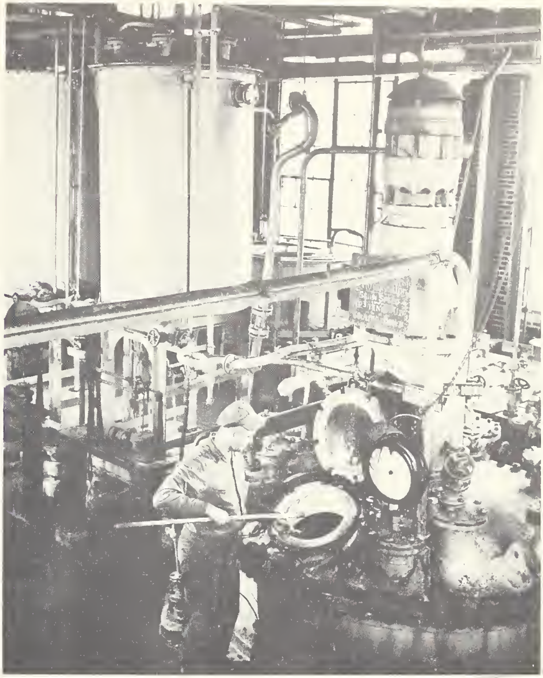
DETERGENTS, EMULSIFIERS, AND EMULSION PRODUCTS AS MARKET OUTLETS FOR FATS AND OILS



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DETERGENTS, EMULSIFIERS, AND EMULSION PRODUCTS AS MARKET OUTLETS FOR FATS AND OILS

Part I. Synthetic Detergents
By Morris W. Sills, agricultural economist

Part II. Emulsifiers and Emulsion Products
By Harry O. Doty, Jr., agricultural economist

UNITED STATES DEPARTMENT OF AGRICULTURE
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PREFACE

The two reports--Part I and Part II--included in this publication are based on a study undertaken by the Fats and Oils Branch, Production and Marketing Administration, at the suggestion of members of the fats and oils industry engaged in the processing and marketing of inedible fats and oils and their derivatives. A report entitled "Marketing of Nondrying Industrial Fats and Oils as Affected by Processing Methods," issued in May 1952, dealt with the market for inedible fats and oils as affected by commercial processing methods. Part I of this publication is concerned with the potential market of inedible fats and oils as affected by synthetic detergents. Part II is concerned with the probable effect of emulsifiers on the fats and oils market.

Two of the most important outlets in the industrial market for nondrying inedible fats and oils are (1) detergents and (2) emulsifiers and emulsion products. These outlets are described briefly in this publication.

Because of the difficulty in marketing inedible tallow and grease in 1949, even at the low prices then prevailing, funds were earmarked by Congress that year for research directed toward an expansion of market outlets for inedible fats and oils.

In 1950 and 1951 a survey of the fats and oils processing industries was carried out through a research contract with John W. McCutcheon of New York City. The contractor furnished estimates of costs from information available to him. He also brought together the technical material (with certain exceptions) presented in this publication and reviewed the manuscript.

Acknowledgment is made to the following for their assistance and contributions to the study and these reports: C. B. Gilliland, Chief, Research Division, and Donald Jackson, project supervisor, both of the Fats and Oils Branch; John W. McCutcheon, consulting chemist, New York, the contractor; and Daniel Swern, Fats and Oils Division, Eastern Regional Research Laboratory, Bureau of Agricultural and Industrial Chemistry.

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The study on which this report is based was conducted under authority of the Agricultural Marketing Act of 1946 (RMA, Title II).

CONTENTS

SUMMARY

Because of a declining market for fats and oils in the manufacture of soap and the outlook for continuing large supplies of fats and oils, producers are searching for expanded markets for new and improved markets for fats and oils. Two major possibilities comprise synthetic detergents and emulsifiers, closely related chemically but having, for the most part, different fields of use.

Inedible tallow and grease, which find their major market in the soap industry, constitute one of the major types of fats and oils affected by a declining soap market. Since the end of World War II, there has been a steady increase in the use of synthetic detergents made from petroleum derivatives and coconut oil fatty acids, and the use of soap has declined somewhat. Over the same period, the production of tallow and grease has increased by about 700 million pounds. Consequently, the percentage of the tallow and grease production used in soap has steadily declined.

SYNTHETIC DETERGENTS have been the object of considerable research the last two decades. This research has shown favorable results both in household and industrial markets. Synthetic detergents for the household market are mostly supplied by soap companies, whereas those for the industrial market are supplied both by the soap companies and by members of the chemical industry.

From a market standpoint, the two most important types of detergent products are alkyl sodium sulfates made from the alcohols of fatty acids and the alkyl aryl sodium sulfonates made from coal tar or petroleum derivatives.

Production costs are lower for petroleum-derived detergents than for those derived from fats. In the fats-and-oil field, tallow and grease are about the cheapest raw materials available but, except in special cases, tallow and grease now constitute, at the most, no more than 50 percent of the fats and oils involved; coconut oil, or other lauric acid-bearing oil, is used in quantities approximating at least 50 percent. Thus, under present techniques, imported oils will of necessity hold at least one-half of the market for synthetic detergents based on fats and oils.

A pound of fat converted into a synthetic detergent goes about 3.5 times as far in detergent power as a pound of fat converted into soap. Even if all synthetics currently used were fat-based, not more than 300 million pounds of fats would be required in the process. Therefore, if synthetic detergents made under present techniques increase in use, tallow consumption in the manufacture of products for cleaning purposes will be reduced.

The more stable prices for petroleum-derived products than those for tallow and grease constitute an attractive consideration in detergent

production. It is true, however, that the present and prospective abundant supplies of tallow and grease in relation to their reduced domestic demand for soapmaking have resulted in more stable prices for these commodities, thereby placing tallow and grease as raw materials for the manufacture of synthetic detergents in a more favorable position than that occupied during World War II and the early postwar years.

Raw materials used in detergent production are usually not interchangeable, although in some cases it is possible to interchange materials of the same general class, such as one type of fat for another or one petroleum derivative for another.

EMULSIFIERS commercially available nearly all contain some derivative of fats or oils. It is estimated that the total consumption of emulsifiers, at the present time, is in the neighborhood of 360 million pounds, including "captive" consumption. In the fat-based emulsifiers the proportional quantity of fats and oils required varies widely. Some emulsifiers are produced wholly from fats and oils derived materials, whereas others contain them at very low levels (less than 10 percent). Furthermore, for industrial usages fat-derived emulsifiers are frequently used in conjunction with larger quantities of other fats or oils materials used in making the emulsions. In some cases emulsifiers may reduce the amount of fats or oils required to achieve a given product characteristic. Thus, the fats-and-oils industries are interested in all the ramifications of the emulsifier market--in every improvement in emulsifiers and in every new use. Each emulsifier has unique characteristics. The difference in character may improve the market for the final emulsion product, either through higher quality or lower cost.

The individual emulsifiers available commercially number at least 600, although many thousands can be made. New emulsifiers are appearing at an ever-increasing rate. The following four types of emulsifiers account for most of the market today: Soap, sulfated and sulfonated oils, modified fatty amides, and fatty acid esters. Soap ranks first in order of volume and makes an effective, cheap emulsifier which is stable under special conditions of use. Soap is used in insecticides, in bituminous road surfacing, and elsewhere. Pure kettle soap has an equivalent fat or oil content of about 65 percent. Edible emulsifiers perhaps account for one-third of all emulsifiers used. All of these edible emulsifiers are esters, and often they are formed within a product during the course of manufacture instead of being added separately afterwards. Including the latter product, esters probably rank close to soap in volume. Animal and vegetable oils as well as mineral oils are sulfated and sulfonated to form emulsifiers. Sulfated castor oil (turkey-red oil) is commonly employed in textile dyeing. Lubricants frequently contain sulfonated mineral oils. Modified fatty amide emulsifiers are used extensively in cosmetics and find a host of other industrial uses.

