the *cis-cis* 9,12-octadecadienoic acid, the isomerization must be kept low. This of course results in a non-selective hydrogenation with the product being waxy. Therefore some compromise must be made and the hydrogenations are carried out under conditions that do not cause too much isomerization or produce too much saturated material.

Recent Progress in Hydrogenation Processes

Most of the edible oil hydrogenation is carried out by a batch process. However a number of studies have been made and patents issued covering the continuous hydrogenation process. In one variation of this process, the catalyst is mixed with oil and the mixture pumped or sprayed into a reaction chamber that contains the hydrogen under pressure. The oil-catalyst slurry may be agitated in the reactor. The catalyst is filtered from the oil continuously and the catalyst may be returned to the start of the cycle for reuse. Another process involves the use of a fixed catalyst bed. The oil and hydrogen are pumped through the bed, where the reaction takes place. There are several difficulties involved in the use of a continuous process, not the least being analysis and control. A continuous reading of the refractive index will indicate the iodine value of the stream of hydrogenated product. However since the iodine value is not the only criterion for the hardness of the oil, some other measurement should be made. It has been reported that a continuous measure of the *trans* acids may be performed on the oil stream by the infrared absorption at 10.36 microns. This would give a somewhat better indication of the consistency of the product. However it would appear that perhaps a combination of refractive index and *trans* content would permit very close analytical control over the product stream. In the operation, various catalyst poisons may alter the catalyst efficiency for both hydrogenation and isomerization, so both types of measurement appear to be necessary.

Hydrogenation in solution seems to be of considerable interest. Solvent extracted oils are becoming more prevalent and since micella refining has several obvious advantages, it should be possible to hydrogenate the oil in the extracting solvent. There have been many claims as to the superiority of the products by solvent hydrogenations but one advantage apparent from the studies is that the reaction may be carried out at a much lower temperature. There are also other advantages such as less oil loss on the catalyst filters and easier filtering because of lower viscosity. Among the disadvantages would be the increased bulk of material for a given amount of oil and the possibility of catalyst poisons in the solvent. The continuous hydrogenation of fats in the extracting solvent should be an efficient process since the process could be operated at low temperatures and in a fixed-bed operation would permit faster reaction because of the decreased concentration of oil compared to catalyst. These are only suggestions of the possibilities that exist in the field of edible-oil hydrogenation.

For almost fifty years the fat and oil industry has hydrogenated, using empirical conditions with very little understanding of the reaction. Research investigations were limited because there was very little incentive to change a process that worked and was very cheap compared to the raw-material cost. Lack of good analytical methods also deterred research. The latter problem has now been largely solved and work in the field of nutrition has given an impetus to the study of the reaction, so that the future should bring a complete picture of the most important chemical reaction the industry performs, hydrogenation.

Emulsifiers [1]

GEORGE Y. BROKAW, Distillation Products Industries, Rochester, N. Y.

THE TREND of modern technology is to use newer techniques and newer materials to provide more desirable items for the consumer. Food technology, even food emulsion technology, is no exception even though it has been with us as long as any, and even though it is subject to as many restrictions as any. Presumably man drank milk very early in history, and milk is certainly a complex food emulsion. Interestingly, milk and milk derivatives are among the more highly regulated of our food products.

The regulations which affect edible emulsifiers, and of course all foods, are based on the factors of safety, food identity, and economic protection. Perhaps the most important Federal regulation affecting all three factors is the Food, Drug, and Cosmetic Act of 1938 and amendments, especially the Food Standards provisions and the Food Additives Amendment of 1958. State regulations, governing intrastate commerce not subject to Federal regulation, are sometimes diverse and nonuniform as would be expected by their origin.

[1] Communication No. 270 from the Research Laboratories of Distillation Products Industries, Division of Eastman Kodak Company, Rochester, N.Y.

