol and carboxylic ester linkages, as well as from the polyol residue.

Glycerol Esters

Bertholet prepared glycerol mono- and di-esters of fatty acids in 1853 by heating equal parts of glycerol and fatty acid to about 200C in sealed tubes. Typical of modern practice is the direct esterification of equimolar quantities of fatty acid and glycerol at 250C for 2–3 hr to produce a reaction mixture of monoglycerides and diglycerides with minor quantities of glycerol, free fatty acid, water, and

TABLE II

HLB Values-Commercial Emulsifiers

Name	Chemical designation	HLB
Atlas G-1706	POE sorbitol beeswax derivative	2
Atlas G-1704	POE sorbitol beeswax derivative	3
Atlas G-1727	POE sorbitol beeswax derivative	4
Atlas G-2180	Propylene glycol monostearate	3.4
Aldo 33	Glycerol monostearate	3.8
Span 60	Sorbitan monostearate	4.7
Polysorbate 60	POE (20) sorbitan monostearate	14.9
PEG 400 Mono-oleate	POE mono-oleate	11.4
Polyoxyethylene (40) stearate	POE (40) stearate	16.9
	Sodium lauryl sulfate	App. 40

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• *Emulsifiers . . .*

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triglycerides. About 80% conversion to monoglyceride may be obtained by use of excess glycerol, conducting the reaction at reduced pressure, directing a stream of inert gas or steam to remove water from the reaction, or by use of solvents. Catalysts include acids, bases, metals, metal oxides, etc.

The alcoholysis or glycerolysis of fats is probably the most important industrial method for the preparation of partial glycerides. The fatty acid composition of the resultant partial glyceride is that of the starting fat. The reaction is normally conducted at 180–250C in the presence of alkaline catalysts including NaOH, $Ca(OH)_2$, sodium methoxide, soaps, potassium carbonate, and trisodium phosphate. The resultant product of the reaction is a mixture comprised of about 45% mono-, 44% di-, and 10% triglycerides and is commonly referred to as "monoglycerides." Products with more than 90% monoglyceride content are readily obtained by molecular distillation of the reaction mixture.

The proportion of mono- to di- and triglyceride may be controlled, depending on the relative proportion of reactants, temperature, time, catalysts, and use of stripping steam or inert gas. Also the amounts of 1- and 2-monoglyceride in the product may be varied, which emphasizes the importance of control of all these factors. Normally about 90% of the total monoglyceride obtained is the *alpha* or 1-glyceride and 10% *beta* or 2-glyceride.

Brandner and Berkmeier (6) have determined the relative esterifiability of the primary and secondary hydroxyls. At 200C the factor favoring the primary hydroxyl is about 2.3; at 100C, 4.5. It is evident that monoglycerides prepared at elevated temperatures are not at equilibrium at room temperature, and isomerization takes place, which must be considered in specifications for such products. Also the reaction between triglycerides and glycerol is reversible, especially in the presence of catalysts and at elevated temperatures. This further illustrates the need for complete removal of catalyst and good control of temperature.

Acids other than the fatty acids, including acetic, lactic, tartaric, citric, succinic, adipic, etc., are utilized to produce substituted partial glycerides as the acetoglycerides, lactated monoglyceride, etc., with useful surfactant and related properties. Acetoglycerides may be prepared either by esterification of the partial glyceride with acetic acid or by the interesterification of triglycerides or partial glycerides and triacetin (7).

The so-called lactated or lactylated monoglycerides such as glycerol lactate palmitate are obtained by direct esterification of fatty acid (palmitic acid), glycerol, and lactic acid at 180C for 12 hr in CO_2 with total reflux.

Glycerides containing fatty acid and lactate residues in predetermined positions have been prepared from blocked glycerol derivatives (8).

Contrary to popular opinion, the acetoglycerides and lactated glycerides are not appreciably more hydrophilic than the glycerol partial esters. The reaction of diacetyl tartaric anhydride with glycerol monostearate at 100–130C yields the diacetyl tartaric acid monoglyceride ester.