All emulsifiers serve the purpose of permitting water and oil to be mixed smoothly together by the suspension of fine droplets of one of the two within the other. This procedure, with innumerable variations and complications, is a basic requirement in a large proportion of our industrial processes. Examples of such products are margarine, salad dressing, candy, ice cream, bake goods, paint, cosmetics, pharmaceuticals, insecticides, textile oils, and lubricating greases.

The variations in uses, in qualities of products, and in possible emulsifiers make almost infinite potential combinations. Also, two or more emulsifiers often are used together. Each improved adjustment among these factors may be of benefit to the product and to the market.

Costs of emulsifiers are mostly for raw materials. Total costs per pound vary widely, and emulsifier costs per pound of emulsion product vary far more widely. A cost range from 25 cents to 50 cents per pound includes most emulsifiers that are important marketwise. Their use, however, may vary from less than 1 part in a thousand up to 10 percent or more of the weight of the product. Raw materials used in emulsifier production usually are not interchangeable. The substitution of one raw material for another virtually represents a change in product.

DETERGENTS, EMULSIFIERS, AND EMULSION PRODUCTS AS MARKET OUTLETS FOR FATS AND OILS

PART I. SYNTHETIC DETERGENTS

By Morris W. Sills, agricultural economist,
Production and Marketing Administration

INTRODUCTION

Synthetic detergents made from fats and oils, particularly coconut oil, have been available since the early 1930's. Synthetic detergents made from petroleum and coal-tar products began to appear on the American market about 10 years prior to World War II. Since the war there has been a steady increase in the use of total synthetic detergents, for both household and industrial purposes. In 1951, the estimated sales of synthetic detergents were 1.35 billion pounds, or more than 38 percent of the total weight of all the soaps and synthetic detergents used. Estimated sales in 1952 reached 1.7 billion pounds, or 45 percent of the total weight of all soaps and synthetic detergents.1/

The major market for inedible fats and oils is the soapmaking industry. Two comparisons are necessary to describe this market: (1) The proportion of all soap fats that is represented by tallow and grease; and (2) the proportion of total tallow and grease production that is used in soapmaking. In 1951, tallow and grease represented about 80 percent of the fats and oils used in soapmaking, the percentage having varied between 73 percent and 80 percent since 1942. During the decade of the 1930's, the corresponding figures fluctuated roughly between 47 percent and 60 percent. In 1941 and 1942 the quantity of tallow and grease used in soapmaking exceeded the production, making it necessary to draw on carryover supplies and imports. Since 1942, the use of tallow and grease in soapmaking in relation to production has been declining. In 1951, however, the contribution of tallow and grease to soapmaking required only 54 percent--the lowest annual figure in the last 20 years--of the inedible tallow and grease production. The next lowest figures were 61.5 percent and 61.8 percent for 1949 and 1950, respectively. The 54 percent of tallow and grease production consumed in soapmaking in 1951 represented four-fifths of the domestic consumption. One-third of the production was exported.

The highest annual figures for the use of fats and oils in soapmaking in the United States were for 1941, 1944, and 1947. In each of those years more than two billion pounds were used. The corresponding high years for the use of tallow and grease in soapmaking were 1942, 1944, and 1947--slightly more than 1.5 billion pounds were used in each of these years. Since 1947 the level for all fats and oils used in

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1/ Based on data published by the Association of American Soap and Glycerine Producers, Inc.

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soapmaking has fallen by 25 percent, and the level for use of tallow and grease has fallen 20 percent. Expansion of the market for synthetic detergents clearly has had an adverse effect on the market for soaps, and through that on the market for inedible tallow and grease and other inedible fats.

The particular product that should be considered the first synthetic detergent and when it was first produced may be a matter of conjecture. Germany is credited with having made detergents from coal tar to supplement inadequate supplies of fats and oils during World War I. During the period 1930-40, soap companies and chemical companies in the United States did considerable research on detergents. Both shampoos and synthetic powders to compete with soap began to appear on the American market in the decade prior to World War II. Synthetic bars also were attempted but none has yet appeared commercially in competition with bar soap. However, two different brands of bar synthetic detergents are now being test-marketed in several cities. If these synthetic bars prove satisfactory during the test, it is almost certain that they will be marketed on a national scale.

Synthetic detergents have one property that makes them highly desirable for use with hard water. Their calcium and magnesium salts are soluble in water; therefore, their use does not form a grease ring on the dishpan nor do they dull the colors of washable fabrics. Also, the great number of closely interrelated chemicals that have definite detergent powers furnishes a wide choice for specialized uses. Several disadvantages are apparent, especially for household use.

Some synthetic detergents create excessive quantities of suds when used in automatic washing machines. If too much of the water is turned into suds the cleaning action may be decreased; also, additional rinsing is required and the normal rinsing cycle of the washing machine may be inadequate. Some synthetics cleanse without creating suds but it appears that great numbers of housewives look with disfavor on such synthetics.

Most synthetics have a much stronger defatting effect than does soap. These synthetics deplete the natural oils in the skin, causing what is sometimes known as dishpan hands. Also, the synthetics extract the lubricating oils from machine bearings which come in contact with them.

The disadvantages in one way may, of course, become advantages in other ways. To some extent correction of disadvantages lies in selecting the appropriate type of detergent for each use. The figures previously mentioned indicate that, in marketing terms, the advantages of synthetics have overbalanced the disadvantages enough to increase the synthetic market at a rapid rate, whereas the soap market has been slowly decreasing.

Thus, current and potential activity in the synthetic market becomes a vital factor in the marketing and the value of inedible fats and oils.

By the same token, such activity becomes a very important influence on the market position of the whole domestic fats and oils production.

Scrutiny of the current position of all the important detergents may at the same time help to disclose areas of potential advantage for fats and oils derivatives.

SYNTHETIC DETERGENT MARKETS

Since synthetic detergents were introduced to the American market during the 1930's they have had an ever-expanding market. Although their original development and application was in the textile industry, they have experienced a phenomenal growth in other industries during recent years.

One of the largest markets to develop has been in the sale of detergents in household packages. This market has been captured by the soap companies that make detergents because they already possessed the marketing machinery for the distribution of such products. Although the number of detergent types is legion, the retail sale of household detergents is restricted almost 100 percent to two basic types of products, the alkyl aryl sodium sulfonates and the alcohol, or alkyl, sulfates.2/ From studies based principally on annual reports of the U. S. Tariff Commission and on the monthly reports of the Association of American Soap and Glycerine Producers, Inc., an estimated 1.35 billion pounds of detergents were produced and sold in 1951, and in 1952 1.7 billion pounds were marketed. Household use comprised a large proportion of the sales--estimated to be at least a billion pounds. The estimated growth of the market for both industrial and household detergents during the period 1939 to 1951 was as follows:

Bulk synthetic detergent production in millions of pounds1/

Market	1939	1940	1941	1942	1943	1944	1945	1946	1947	1948	1949	1950	1951
Retail	100	100	100	100	100	100	150	300	525	775	825	900	1000
Industrial	70	80	80	80	100	140	150	150	175	200	250	300	350
Total	170	180	180	180	200	240	300	450	700	975	1075	1200	1350

1/ These data are estimates made by John W. McCutcheon, consulting chemist. They are based on data published by the U. S. Tariff Commission.

2/ Alkyl aryl sodium sulfonate is derived from either coal tar or petroleum sources. Alcohol sulfate is derived from natural fats to form the active ingredient for a synthetic detergent. In technical nomenclature, the correct term is "alkyl sulfate."