Acceptable Emulsifiers and Stabilizers

The above preamble on regulations recognizes that the very definition of "edible" emulsifier requires a knowledge of the Food Additives Amendment of 1958. In fact the lists of materials published in the Federal Register serve as guides to acceptable food emulsifiers and are used for that purpose here. Tables I through V show listed materials which are indicated as emulsifiers or stabilizers, and which are direct additives to foods. No attempt has been made to assemble a list of indirect additives (e.g. via packaging materials). Materials under "prior sanction" do not appear on these lists, and therefore have been omitted from this compilation.

Table I shows the emulsifiers and stabilizers which were on the original list of materials "generally recognized as safe." The first three classes of materials contain the terminology ". . . from the glycerolysis of edible fats or oils." This terminology is due, in part, to an earlier unrecognized contaminant in certain fatty acids which could cause a pericardial edema in young chickens. Steps are underway to

TABLE I

Materials Approved as "Generally Recognized as Safe" (Federal Register, November 20, 1959, p. 9369)

1. Diacetyl tartaric acid esters of mono- and diglycerides from the glycerolysis of edible fats or oils	4. Propylene glycol
2. Mono- and diglycerides from the glycerolysis of edible fats or oils	5. Glycerol monostearate
3. Monosodium phosphate derivatives of mono- and diglycerides from the glycerolysis of edible fats or oils	6. Agar-agar
	7. Locust bean gum
	8. Carragheenin
	9. Guar gum

define and overcome this problem, and Table IV shows the beginning of its resolution. Commercial fatty acids claimed to be suitable under the definition shown in Table IV made their appearance in June of this year.

Table II shows the emulsifiers and stabilizers which appeared on a supplementary proposed (but not yet ordered) list of materials "generally recognized as safe."

Table III shows materials approved on a limited or tolerance basis. Table IV shows materials which may be used until March 5, 1961, unless earlier action is announced.

Table V shows materials for which petitions have been sumitted but not yet approved.

These lists were prepared from the Federal Register, but originals, the Food and Drug Administration, and the manufacturers should be consulted, if in doubt. This is particularly true for materials which may be under "prior sanction," and which are not listed here. Please note also that the status of many of these materials is fluid and that the above tables are up to date to and including June 21, 1960.

TABLE II

Materials Proposed but Not Yet Ordered as "Generally Recognized as Safe" (Federal Register, February 2, 1960, p. 881)

1. Lecithin	8. Karaya gum
2. Acacia	9. Tragacanth gum
3. Ammonium alginate	10. Methyl cellulose (as defined)
4. Calcium alginate	11. Sodium carboxymethylcellulose (as defined)
5. Potassium alginate	
6. Sodium alginate	12. Sodium caseinate
7. Ghatti gum	13. Sodium pectinate

Emulsion Theory

So much has been written on general emulsion theory that this presentation will serve only as a reference. The American Chemical Society Monograph #135 by Paul Becher (1) covers emulsion theory, chemistry, techniques, and applications, and it contains more than 850 references to other literature. Additional theory references should be consulted on nonaqueous micelles (2,3) which, in this author's opinion, will receive more attention in the future. Some reference to application theory is included in the next section.

TABLE III

Materials Approved with Tolerance Limits

Emulsifier	Maximum level	Food	Federal Register	
			Date	Page
Glycerol lactostearate and mono- and diglycerides (as defined)[a]	8%	Shortening	10-13-59	8293
Sodium lauryl sulphate (as described)	125 p.p.m.	Liquid egg white	4-18-60	3024
Sodium lauryl sulphate (as described)	125 p.p.m.	Frozen egg white	4-18-60	3024
Sodium lauryl sulphate (as described)	1,000 p.p.m.	Egg white solid	4-18-60	3024
Cholic acid	0.1%	Dried egg white	11-20-59	9370
Desoxycholic acid	0.1%	Dried egg white	11-20-59	9370
Glycocholic acid	0.1%	Dried egg white	11-20-59	9370
Ox bile extract	0.1%	Dried egg white	11-20-59	9370
Taurocholic acid (or sodium salt)	0.1%	Dried egg white	11-20-59	9370

[a] See also Tables IV and V.