There has been some resurgence of interest in the polyglycerol fatty acid esters. When glycerol is heated in the presence of either alkaline or acidic catalysts, it polymerizes with intermolecular loss of water to form polyglycerols. In the presence of sodium hydroxide or sodium acetate and at temperatures of 250–275C, polymers of 2–30 moles of glycerol have been obtained. The ether linkages are asserted to form linear chains (9), although branched chains attributable to further anhydrization are known to be present.

The periodate consumption is higher than calculated by assuming two pairs of vicinal hydroxyl groups, which is the number present in any linear polyglycerol. Progressively more branching occurs as the polymer length is increased from triglycerol to the apparent decaglycerol. Other calculations and data make it appear probable that considerable anhydrization occurs concurrently with the polymerization to form stable, six-membered, dioxane-type ethers (10).

Esterification of the polyglycerol is normally conducted at 190–220C with basic catalysts. Additional anhydrization results as a side reaction. As with other nonionic emulsifiers, a variety of products can be made by control of the degree of polymerization, extent of esterification, and selection of fatty acids and triglyceride. In the last instance, mixed glycerol-polyglycerol esters are formed. Minor proportions of polyglycerol esters can be found in virtually all partial glycerides (11).

Glycol Esters

Direct esterification of ethylene glycol or propylene glycol with molar equivalents of fatty acids at temperatures of 170–210C, in the presence of alkaline or acidic catalysts, produces mono- and diesters of the glycol. Commercial grades of glycol esters, including so-called propylene glycol monostearate (PGMS), usually are comprised of about 55–63% monoester; the balance consists of diester and lesser amounts of free fatty acid and free glycol. An excess of glycol leads to higher monoester content. A product with 69% ethylene glycol monopalmitate results from reacting three moles of ethylene glycol with one mole of palmitic acid at 180C for 4 hr with 0.1% camphorsulfonic acid catalyst. Ten moles of ethylene glycol to one mole of fatty acid produce substantially pure monoester. Glycol esters have been prepared by direct reaction of ethylene oxide and propylene oxide with fatty acids.

There is currently a petition before the Food and Drug Administration to seek approval of 1,3-butylene glycol mono- and diesters of edible fatty acids as a direct food additive.

The two hydroxyl groups of ethylene glycol are equally reactive, but the reactivity of the primary hydroxyl of propylene glycol has been shown to be about three times that of the secondary OH (12).

Alcoholysis of triglycerides with glycols leads to mixed partial glycol-glycerol esters or PGME.

Tetritol and Pentitol Esters

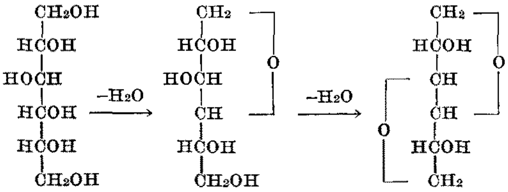
Benson (13) cites conditions and lists examples of the esterification of erythritol, xylitol, and pentaerythritol, but concludes that none of these esters has achieved commercial significance as surfactants.

Hexitols and Anhydrohexitols

Partial esters of the hexitols, sorbitol, and mannitol may be obtained by *trans* esterification, using solvents such as phenol, pyridine, dimethylformamide, etc.; and esterification to the hexa-acetate with acetic anhydride is known. However the unmodified hexitol esters are not of commercial significance.

Much more important are the anhydrohexitol esters which are produced by direct reaction of hexitol with fatty acids, during which internal ether formation occurs as well as esterification. Schwartz et al. (1) say that these are among the best known and most widely used nonionic surfactants which do not contain the polyethanoxy chain.