The large expansion in the retail synthetic detergent market immediately after World War II can partly be accounted for by two factors: (1) The fats and oils shortage (and consequently the soap shortage) during this period made an opening for the new product; and (2) a very extensive advertising and marketing campaign induced consumers to give extended trials to synthetics as substitutes for the scarce soap.

Data published by the Association of American Soap and Glycerine Producers, Inc., since 1948 give some indication of the growth of the synthetic detergent market in comparison with the soap market.

Soap and synthetic detergent sales, 1948-52 1/ (1,000 pounds)

Sale of--	1948	1949	1950	1951	1952
Hard soap	2,491,380	2,440,024	2,439,259	2,015,380	1,824,224
Synthetic detergents	401,685	702,136	1,070,688	1,217,022	1,530,119

1/ The data in this tabulation are based on actual sales of producers as reported to the Association of American Soap and Glycerine Producers, Inc. These data represent, for the most part, sales that eventually found their way into retail channels.

These figures must be considered with some reserve as many synthetic detergent manufacturers and some soap manufacturers are not members of the association. The data do show, however, that synthetic detergent sales have had a tremendous growth since 1948 and soap sales have shown a loss. The great increase in over-all detergent consumption has been supplied by the synthetic detergents. Most of the increase in demand has been due principally to an increase in population, but there has also been a larger per capita consumption.

Since a large share in the increase of detergent use is attributed to an increased population, it appears that synthetics in 1951 were keeping soap out of some of its traditional uses to the extent of about 350 million pounds of domestic fats annually. A slight offset would be the quantity of domestic fats and oils going into synthetics. It is estimated that this quantity would be not more than 10 million pounds of domestic fats, to be deducted from the 350 million pounds. The total quantity of fats used in detergents, however, would be much higher than this when the imported lauric acid-bearing oils such as coconut, palm kernel, and babassu are included.

The great inroads of synthetic detergents have been in the field of granulated powder. The field is attractively large and growing and it is ideally suited for the incorporation of the necessary builders or fillers. An analysis of trends from nine market survey reports 3/ shows

3/ Soap and Sanitary Chemicals. p. 87. March 1951.

that in the category of soaps for fine fabrics the use of synthetic detergents increased from 28.6 percent in 1947 to 37.3 percent in 1950. In the category of soaps for dishes the use of synthetic detergents increased from 36.4 percent in 1947 to 56.8 percent in 1950. These figures indicate an average increase of about two percent a year in the use of synthetic detergents for fine fabrics and about six percent a year, with some indication of levelling off, for dishes. These uses represent an added displacement of about 30 million pounds of fats and oils a year. How far soap powders will be displaced is highly speculative. Nearly all the detergents going into this granulated and powdered field are alkyl sulfates and alkyl aryl sulfonates, both of which, in chemical terms, are anionic (negative electric charge) compounds.

Another type termed nonionics (neutral electric charge) also has been developed in the field of powdered synthetic detergents, but this type has gained only a relatively minor success. To a great extent the nonionics are special purpose detergents and have not been able to invade the market of household detergents in a major way. Nevertheless, improvements in special purpose detergents have led to some competition between synthetics in addition to that between synthetics and soap. The competition has developed principally in detergents for dishes. Several liquid dishwashing detergents have been developed and marketed. In 1950 the leading examples on the market were probably about equally divided between anionic and nonionic based materials, although during the last 2 years the anionic type has been gaining and, at the present time, this type appears to be outselling the nonionic type. The reason appears to be that most housewives like a detergent that foams, and the triethanolamine salts of the sulfated lauryl alcohol and alkyl aryl sulfonates do produce a high foam. Most of the leading manufacturers of both soaps and synthetic detergents concede that foam power is a necessary specification of a product for retail sale, even where the detergency of a nonfoaming product may be as good or better than the foam-producing product.

Fat-based and nonfat-based nonionics also are making some inroads in the detergent fields for laundry purposes. One such fat-type nonionic, fatty alkanolamide, is made by dehydrating the amine salt of a fatty acid. This class of product is very popular and useful as a textile wetting agent and emulsifier. Another principal class of nonionic detergent is made from tall oil by combining ethylene oxide with it to give the product water solubility. A nonionic nonfat type is made by reacting an alkylated phenol with ethylene oxide. The general characteristics of these products are that they are substituted amide ester-type or ether-type compounds not ionized in water, and therefore are stable in all strengths of salt solutions. They are compatible with cationic-type materials, including the quaternary ammonium compounds, and also with soap. A fatal drawback from a market standpoint, according to soap manufacturers, is their nonfoaming property, plus the fact that most of them are liquid.

Although no synthetic toilet bar has appeared, about 80 percent of the synthetic detergent manufacturers interviewed in this survey expressed the opinion that synthetics are about to make inroads in the field of toilet soaps. Most of the manufacturers considered the appearance of the synthetic toilet bar as inevitable, but they gave no indication as to how long it might be before this happens. Laboratory work on the development of a synthetic bar has been in progress to a limited extent for several years. 4/ The major factor working against the use of synthetics in a toilet bar is the fact that synthetics do not precipitate like soap in the rinsing process, and therefore the skin feels slippery because traces of the cleansing agent remain on it. Actually, synthetics rinse just as freely as soap, but in the case of soap, the residual traces are destroyed immediately by rinsing. This gives a soap-free feeling which is not obtained with synthetics.

The most complete change from conventional fat-based soap to synthetic detergents has probably been in the field of abrasive cleaners or scouring powders. Scouring powders normally contain only a small percentage of detergent. In some cases as little as 3-percent soap has been relied on for the detergent action. Because soap will react with lime to form an insoluble soap sediment, however, these small portions of soap may be largely destroyed in use with hard water.

At the present time, the status of fats and oils in synthetic detergents is determined largely by the strong position of the alkyl aryl sulfonate class of petroleum derivatives which is well established in the American market. A principal reason for this strong position is the competitive price structure of the petroleum-derived materials in relation to both soaps and fat-derived synthetics. Although prices of fats and fatty acids have varied widely since 1939, the prices of alkyl aryl sulfonates have remained relatively constant. Oleic acid, for example, has ranged from 7 cents to 34 cents per pound during this period and the price of the alkyl aryl sulfonates has remained near 13 cents. Other fats and fatty acids have varied proportionately with oleic.

Tallow and grease, with a small percentage of coconut oil to increase lather, are the basic raw materials in soap manufacture. In fat-based synthetics, the lauric acid oils have had almost complete control of the market despite the technical feasibility of using 50-percent tallow. However, the present prices of tallow and coconut oil make tallow an attractive raw material for fat-based synthetics, and there is some indication that tallow alcohols may take the place of part of the lauric acid alcohols used in the alcohol sulfates.

4/ Two synthetic bars have recently been developed and are now available in restricted areas.

The detergent value of fats or oils converted to synthetics is about 3.5 times as great as the equivalent fat converted to soap. For this reason, even were all synthetics fat-based, not more than 300 million pounds of fat would be required, and in the present state of technical knowledge at least 150 million pounds of this volume would have to be lauric acid oils.

Increases in the use of any type of synthetics, therefore, will hold the use of tallow and grease to a smaller total than it otherwise would be, and the stable prices of petroleum derivatives offer marketing and promotion advantages that the soap manufacturer has not enjoyed.

PRODUCTION COSTS [5]

A cost comparison between the two major types of detergents--fat-based alkyl sulfates and petroleum-based alkyl aryl sulfonates--is significant.