Application

Regulations also apply to application; in this latter case the primary Federal concern is the Standards of Identity. No material, no matter how safe or valu-

TABLE IV

Materials Permitted on Extension Basis [a]

Material	Maximum level	Food	Federal Register	
			Date	Page
Mono- and diglycerides prepared from oleic acid (as defined)[b]	....	Foods and food components	4-22-60	3525
Glycerol monooleate (as defined)	3.5 p.p.m.	Fluid milk (via vitamins)	2-3-60	1074
Lactic acid esters of mono- and diglycerides derived by the glycerolysis of edible vegetable and animal fat[c]	....	Emulsifiers in foods in accordance with good manufacturing practice	6-15-60	5339
Hydroxylated lecithin	0.5%	Nonstandardized foods	4-22-60	3525
Calcium stearyl 2-lactylate	0.5%	Egg white solids	4- 5-60	2837
Calcium stearyl 2-lactylate	0.05%	Liquid and frozen egg white	4- 5-60	2837
Calcium stearyl 2-lactylate	0.35%	Nonstandard bakery products	4- 5-60	2837
Polyoxyethylene (20) sorbitan monooleate	0.1%	Frozen desserts (not water ices)	2-27-60	1944
Polyoxyethylene (20) sorbitan monooleate	0.1%	Imitation ice cream	2-27-60	1944
Polyoxyethylene (20) sorbitan monooleate	0.05%	Pickles	2-27-60	1944
Polyoxyethylene (20) sorbitan monooleate	9 pts. to 1 pt. flavor	In flavored foods	2-27-60	1944
Polyoxyethylene (20) sorbitan monooleate	....	Solubilizer in essential oils	4- 5-60	2837
Polyoxyethylene (20) sorbitan monooleate	as described	Vitamin preparations	4-22-60	3525
Polyoxyethylene (20) sorbitan monooleate	0.26 p.p.m.	Milk (via vitamin D concentrates)	4-22-60	3525
Polyoxyethylene (20) sorbitan monostearate	0.475%	Cakes	2-27-60	1944
Polyoxyethylene (20) sorbitan monostearate	0.45%	Cake icing	2-27-60	1944
Polyoxyethylene (20) sorbitan monostearate	0.5%	Confectionery coating	2-27-60	1944
Polyoxyethylene (20) sorbitan monostearate	0.2%	Sugar confectionery pan coatings	2-27-60	1944
Polyoxyethylene (20) sorbitan monostearate	0.4%	Whipped toppings	2-27-60	1944
Polyoxyethylene (20) sorbitan monostearate	9 pts. to 1 pt. flavor	In flavored foods	2-27-60	1944
Polyoxyethylene (20) sorbitan tristearate	0.1%	Frozen desserts (not water ices)	2-27-60	1944
Polyoxyethylene (20) sorbitan tristearate	0.1%	Imitation ice cream	2-27-60	1944
Sorbitan monostearate	9 pts. to 1 pt. flavor	In flavored foods	2-27-60	1944
Sorbitan monostearate + polyoxyethylene (20) sorbitan monostearate	0.475%	Cakes	2-27-60	1944
Sorbitan monostearate + polyoxyethylene (20) sorbitan monostearate	1.0%	Confectionery coating	2-27-60	1944
Sorbitan monostearate + polyoxyethylene (20) sorbitan monostearate	0.4%	Whipped toppings	2-27-60	1944
Polyethylene glycol 400 monooleate	10% of fat	Calf-feed milk replacer	4- 5-60	2837
Ethyl cellulose	35%	Dry vitamin preparations	2-27-60	1944
Methylethyl cellulose	3%	Vegetable fat whipped toppings	4-22-60	3525
Propylene glycol ether of methyl cellulose[d]	....	Foods	2- 6-60	1074
Oxidized starch	....	Prepared foods	5-21-60	4505

[a] Permitted until March 5, 1961, unless earlier action is announced. [b] Oleic acid must be derived from edible fat or oil and must be tested and found free of chick edema factor. [c] See also Tables III and V. [d] See also Table V.