Formation of internal ether linkages characteristic of these sugar alcohols occurs under the influence of heat and catalyst as represented below:



Sorbitol 1,4 Sorbitan Isosorbide

Lesser amounts of the 1,5 sorbitan, etc., are also formed. In general, anhydrization increases with temperature during esterification. Reaction temperatures range from 180C to 285C. Preferred temperatures are in the range of 225C to 250C. Catalysts used include sulfuric and phosphoric acids, alkali, e.g., NaOH, or no catalyst other than the fatty acid. When NaOH is used the actual catalyst is the soap formed by the fatty acid.

Anhydrohexitol esters are prepared from a variety of fatty acids. The resulting products are complex mixtures of components with varying degrees of anhydrization and esterification. Having arrived at a desirable composition, combined statistical-chemical control programs mating raw material acceptance plans, in-process control, and product qualification are essential to assure consistent emulsifier composition. The *trans* esterification of hexitol with triglycerides (for instance, the interaction of one mole of coconut oil with two moles of sorbitol to give a mixed coconut-monoglyceride, mono-coconut sorbitan ester) serves as an example of the complex compositions that may be encountered.

Anhydrohexitol esters may also be prepared by the separate anhydrization of hexitols followed by esterification.

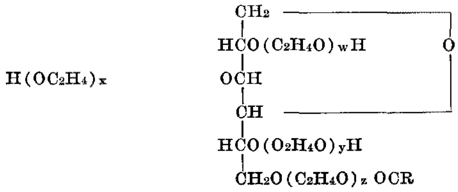
Sugar Esters

Sugar may be reacted with triglyceride fats or fatty acids to form the sucrose esters, etc. Because the sucrose and other sugars are insoluble in fats or fatty derivatives, a mutual solvent is required to avoid charring. Dimethylformamide has been used most extensively. The residual dimethylformamide must be removed completely if the sugar esters are to be used in food. The sugar esters have not achieved wide commercial acceptance.

Polyoxyalkalene Polyol Esters

With the exception of some of the polyglycerol esters, the unmodified polyol esters described thus far are primarily lipophilic in nature with an HLB number on the order of 5 or less. They can be made hydrophilic, i.e., HLB in excess of 10, by attaching the requisite number of moles of ethylene oxide. Virtually any desired HLB may be obtained by control of the degree of alkoxylation.

Polyoxyethylene anhydrohexitol fatty acid esters are the most important commercial oxyalkylated esters. Preparation of POE (10) mannitan monostearate, as described by Griffin (14), consists of reacting 10 moles of ETO with 1 mole of mannitan monostearate in the presence of Na methylate at 100C under pressure. Oxyethylene chains attach at the site of each hydroxy group of the ester. The sum of all the oxyalkylene chain lengths equals the average number of moles of ETO attached per mole of hexitol. The formula of a representative component of POE (20) sorbitan monostearate is shown.



where $w + x + y + z = 20$ *moles* ETO

Polyoxyalkalene polyol esters may also be made by first reacting ETO with the polyol, followed by esterification with fatty acids, or by using the dendro[2] polyol to alcoholize fatty esters.

POE (3) glycerol stearate may be produced by first reacting ETO with glycerol. The catalyst (Na methylate) may also be used to catalyze the esterification with stearic acid.

Methylglucoside esters, sucrose esters, glucose esters, polyol glucoside esters prepared from starch, and many others have been ethoxylated to produce commercial products.

Quality Control

Only representative examples of the principal types of nonionic emulsifiers have been listed. However, this directs attention to the many variations in formulation possible in this class. We have previously described a "grid" (15) in which we have attempted to use methods that are not random in nature to predict the combination of the many variables best suited for a particular application. The very complex composition and the many degrees of freedom which make the nonionics so versatile demand the utmost in control of all the many production variables to assure products that are uniform in composition and performance.

Application studies to determine optimum emulsifier systems may be based on prior knowledge, HLB requirements, and planned experimental design. Once a user selects a system he must be assured of consistent emulsifier performance. Consistent performance is dependent upon uniform composition. Manufacturing and quality control procedures must be geared to supply this uniformity. There are three important quality phases in the manufacture of emulsifiers: raw materials selection, controlled manufacturing procedures, and final acceptance qualifications.