The alkyl aryl sulfonate (made from petroleum sources) is less expensive to produce than is the (alcohol or) alkyl sulfates made from coconut oil. It is almost impossible to figure exact costs of the alkyl aryl sulfonates without becoming specific in regard to the type of refinery, quality of waste gas, and marketability of the propane as a fuel. Nevertheless, an estimate of production costs (September 1950 prices) per thousand pounds of active ingredients for the two types is as follows:

Detergents from petroleum sources

Cost item	Estimated cost
Labor	$ 4.80
Dodecylbenzene, 720 pounds	108.00
Acid and alkali	68.20
Service	14.00
Overhead	4.80
Repairs and maintenance	0.66
Amortization of plant (10 years)	3.30
Total net cost (1,000 lb. active ingredients)...	$203.76

5/ The costs represent estimates based on September 1950 prices.

Detergents from coconut oil

Cost of producing alcohol, 745 pounds:

1,000 lb. coconut oil @ 20¢	$200.00	
Sodium, 415 lb. @ 16¢	66.50	
Miscellaneous supplies	20.00	
Labor	6.00	
Steam and power	1.50	
Repairs and maintenance	1.00	
Overhead	6.00	
Amortization of plant (10 years)	8.00	
Total cost of alcohol	$309.00	
Credit for glycerine	65.00	
Net cost of alcohol	$234.00	$234.00

Cost of sulfating alcohol, 745 pounds:

Labor	$ 4.80	
Acid and alkali	68.20	
Services	14.00	
Overhead	4.80	
Repairs and maintenance	0.66	
Amortization of plant (10 years)	3.30	
Net cost of sulfating	$ 95.76	$ 95.76
Total net cost (1,000 lb. active ingredients)		$329.76

The cost of producing an alkyl sulfate from tallow is comparable with the production costs from coconut oil. The difference is the price between the two raw materials and the glycerine credit. More glycerine is derived from coconut oil than that from tallow. With tallow at 16 cents per pound (September 1950) the total cost of producing 1,000 pounds of an alkyl sulfate from tallow is estimated at $313.11 as compared with $329.76 for producing a similar quantity from coconut oil. At present prices of tallow (5 cents per pound), coconut oil (17 cents per pound), and glycerine (31 cents per pound), and assuming that all other costs are the same as they were in September 1950, the cost of producing 1,000 pounds of an alkyl sulfate from tallow is estimated at $217.91 as compared with $318.26 for producing a similar quantity from coconut oil. It must be remembered, however, that the properties of the two fats are different and that tallow at present can only be substituted for coconut oil to an estimated maximum of 50 percent. Up to that maximum any substitution will depend on the price relationship between tallow and coconut oil.

The present and anticipated high level of tallow and grease supplies should result in prices that make these commodities attractive raw materials for the development of fat-based synthetic detergents and other new products and markets based on fats and oils.

SYNTHETIC DETERGENTS, BY CLASS AND TYPE

Synthetic detergents constitute three classes, previously mentioned, depending on whether the active ingredient is electrically charged positively or negatively, or is neutral. The three classes are technically designated as cationic, anionic, and nonionic, respectively. Insofar as competition with fats and oils is concerned, the anionics are of major importance. They contain practically all the important retail products and the major portion of the important industrial products. In volume they constitute the largest class, by far. They are the products that compete with soap and, to the extent of their competition, replace fats and oils in their traditional market.

Anionic detergents

Although there are at least five types of anionic detergents on the market, only two types, the alkyl sulfates and alkyl aryl sulfonates, supply almost 100 percent of the retail market.

Alkyl sulfate. An alkyl sulfate is a sulfated derivative of a fatty alcohol. An alkyl sulfate was the first type of detergent available in the United States on a commercial scale, being introduced about 1930. Its manufacture depends on: (1) High pressure hydrogenation of fatty acids to form fatty alcohols, with the oxides of chromium and copper as catalysts; or (2) sodium reduction. The alcohol is sulfated by either a batch or continuous process. The finished product for retail distribution is usually manufactured as a 30-to-35 percent active base, with sodium sulfate added as a builder, or as a 20-percent active base with sodium sulfate and sodium tripolyphosphate plus other materials as builders. For industrial purposes it is usually sold unbuilt in 30-to-90-percent active form.

The alkyl sulfate has stood the test of time in regard to stability, foam power, freedom from odor, compatability with builders, nonhygroscopic properties, ability to withstand spray drying conditions without undue decomposition, and market availability of raw materials.

Alkyl sulfates are used industrially in the preparation of emulsions of oils in solvents for important markets, including textile scouring and finishing. Alkyl sulfate from oleic acid is widely considered the most suitable type for such textile use because it rinses well. The alkyl sulfate from stearic acid is advantageous for white wash if used at high temperatures, as in commercial laundries. For household-type detergents (by far the most important outlet), the alkyl sulfate of lauric acid, which must be obtained from coconut, babassu, or palm kernel oil, is desirable. However, the low price and huge supply of tallow makes it an attractive raw material, and tallow acids are being substituted for the lauric acid in increasing quantities.

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Fatty acids used in the manufacture of alkyl sulfates are in practice limited to oleic, palmitic, stearic, and lauric acids. The fact that coconut oil is the common source of lauric acid means that, whereas this widely used class of detergents is fat-based, it serves only very slightly at present as a market outlet for tallow and grease, or for any domestic fats and oils.

Alkyl aryl sulfonate. The alkyl aryl sulfonate type of detergent is derived from petroleum products, with benzene being the most important raw material from an economic viewpoint. The manufacture involves three steps: (1) The chlorination of a kerosene fraction; (2) condensation of alkyl chloride with benzene or toluene; and (3) the sulfonation of the alkyl aryl compound. 6/ The third step may be carried out either by the manufacturer of the alkyl aryl or by the soap companies that complete and distribute the product. As the final step, alkyl aryl sulfonate is mixed with builders to give the degree of detergency desired.

Sulfated and sulfonated amides and amines. Sulfated and sulfonated amides and amines constitute another type of anionic detergents based on fats and oils. The most important member of the type is made by condensing acid chloride of red oil (oleic acid) with methyl taurine and neutralizing to the sodium salt. It can be used in either acid solutions or hard water, and is resistant to metallic salts. It has special application to the textile industry because of these properties and also because of its solubility in water and easy rinsing. It is very efficient in the removal of liquid soils, such as grease and spindle oils.

Miscellaneous types. Other types of detergents include sulfated and sulfonated esters and ethers, alkyl sulfonates, and a number of special types which are difficult to classify for market purposes.

The sulfated and sulfonated esters and ethers on the one hand are fat-based detergents that are partially stable to acids and alkalies. They have only a small place in the present market.

The alkyl sulfonates, on the other hand, are petroleum-derived products. They differ from the alkyl sulfates in that there is no oxygen linkage between the carbon and sulfur atoms. These products were used extensively in Germany during the war to replace soap. American production is now under way; however, alkyl sulfonates represent only a small portion of the entire synthetic detergent market.

6/ For a detailed description of this process, see Soap and Detergents. By E. G. Thomssen and J. W. McCutcheon. MacNair-Dorland Co. New York. 1950.

Cationic detergents

Cationic agents are poor detergents for laundry and other cleaning purposes. They are used primarily as wetting and dispersing agents. Considerable disagreement has arisen over the question whether they should be called detergents. The active ingredient is positively charged and, because of this, cationic detergents are sometimes called invert soaps.

The most important group of cationic agents are what the chemists call "quaternary ammonium compounds" which have considerable value as germicides. In addition to their main roles as germicides they do exhibit some foam power but their detergent action is poor.

Nonionic detergents

The nonionic detergents are commonly considered to be excellent detergents but have limited application because they are liquids. A recent development was the production of a unique type in solid form. How important this type will become remains to be seen.

Nonionics are both fat-based and nonfat-based. The important fat-based types are largely made by dehydrating the amine salt of a fatty acid to form the alkanolamides, although one principal type is made from tall oil by condensing with ethylene oxide to give it water solubility. The principal nonfat-based type is an alkylated phenol condensed with ethylene oxide.