TABLE V
Materials with Petitions Submitted

Material	Maximum level	Food	Federal Register Date	Federal Register Page
Glycol lactostearate (as defined)[a]	8.0%	Shortening	5-11-60	4201
Distilled acetylated monoglycerides (as defined)	5.0%	Nonstandard foods	1-28-60	726
Sorbitan monostearate	0.4%	Whipped vegetable toppings	6-21-60	5589
Polyoxyethylene (20) sorbitan tristearate	0.1%[b]	Frozen desserts	5-13-59	3827
Polyoxyethylene (20) sorbitan monooleate	0.1%[b]	Frozen desserts	5-13-59	3827
Polyoxyethylene (20) sorbitan monostearate	0.20%	Sugar-type confection coatings	4-22-60	3531
Methyl cellulose, U.S.P. (as described)	......	Salad dressing and French dressing	2-17-59	1216
Propylene glycol ether of methyl cellulose[a]	......	Salad dressing, French dressing, and nonstandardized foods	2-26-60	1690
Propylene glycol alginate	......	Nonstandard foods	3-31-60	2735
Propylene glycol alginate	......	Cream cheese and Neufchatel cheese	5- 5-60	3898

[a]Already approved or permitted by different definitions; see Tables III and IV. [d] Total of the two emulsifiers not to exceed 0.1%.

able, can be used in a standardized food unless or until it is included in the Standard. Some proposals below cannot be used at present because of this factor; they are listed, however, since mechanisms exist for amending a Standard to take advantage of newer developments. On the other hand, materials which appear in a Standard of Identity have the status of "prior sanction" when used as described for that food (e.g. sodium sulfoacetate derivatives of mono- and diglycerides in margarine). As reference, Table VI shows classes of foods for which Standards of Identity have been promulgated or tentatively proposed.

TABLE VI
List[a] of Foods Covered by Federal Standards of Identity

Cacao products (chocolate products)	Fruit butters, jellies, preserves, etc.
Cereal flours and related products	Frozen fruits (tentative)
Alimentary pastes	Shellfish
Bakery products	Canned tuna fish
Milk and cream products	Eggs and egg products
Cheeses	Oleomargarine
Frozen desserts (tentative)	Canned vegetables
Dressings for foods	Tomato products
Canned fruits and juices	

[a]From Commercial Clearing House Inc. (CCH), Vol. 1, pp. 1405–1750.

Salad Dressings and Oils. Mayonnaise is one of the most interesting of food emulsions. The phase ratio (oil to water) borders on the limit of, or appears to defy, some rules of emulsion theory. A combination of emulsifier usage and technique makes a good product. These factors are reviewed by Becher (1) (pp. 261–264), Brown (4), and Gunther (5). Becher emphasizes the role of mustard and egg yolk as emulsifiers and the importance of technique; Gunther describes the peculiarities of egg lecithin. Gunther noted that soy lecithin cannot be used as a direct substitute although certain protein complexes of soy lecithin showed promise; egg lecithin is a protein complex which imparts oil-in-water characteristics to an otherwise water-in-oil type emulsifier.

Other salad dressings have less oil and some of them use hydrocolloid stabilizers. Homogenization is used for maximum stability in some instances. Salad oils may contain pour point depressants which are usually surface active in nature. Consumer salad oils usually do not contain added emulsifier as do household plastic shortenings since such emulsifiers reduce the smoke point, and these oils frequently are used for deep fat frying or other high temperature cooking purposes.

Margarine. Good references to margarine manufacture exist (4,6,7,8). Emulsifiers are used to prevent "weep" and to control spatter and foam. The latter two tend somewhat to be contradictory, since fine emulsions control spatter whereas coarse emulsions reduce foam. Moderately coarse emulsions (most of the water droplets larger than 2 microns diameter) are usually preferred in order to give better flavor release and to prevent too greasy a mouth feel.