The problem is further complicated because throughout the manufacture of emulsifiers, beginning with some of the raw materials themselves, one is not dealing with pure chemical compounds. The ingredients of many commercial emulsifiers include materials such as fatty acids, fatty esters, etc. In these there is inherent variability resulting from factors such as climatological or processing conditions. The manufacturer must assure uniform quality

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[2] The term dendro has been used to describe products in which the polyol is ethoxylated and this material is then esterified. Catenyl, as in 20 catenyl sorbitan monostearate, would describe a product in which the esterification is followed by ethoxylation.

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at the raw material stage. Adequate specifications must be established. Vendors must be carefully screened and approved. Quality acceptance tests must be designed to ensure that specifications of raw materials are met. Chemical properties such as acid number, hydroxyl number, etc., are not always adequate to assure consistency.

Color stability is important since raw materials may contain trace compounds which develop unsatisfactory colors in the final product. While this is a common problem with natural raw materials such as fats and oils, it is also true of synthetic materials like fermentation-lactic acid which can contain materials detrimental to final-product color. In some cases it is necessary to measure the distribution of constituents by gas-liquid chromatography (for example, fatty acid distributions). Where necessary, acceptance criteria may be based on this newer tool. Blends of several types of raw materials are necessary in some cases as a means of obtaining proper control.

In manufacture, standard operating conditions must be adhered to. For example even slight differences in reactor design must be taken into account in preparing manufacturing procedures. Such procedures must not only specify the manufacturing conditions, i.e., temperature and pressure, but also include chemical control analyses, method and frequency, and control criteria.

Control problems may be more fully appreciated from some examples. In the manufacture of sorbitan esters, both esterification and formation of ether bonds must be controlled. If rigorous control of conditions is not exercised, the final product may not have the desired final properties; during ethoxylation of esters, varying sets of conditions can give the same final average ethoxy length, but only an exacting manufacturing control can give consistent distribution of chain length from batch to batch.

Once the product has been manufactured, detailed final acceptance tests which fully characterize the resultant product must be met. These final analyses measure not only the effect of the manufacturing operation but to some extent the characteristics of the original raw materials. Only after assurance that final laboratory analysis meets specifications requirements can the product be released for shipment.

Each batch's adherence to specifications can ensure its satisfactory performance, but this should not be the last step in a full quality assurance program. Statistical data reduction techniques, like cumulative sum and Shewhart control charts, should be exercised on a regular basis. Periodic computer evaluations, involving more advanced statistical techniques, such as multiple regression, can evaluate long-term product uniformity and point out areas for further improvement.

In addition to normal specification requirements, a program to establish stability characteristics must be conducted. Not only is it important that a product meet specifications when manufactured, but chemical and physical properties of the material must remain stable over an extended period of time.

Control also must be maintained over analytical measurements. If analytical results are erroneous, the whole program fails. When emulsifiers are manufactured at more than one location, it is most important to have detailed interlaboratory evaluation programs. Such programs help to ensure that laboratory analyses are being properly performed.

It is obvious that differences between various sources could seriously affect performance. There is need for greater consistency between manufacturers. Perhaps what is really needed is more apt characterization of materials such as emulsifiers, so that when one speaks of PGMS, it will be with some specificity and will not include the four existing commercial varieties available; and a food additive order should not have to utilize something like a Reichert-Meissl value in an attempt to characterize acetoglycerides.

People often ask, "What's new in emulsifiers?" Periodically someone makes a splash with a new emulsifier or line of products, and there is a flurry of activity to evaluate these products. After a short while each finds its own level in the market place, and the old stand-bys continue to be used. This is not to say there is no place for new products. There is. There is also room for improvement in the myriad existing materials.

What is new in emulsifiers is a better understanding of their functions, an increased sophistication in ascertaining optimal combinations for specific applications, and improved and automated control procedures to assure the user of uniform products to give consistent performance.

ACKNOWLEDGMENT

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