One of the disadvantages of the nonionics is their inability to attain the foaming characteristics of other detergents in the household field. Some types have found special applications where the forming of suds is a nuisance in automatic clothes-washing machines and automatic dishwashing machines.

INTERCHANGEABILITY OF RAW MATERIALS

In most cases a synthetic detergent is made for specialized use and calls for a specific type of raw material. Some of the synthetic detergents are even manufactured and marketed for one specific purpose. In general, raw materials are not interchangeable, although in the manufacture of some types of detergents it is possible to use different raw materials of the same general type. An example is the alkyl sulfates, in which fatty alcohol from tallow may be partially substituted for the fatty alcohol from coconut oil. In the manufacture of the two most important synthetic detergents--alkyl sulfates and alkyl aryl sulfonates--raw materials are not interchangeable. These detergents are two entirely different types of products, and they require different types of processing equipment.

Thus, the two types of raw materials cannot compete in precisely the same product. Nevertheless, various <u>products</u> of the two <u>can</u> compete technically in the detergent field. The major fats-and-oils marketing problem involved is the fabrication of tallow and grease into forms of technically efficient detergents that can compete for a substantial share of the market.

NEED FOR FURTHER RESEARCH

This study has shown that one of the major factors causing the huge surpluses of domestic fats and oils, particularly tallow and grease, is the synthetic detergent market. Synthetic detergents can be, and usually are, tailored to meet the specifications of a particular market. Therefore, it behooves the producers of fats and oils and fats and oils products to have a thorough knowledge of every segment of the synthetic detergent market, in order that they may organize and plan their marketing operations to meet the demand from every segment of the market.

It appears that additional market research on fats and oils is needed in the field of synthetic detergents. Such research should be directed toward a determination of how fats and oils can compete with nonfat materials in each market for synthetic detergents. In order that the competitive position of fats and oils, and particularly tallow and grease, may be maintained and improved in the detergent industry, some of the specific areas which need to be studied are: (1) Uses for synthetic detergents, (2) competition between fat-derived and nonfat-derived detergents, (3) competition between the various fats and oils in the manufacture of synthetic detergents, and (4) the potential competition between soap and synthetic detergents in the toilet bar field.

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APPENDIX

Table 1.--Factory production and consumption of inedible tallow and grease for specified uses and percentages of production of tallow and grease used in soap and of all fats and oils used in soap, by years, 1931-51

Year	Factory production	Percentage of tallow and grease production used in soap	Factory consumption of inedible tallow and grease used for-- Soap	Fat splitting	Refining	Sulfonation	Lubricants and grease	Paint and varnish	Printing ink	Pressing	Other	Other fats and oils consumed in soap	Total fats and oils consumed in soap	Tallow and grease as percent of total consumption in soap
	1,000 pounds	Percent	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	1,000 pounds	Percent
1931....	951,125	68.7	653,117	1/	1/	1/	1/	112	378	1/	123,475	737,183	1,390,300	47.0
1932....	920,541	75.2	692,910	1/	1/	1/	1/	46	298	1/	95,502	682,506	1,375,416	50.4
1933....	964,592	65.7	633,577	1/	1/	1/	1/	156	355	1/	137,607	678,096	1,311,273	48.3
1934....	1,087,861	74.1	805,640	1/	1/	1/	1/	179	383	1/	150,524	668,745	1,474,385	54.6
1935....	638,720	119.2	761,088	1/	1/	1/	1/	183	358	1/	155,963	551,669	1,312,757	58.0
1936....	773,398	98.1	758,734	1/	1/	1/	1/	229	475	1/	170,057	635,805	1,394,539	54.4
1937....	722,834	97.9	707,756	1/	1/	1/	1/	301	516	1/	182,342	768,000	1,475,756	48.0
1938....	822,137	97.1	798,623	1/	1/	1/	1/	261	424	1/	146,520	669,912	1,468,535	54.4
1939....	957,501	94.6	905,897	1/	1/	1/	1/	144	450	1/	178,515	747,807	1,653,704	54.8
1940....	1,154,689	90.4	1,043,342	1/	1/	1/	1/	235	411	1/	197,199	679,292	1,722,634	60.6
1941....	1,321,271	103.5	1,367,790	1/	1/	1/	1/	514	476	1/	291,970	776,067	2,143,857	63.8
1942....	1,456,954	104.9	1,527,897	312,349	3,410	4,434	12,381	366	427	1/	233,385	343,142	1,871,039	81.7
1943....	1,411,407	96.4	1,360,097	199,506	7,048	6,283	47,667	112	399	126,505	29,898	355,334	1,715,431	79.3
1944....	1,630,402	93.8	1,529,749	215,363	9,181	4,718	58,251	48	305	99,114	26,184	471,862	2,001,611	76.4
1945....	1,462,372	93.4	1,363,934	277,186	8,968	5,179	64,103	69	279	111,784	28,350	393,572	1,757,506	77.6
1946....	1,398,805	86.5	1,209,839	296,990	6,742	7,410	57,741	100	312	82,320	31,958	312,486	1,522,325	79.5
1947....	1,660,947	91.9	1,525,747	193,031	7,581	6,653	71,638	60	284	61,458	36,649	602,262	2,128,009	72.7
1948....	1,656,805	87.6	1,451,756	186,928	7,202	6,543	63,370	47	265	52,289	36,385	497,361	1,949,117	74.5
1949....	2,188,930	61.5	1,345,599	168,620	335,452	5,548	36,565	16	36	53,705	36,684	402,372	1,747,971	77.0
1950....	2,220,367	61.8	1,371,976	229,088	309,329	5,637	37,247	15	1/	71,069	69,415	412,868	1,784,844	76.9
1951....	2,198,810	54.3	1,194,815	242,597	265,075	6,249	40,426	1/	1/	75,697	101,342	307,037	1,501,852	79.6

1/ Not shown separately.

Source: Bureau of the Census.

DETERGENTS, EMULSIFIERS, AND EMULSION PRODUCTS AS MARKET OUTLETS FOR FATS AND OILS

PART II. Emulsifiers and Emulsion Products

By Harry O. Doty, Jr., agricultural economist, Production and Marketing Administration

INTRODUCTION

A potentially important industrial market for fats and oils is in the field of emulsifiers and emulsion products. This market outlet is of interest to producers and processors of fats and oils whether in emulsifiers themselves or in the products that better emulsifiers make possible. Use of emulsifiers does not always increase the use of fats and oils. In some cases emulsifiers may reduce the quantity of fats and oils required to achieve a given product characteristic. The chemistry of the subject has innumerable complexities that need not be mastered by the marketing economist, but a working concept of the type of emulsifiers--their characteristics and uses--is essential in order to visualize the probable conditions and directions of potential development. Thus, marketing interest in the technical aspects of emulsifiers is vital although indirect.

Of the many thousands of emulsifiers that are known, at least 600 are on the market at the present time. These emulsifiers are marketed largely under trade names, and the same emulsifier may be prepared in several strengths or in various forms, such as powders, flakes, pastes, or liquids. In fact, various forms may be offered by a single processor. About 100 companies constitute the emulsifier-producing industry.

Only a very rough estimate can be made of the total current consumption of emulsifiers. This is due to their wide diversity, the relative importance of their different outlets, and the large amount of emulsifiers produced for "captive" consumption. It is estimated that the total consumption of emulsifiers at present is in the neighborhood of 360 million pounds per year, including captive consumption.