Opposing needs such as those above are common in foods, and the principle of balanced emulsification is becoming accepted more broadly in recent years. The HLB System has been a very valuable contribution in this direction, although the technologist should not neglect other balancing factors in his search for a panacea.

Peanut Butter. Brown proposed (9) the use of monoglycerides as stabilizers for peanut butter. The emulsifying action permits more ready mixing of peanut butter with saliva which reduces the otherwise customary stickiness of this product. Monoglycerides recently are finding increased acceptance because of crystal behavior and oil-insolubility as well as because of surface activity. These features are perhaps better illustrated in one approach to a "global spread" (10).

Dairy Products. Brunner (11) used monoglycerides, sorbitan monostearate, and silicones as foam depressants in the vacuum panning of milk. He proposed that the monoglyceride content of sour milk could account for its reduced foaming. This was found to be a real possibility by Jensen (12a and b) who found monoglycerides in rancid milk and traces of monoglycerides in some normal milk (12a) and in a variety of milk products (12b).

Ice cream theory and practice is described thoroughly by Sommer (13), who pointed out that fine division of air bubbles gave a dry appearance to ice cream, and that emulsifiers aided this property. Emulsification theory has evolved recently as represented by Keeney (14) who showed that emulsifiers can destabilize the ice cream emulsion when they produce very great "dryness"; in fact, churning can result. Another instance of opposing needs is thus evident, since "dryness" and churn resistance both are desired.

Work done partly in our own laboratories at Distillation Products and partly elsewhere has shown that unsaturated monoglycerides promote "dryness," fast whip, low overrun, and heavy body; saturated monoglycerides behave quite differently promoting slow whip, high overrun, and foamy light body. This remarkable difference in behavior between saturated and unsaturated monoglycerides suggests that the physical state of the emulsifier may be an important factor in all emulsion technology, And it further supports the contentions in many fields that balanced emulsification is required for best results.

In fact, the above effect holds very well in homogenized whipped toppings. It is of interest that homogenized cream was considered unwhippable until recently when emulsifiers have overcome this technical problem for dairy cream; emulsifiers have been in use some time for homogenized whipped toppings prepared from vegetable or animal fat.

Candy. Chocolate is one of many candy products requiring careful procedures to obtain good results. The only classical emulsifiers currently listed in the Standards of Identity for most pure chocolate and cacao products are lecithin and the monosodium phosphate derivatives of mono- and diglycerides. Emulsifiers are useful in chocolate formulations particularly to control viscosity and reduce fat bloom. In caramels, fat separation or surface oiliness can be reduced by proper emulsification, which also affects consistency in cream fillings.

Baked Goods and Shortening. These products are classified together since most baked goods are emulsified by means of shortening and since most emulsified shortenings are used for baking. Bread, sweet goods, icings, cream fillings, and the like are involved. Many cake mixes use the newer "lactated monoglycerides." The properties affected are dough handling, batter viscosity and appearance, texture, crumb structure, whiteness, softness, and resistance to staling.

Staling appears to occur not necessarily because of moisture loss, but possibly because of moisture migration within the baked item. This has been attributed to or correlated with starch retrogradation, and to other changes in starch as well (15). The role of emulsifiers as anti-staling agents may lie partly in their ability to alter the starch crystallization pattern. At this point we move to some modern and future uses of emulsifiers.

Starchy Foods. A very interesting article on the properties of starch (16) describes the solubilization, gelation, and retrogradation of amylose, and of course, starch has been the subject of books (e.g. 15). Amylose complexes with certain materials to form an insoluble product which does not form a blue color with iodine, and which does not gel when in hot water. Cording (17) used iodine titration to determine the completeness of formation of the monoglyceride-amylose complex in dehydrated potatoes. This treatment resulted in reconstituted potatoes which are mealy rather than pasty or "gluey."