Several factors combine to make market development for emulsifiers an important and specialized task. Because they are used almost entirely by industry, large-scale popular advertising is ineffective. In fact, advertising as such is largely restricted to trade journals. Appeal of an emulsifier to a potential user must rest on demonstrable or largely predictable physical improvements that its use will make possible in a product or process, or that a better new product or process will be made possible by its use. In practice, advertising claims are based for the most part on technical data gathered through laboratory testing or on data supplied by companies using the emulsifiers. Specially trained sales representatives and engineering service to customers appear to be the most effective means of doing the marketing job.

As has happened in some other lines, unjustifiable claims appear to have been made occasionally for some emulsifiers. A reaction reported from the trade is that this hurts the market for emulsifiers.

Sources of raw materials used in emulsifiers have had little emphasis except with respect to those uses where public interest or Government responsibility has raised questions of nutrition or health. These questions have been developed most succinctly in hearings held under the authority of the Federal Food, Drug, and Cosmetic Act, especially the bread hearings on the basis of which an order was issued on May 15, 1952, containing definitions and standards of identity for white bread and certain closely related bakery products.

Emulsifiers are distributed through numerous sales agencies such as chemical distribution companies, private laboratories, bakery supply houses, and by private individuals. Nevertheless, most manufacturers distribute their emulsifiers directly to consumers--usually companies manufacturing emulsion products. Strategically placed warehouses maintain good distribution. Since practically all emulsifiers are shipped in kegs, drums, or carlots, the cost of their physical distribution is of minor importance in total cost. Large quantities of emulsifiers never go through trade channels because manufacturers of shortening and margarine for the most part manufacture the edible (monoglyceride and diglyceride) emulsifiers they use as one step in their processing procedures.

PRODUCTION COSTS

The cost estimates given in the following tabulations for different types of emulsifiers are based on the output of a 10-ton per day plant, with the exception of distilled monoglycerides which are based on the output of a 4,800-pound per day plant. The costs presented here are estimates based on May 1, 1953, prices. In some cases, the input factor is an unprocessed fat or oil, and in other cases it has already been subjected to one or more processes. It is not feasible, using the available cost data, to determine the costs of putting a pound of fat or oil through all the processes necessary to convert it into the various emulsifiers. There are also other raw materials used in addition to fats or oils and their derivatives. In all cases, the cost of the emulsifier is chiefly the cost of ingredients.

Distilled monoglycerides of fatty acids
(90 percent purity)

Materials:

Tallow, edible ...... 821 lb. @ 7¼¢ lb.	$ 59.52
Glycerine, high gravity .... 179 lb. @ 44¢ lb.	78.76
Esterification costs	5.00
Distillation costs (allowing 50-percent increase for recycling)...	15.00
Royalty fee	10.00
Plant amortization (10 years)	12.00
Cost per 1,000 pounds	$180.28
Cost per pound	.180

Polyoxyethylene glycol ester of stearic acid
(15 moles ethylene oxide)

Materials:

Stearic acid, triple pressed .... 290 lb. @ 14½¢ lb.	$ 42.05
Ethylene oxide ...... 710 lb. @ 19¢ lb.	134.90
Labor	1.60
Utilities (power, steam, and water)	.20
Repairs and maintenance	.20
Overhead	1.60
Plant amortization (10 years)	.60
Cost per 1,000 pounds	$181.15
Cost per pound	.181

Propylene glycol monostearate

Materials:

Stearic acid, triple pressed .... 823 lb. @ 14½¢ lb.	$119.34
Propylene glycol .... 232 lb. @ 18¢ lb.	41.76
Labor	1.20
Utilities (power, steam, and water)	.30
Repairs and maintenance	.10
Overhead	1.20
Plant amortization (10 years)	.40
Cost per 1,000 pounds	$164.30
Cost per pound	.164

Diethanolamide of stearic acid

Materials:

Oleic acid, double distilled .... 756 lb. @ 13½¢ lb.	$102.06
Diethanolamine ...... 295 lb. @ 27½¢ lb.	81.13
Labor	1.20
Utilities (power, steam, and water)	.30
Repairs and maintenance	.10
Overhead	1.20
Plant amortization (10 years)	.40
Cost per 1,000 pounds	$186.39
Cost per pound	.186

SOURCES OF EMULSIFIERS

Edible fat-based emulsifiers are confined to fatty acid esters. Such emulsifiers account for perhaps one-third of all emulsifiers used. They are extensively used in shortening, other foods, cosmetics, and pharmaceuticals. It is estimated that 80 million pounds per year of commercial monoglyceride esters are being used in shortenings. These are, for the most part, made during the shortening manufacturing process from edible vegetable oils or lard. Ester-type emulsifiers are produced also by esterification of fatty acids with polyhydric alcohols, such as glycerine, several glycols, manitol, sorbitol, pentaerythritol, and others. These emulsifiers may be either edible or inedible, depending on the fatty acids and polyhydric alcohols from which they are made. Present production of polyhydric alcohol esters is estimated to consume 30 million pounds of animal fats per year, of which probably 15 million pounds are converted to monoglycerides. Included in this figure are the distilled monoglycerides (90 percent purity), production of which, at the present time, is under 5 million pounds going chiefly into the new prepared bake goods mixes. Another class of ester emulsifiers containing some fat, and currently used in numerous edible products, but not recognized as optional ingredients in the standards for breads entering interstate commerce recently promulgated under authority of the Federal Food, Drug, and Cosmetic Act, is that of the polyoxyethylene fatty acid esters.

The principal inedible fat-based emulsifiers are soaps, followed by sulfated and sulfonated oils. It is estimated that at the present time about 150 million pounds of soap per year are being used as an emulsifier. In addition, there are inedible fatty acid esters and fatty amide emulsifiers. It is estimated that not more than 20 million pounds of domestic fats, split chiefly between stearic and oleic acids, are used to produce fatty acid esters and fatty amides for incorporation into synthetic detergents.

SOURCES OF RAW MATERIALS USED

With the exception of most monoglycerides and diglycerides, which are mostly manufactured directly from fats and oils, the fatty raw materials used in the production of emulsifiers are in the form of fatty acids. These fatty acids are produced from animal fats and vegetable and fish oils. When stearic acid is used as a raw material for emulsifiers to be incorporated into edible, cosmetic, or pharmaceutical products, usually only triple pressed stearic acid is used. Monoglyceride and diglyceride edible emulsifiers are largely prepared from oils similar to those used in the final emulsion products. For example, cottonseed oil is used in emulsifiers for shortening, and lard is used in those emulsifiers going into a lard product. Tallow and grease are important sources of fatty acids for inedible emulsifiers, along with other materials such as vegetable oils, vegetable oil foots, and tall oil. The main advantage of vegetable oil foots and tall oil is their low price in comparison with prices of other fats and oils. Foots are obtained as a byproduct of the refining of vegetable oils, mainly cottonseed and soybean oils. Tall oil is recovered chemically from the spent alkaline liquor of the sulfite papermaking process after the wood has been cooked to a pulp.

Ethylene oxide is a product of the petroleum chemical industry. Petroleum sulfonates are formed in the acid refining of white mineral oil. Alkyl phenol products are derived from the coal tar industry, although synthetic benzene may make this material also available from the petroleum industry. Glycerine is chiefly derived from fats and oils as a byproduct of the soap industry but about 25 percent of the total production is available as synthetic glycerine from petroleum sources.

The varied properties imparted to emulsifiers by the several types and qualities of raw materials and the diverse requirements in industry result in the employment of many kinds and grades of ingredients. For example, a company producing emulsifiers from oleic acid will use a high grade odorless oleic acid of the elaine type for the cosmetic trade or a low-grade oleic acid for cutting oil emulsions. Materials used in the dry-cleaning trade must be odorless. For this reason, low-grade oleic acid soaps have been found objectionable.

Each type emulsifier has its own special qualities to such an extent that the substitution of one raw material for another virtually represents a change in product. For that reason, a company contemplating such a substitution, whether for cost reasons or otherwise, usually brings out a new emulsifier rather than make a change in raw materials for a product under an established trade name.

PRESENT MARKET FOR EMULSIFIERS AND EMULSIONS

As a marketing outlet, the emulsion field is broader than the technical meaning of the term "emulsion" signifies. The product may be technically an emulsion or a colloidal suspension, or a combination of the two. In an emulsion, fine droplets of one liquid are dispersed and suspended in another liquid, whereas, in common usage, the trade and industry may include borderline cases of solids suspended in liquid. Most of the common emulsions are comprised of water and oil, and frequently the two components of any emulsion are referred to as the "oil" and "water" phases. So long as at least one of the ingredients is a liquid in which other material is suspended, the mixture may appear in the trade as an emulsion. An oil-and-water emulsion may have oil dispersed in water, or water dispersed in oil, or a mixture of the two relationships. In general, the greater the proportion of oil the more the emulsion behaves like oil, and the greater the proportion of water the more the emulsion behaves like water. Many emulsifiers tend to promote oil-in-water emulsions, whereas many others have an opposite tendency to promote water-in-oil emulsions. Although the classification holds for no emulsifiers in all circumstances, it obviously is very important both in their marketing and their use.

In many processes using fats and oils--such as the mixing of paints and varnishes, and making bakery products, lubricants, and pharmaceuticals--there arises repeatedly the need to put together two or more materials that are difficult to mix. It is here that emulsifiers play their important role of bringing together the oil and water phases to form an emulsion. In many individual cases, a better mixture in some specific sense, such as uniformity, permanency, texture, or cost, can improve a process or a product. It may improve the product's competitive position in the market, or it may make a new product available. The central interest here is in the directions and the degrees in which improved emulsions can be expected to improve the market for fats and oils.

Emulsions are by no means new, having always existed in nature. Good examples are milk and egg yolk. The first major industrial development of an emulsifier was the sulfonation of castor oil, commonly called turkey-red oil, which came into use for textile dyeing in 1875. This was followed in 1898 by the Twitchell reagent, an emulsifier used in fat splitting. These two emulsifiers are still used in large quantities today. Only in the last 50 years has the study of the physical principles of emulsifiers and emulsification made possible the production or manipulation of emulsions in a broad way.

In the last 25 years, new types of emulsifiers and new emulsion products have been developed at an ever-increasing rate. Following the commercial development of the emulsifier lecithin (derived from the gummy material found in vegetable oils) in Europe shortly after World War I, two of the basic contributions were: (1) The production of mono-glycerides and diglycerides; and (2) the production of polyoxyethylene glycol from ethylene oxide.

Edible monoglycerides and diglycerides are made entirely from fats and oils but with additional glycerine added. Their first market, and still their most important one, in vegetable shortening was opened in

1933. Recently, monoglycerides and diglycerides have been modified to produce emulsifiers with slightly different properties making them more desirable for use in certain other edible products. For example, monoglycerides have been distilled, giving a product with 90 percent purity, and derivatives such as diacetyl tartaric acid esters of monoglycerides and diglycerides have come into use.

Just before World War II, ethylene oxide, produced from petroleum or natural gas, was polymerized by means of a catalyst to form polyoxyethylene glycol. The commercial development of this product in the United States opened up a whole new field of emulsifiers.

CHARACTERISTICS OF EMULSIFIERS AND EMULSIONS

Ever wider market potentialities for emulsions are opened by the utilization of traits peculiar to individual emulsions. Offhand it may appear paradoxical that often the same trait in two emulsions may give practically opposite effects. For example, some liquids dispersed in other liquids as emulsions have penetrating powers exceeding those of any practicable solutions of the same materials, while the emulsion of two liquids in other cases prevents penetration, permitting a thin film to be applied over porous surfaces; some emulsions reduce or disguise tastes and odors, and other emulsions enhance flavors and aromas. Penetration may be desirable in an insecticide but undesirable in a paint, or it may be desirable in a paint for one use but not for another. Accented flavor may be an asset in bake goods but a disadvantage in a pharmaceutical product.

Emulsions have various other traits that often contribute to their usefulness in specific uses. They may permit chemical solvents to be replaced by water. This will cut costs and may reduce fire hazard and eliminate toxicity of the product. In some instances, a chemical reaction that is to be made between two materials can be speeded up or otherwise improved by first forming an emulsion of the two. One effect will be to reduce the size of suspended droplets, thus increasing the area of contact over what it would be in a coarser mixture. Where the joint action of the two materials on a third is desired, an emulsion of the two will often permit a convenient application. This is the case in many cleansers and polishes.

Emulsions also have certain disadvantages. Many of them are more difficult to prepare than are various solutions of the same materials. Also, many of them are sensitive to heat, cold, or vibration, and, with the passage of time, some emulsions separate into layers, discolor, or change consistency. Thus, they may be difficult to handle, transport, store, stock, or display.

Stability of emulsions obviously is of vital importance throughout their production, distribution, and utilization. The period during which stability must be maintained may vary, however, from a few seconds to several years. An insecticide may require stability for a few seconds, whereas a cosmetic may require it for a year or more.

Some of the important factors affecting stability are: Quantity and type of emulsifier used; acidity, alkalinity, or other characteristics of the materials incorporated with the emulsion (as in cosmetics); amount of reaction between emulsion and container; evaporation; bacterial activity; amount of vibration; and temperature level and changes. Also, the basic physical characteristics of the materials to be emulsified will affect the stability of the emulsion. For example, as a general rule, the more viscous the materials emulsified the more viscous and the more stable will be the emulsion.

The nature and action of emulsifiers is affected to a considerable extent by the kind of electrical charges that their molecules carry when in contact with the emulsion materials. Like other surface-active materials, emulsifiers may be anionic (with a negative charge), cationic (with a positive charge), or nonionic (showing neither negative nor positive force). But whereas most important detergents are anionic and most germicides are cationic, most emulsifiers are nonionic. In general, an emulsifier carrying either a positive or a negative electric charge has a greater possibility of running into trouble than one that is neutral (nonionic). If one carrying a charge comes in contact with material carrying an opposite charge, its characteristics and action will be altered and the emulsion may be modified or destroyed. This becomes vital in practice where emulsions are mixed with various other ingredients, as in paints. Also, cationic emulsifiers cannot be used with many of the phosphate compounds. An anionic emulsifier, such as soap, cannot be used with a cationic germicidal substance because a precipitate is formed, destroying the emulsion.

CLASSES OF EMULSIFIERS

Although it is literally possible to manufacture thousands of different emulsifiers at the present time, a preponderant part of the market is accounted for by four types, the most important of which is soap.

Soap is probably the widest used of all the emulsifying agents. It is commonly produced from fats and oils by splitting them into fatty acids and glycerine and saponifying the fatty acids with an alkali such as caustic soda or potash. Pure kettle soap has an equivalent fat or oil content of about 65 percent. Sources of fats and oils most commonly used in the manufacture of emulsion soaps are: Inedible tallow and grease; and vegetable oil foots. Toilet soaps commonly contain 20 percent or somewhat more of coconut oil, and, under special circumstances, relatively small quantities of soybean, cottonseed, linseed, and castor oils, lard and edible tallow are also used in soapmaking. Soap as an emulsifier, may be <u>added to</u> a mixture of liquids to form an emulsion, but frequently soap is actually <u>formed within</u> the mixture by the addition of a fatty acid and an alkaline salt--or by adding one of the two if the other is present. Soap is anionic, unstable in contact with acid materials and makes a cheap and effective emulsifier under special conditions of use. The principal uses of soap as an emulsifier are in situations where acids and inorganic salts are absent--an important use being in bituminous emulsions for roadbuilding.