The amylose complex principle has been tried successfully in alimentary pastes (macaroni, spaghetti, noodles, etc.), a variety of cereal products, pie fillings, and other starch-containing foods. It appears to have general utility where repression of amylose gelation or control of amylose crystallization is desirable.

Foam Mat Drying. This is a new process, developed by the Western Utilization Research and Development Division, U.S.D.A. (18), employing edible foaming agents to help in the dehydration of fruit and vegetable juices, purees, and the like, to give reconstitutable powders of very good quality.

Fat Separation. This is a general problem in some of the foods listed above. However it is recognized that additional advances in many foods including certain meat products and frozen liquids such as soups, sauces, etc. can be realized by the proper use of emulsification materials and techniques.

The Future. The types of emulsifiers available for food technology are quite limited by virtue of the various legislative regulations, both Federal and State. One particular area that has been affected is that of water-soluble or oil-in-water type emulsifiers. Extensions have alleviated some of these problems temporarily, and this author shares the view that a reasonable number of such products will find acceptance where the need exists. Increased information on present products and development of new products will have a large part to play; the sugar esters are just one example of such new classes of products on the horizon.

New applications, even new principles of application, are being found, some of which have rather far-reaching implications. More precise control of starch behavior, improvements in dehydration and reconstitution, and overcoming of some of the problems in freeze preservation are among the fields where considerable change can be expected.

Much has occurred in food emulsion technology in the twelve years since the first A.O.C.S. Short Course in 1948. Even more can be expected to occur in the next twelve years, particularly in the areas of regulatory interpretation, of new applications in our fast moving food technology, and of new materials to give even greater ability to meet these new needs.

REFERENCES

1. Becher, P., "Emulsions, Theory and Practice," American Chemical Society Monograph No. 135, Reinhold Publishing Corp., New York, 1957.
2. Singleterry, C., J. Am. Oil Chemists' Soc., *32*, 446–452 (1955).
3. Debye, P., and Prins, W., J. Colloid Sci., *13*, 86–98 (1958).
4. Brown, L. C., J. Am. Oil Chemists' Soc., *26*, 632–636 (1949).
5. Gunther, J. K., Proc. 1st Annual Am. Oil Chemists' Soc. Short Course, planographed by the University of Illinois, 1948.
6. Andersen, A. J. C., "Margarine," Academic Press, Inc., New York, 1954.
7. Schwitzer, M. K., "Margarine and Other Food Fats," Interscience Publishers, Inc., New York, 1956.
8. Brown, L. C., J. Am. Oil Chemists' Soc., *33*, 506–512 (1956).
9. Brown, L. C. (Pond), U. S. 1,926,369 (1933).
10. Jones, E. P., and Lancaster, E. B. (U. S. Gov't), U. S. 2,754,213 (1956).
11. Brunner, J., J. Dairy Sci., *33*, 741 (1950).
12a. Jensen, R. G., and Morgan, M. E., J. Dairy Sci., *42*, 232–239 (1959).
12b. Jensen, R. G., Gander, G. W., and Duthie, A. H., J. Dairy Sci., *42*, 1913–16 (1959).
13. Sommer, H. H., "Theory and Practice of Ice Cream Making," 6th ed., Olsen Publishing Co., Milwaukee, 1951.
14. Keeney, P. G., and Josephson, D. V., Ice Cream Trade J., May, 1958.
15. Kerr, R. W., "Chemistry and Industry of Starch," 2nd ed., pp. 544–548, Academic Press, Inc., New York, 1950.
16. Elder, A. L., and Schoch, T. J., Cereal Science Today, *4* (7), 202–208 (1959).
17. U. S. Dept. of Agriculture Report CA-E-17, April, 1959 (Eastern Utilization Research and Development Division, Philadelphia, Pa.).
18. Morgan, A. I. Jr., Ginnette, L. F., Randall, J. M., and Graham, R. P., Food Engr., September, 1959.