A second important type of emulsifier comprises sulfated and sulfonated oils. They are anionic and are formed by treating mineral and natural oils with sulfuric acid or sulfuric acid derivatives. Sulfates and sulfonates differ structurally in that in sulfates the sulfur is linked to carbon by the intermediate of an oxygen, whereas in sulfonates the sulfur is attached directly to the carbon. Petroleum sulfonates are formed in the acid refining of white mineral oil and are used very extensively as additives to lubricants. They have the property of holding traces of water in suspension and away from the surfaces where they might cause corrosion. In the same class chemically, but with different raw materials and uses, are the animal and vegetable sulfated and sulfonated fats and oils. Sulfated and sulfonated natural fats and oils are used chiefly in the textile and leather industries. The most popular of these is sulfated castor oil (turkey-red oil).

A third important type of emulsifier comprises the modified fatty amides. The oldest method of preparing amides, and one which is extensively used, involves the dehydration of a soap. The basic patents for this process are held by one company which licenses a number of producers. Amides are modified in numerous ways to form emulsifiers. These amide-derived emulsifiers are nonionic and are made from oleic, lauric, and stearic acids, and occasionally others. They find no use in edible products but are extensively used in cosmetics, textiles, leather, paper, polishes, cutting oils, and insecticides. The ease of their manufacture makes them popular with small companies that do not wish to install expensive equipment.

A fourth important type of emulsifier comprises fatty acid esters which are formed by combining fatty acids with an alcohol. They are nonionic and it is in this type that all emulsifiers going into edible use are found. Common emulsifiers found in this class are monoglycerides and diglycerides of fatty acids, polyhydric alcohol esters of fatty acids, and polyoxyethylene esters of fatty acids. The true importance of this type of emulsifiers would be more apparent if the large amounts of monoglycerides and diglycerides which do not enter the trade, but are formed in one step in the making of shortening and margarine, were considered. This type would then nearly equal the soaps in quantity of emulsifier produced.

Monoglyceride and diglyceride emulsifiers are commonly manufactured by two methods. The first is the reaction of glycerine with the triglycerides constituting a fat or an oil, and the second is direct esterification of a fatty acid with glycerine. Both of these reactions take place in the presence of heat and a catalyst. Commercial monoglycerides and diglycerides contain minor parts of triglycerides, glycerine, moisture, soap, and traces of the catalyst. The product made from fats and oils by customary methods usually will not contain more than 55 to 65 percent monoglycerides; in many instances, it will be as low as 40 percent. Monoglycerides and diglycerides may be edible or inedible, depending upon the raw materials from which they are processed.

Monoglycerides find wide industrial application, the most important of which is the use of edible monoglycerides in foods. Edible monoglycerides find uses in shortening, margarine, peanut butter, frozen desserts, candy, frozen eggs, salad dressing, baked goods, and pharmaceuticals. Some important uses of inedible monoglycerides are in cosmetics, surface coatings, and in the textile and leather industries. By far the most important market for monoglycerides and diglycerides is for use in vegetable shortening. The resulting shortenings permit a much higher ratio of sugar to flour, which is especially important in cakemaking. This higher ratio makes possible a cake that is sweeter, lighter--with greater volume--and more moist than is a standard formula cake.

New developments in the use of emulsifiers have revealed distinct advantages of purer monoglycerides over those of the usual mixture. Indications are that the diglycerides lessen the effectiveness of the monoglycerides. Thus, the purer monoglycerides can be used in much smaller quantities than the usual mixture. Higher purity monoglycerides can be produced by molecular distillation. Produced in this manner, there are on the market monoglycerides which are said to have a purity of over 90 percent. At the present time these monoglycerides represent a relatively new development. As such, there may be a good possibility of improvements in method that would lower their costs. Lowered costs would provide an opportunity for high purity glyceride emulsifiers to break into fields where their less refined forms have been poorly adapted.

Another recent development has been the diacetyl tartaric acid esters of monoglycerides and diglycerides. These modified monoglycerides and diglycerides are said to improve the action of shortening when used in breadmaking.

Ethylene oxide, from which polyoxyethylene esters are made, is a product of the petroleum chemical industry. The variety of ways in which ethylene oxide can be added to fatty and nonfatty materials to make emulsifiers is almost infinite. The I. G. Farben Co. of Germany originally held the basic patents covering many of the processes for manufacturing emulsifiers from ethylene oxide. Manufacturers found it easy to enter the emulsifier business by making arrangements through the U. S. Government's Alien Property Custodian. Probably the simplest way of producing ethylene oxide-based emulsifiers is by producing the straight fatty acid esters of polyoxyethylene glycol. These are usually made by first transforming ethylene oxide to polyoxyethylene glycol. The glycol is sold to small manufacturers who esterify it with a fatty acid to form polyoxyethylene glycol esters. It is possible to make the esters directly from ethylene oxide and fatty acid, under pressure. This direct use of ethylene oxide is somewhat hazardous, however, and requires both considerable know-how and special equipment. It does permit a more varied and versatile group of products than is possible in using the polyoxyethylene glycol. Only a few companies manufacture emulsifiers directly from ethylene oxide.

Ethylene oxide will form emulsifiers with various materials other than fats and oils. For example, it may be added to the alcohols and tall oil. Tall oil is a mixture of fatty acids and resin acids. Ethylene oxide reacts with both the fatty acids and the resin acids. It may also be added to alkyl phenols, to the amides or amines, or to fatty acid polyhydric alcohol esters, such as sorbitan monolaurate, monostearate and others, to increase "water solubility." Furthermore, the almost infinite variety of ways in which ethylene oxide apparently can be added to fatty and nonfatty materials to produce emulsifiers suggests a promising field for research.

A wide variety of alcohols may be used to esterify fatty acids, but in order to form a good emulsifier the alcohol usually must be polyhydric. Fatty acid esters of the more common monohydric alcohols, such as methyl or butyl, are chiefly plasticizers. A typical example of an emulsifier among the polyhydric alcohol esters of fatty acids is glycerol monostearate. The sugar alcohols are of the polyhydric type and are often employed in esterifying fatty acids to produce emulsifiers. The one widely used is sorbitol, which is produced from glucose.

The polyoxyethylene glycol and polyhydric alcohol esters of fatty acids have wide and varied uses. Some of their principal edible uses are in ice cream, bakery products, salad dressings, candy, and pharmaceuticals. They also find use in cosmetics, insecticides, herbicides, various types of lubricants, and elsewhere.

EFFECTS OF EMULSIFIERS ON EMULSION PRODUCTS

Frequently, an emulsion can be formed by the use of much less emulsifier than that actually used. The greater quantity is actually being used to increase the stability of the emulsion or otherwise improve the properties of the product. For example, an increase in emulsifier above the minimum requirement will permit the suspension of smaller droplets, hence a finer mixing of ingredients.

To obtain best results, in some instances two or more emulsifiers must be used together. Some emulsifying agents that are relatively ineffective by themselves are excellent when they are used in combination with small quantities of "emulsion stabilizers." A good example of the use of several emulsifiers jointly is margarine. One emulsifier is the casein in the milk solids employed; another now customarily used, lecithin, is added to reduce spattering when the margarine is used in frying; a third, monoglycerides (and diglycerides), is added to prevent leakage of moisture. The example illustrates the unique effects of each individual emulsifier and often considered as secondary or supplementary effects. A given emulsifier, and an emulsion formed with it, will impart characteristic qualities to products in which the emulsion in turn is incorporated. Any change in these qualities may or may not be beneficial, but emulsifiers can be chosen that do contribute desirable qualities. Some products which do not require emulsifiers are, nevertheless, benefited by having a proper emulsifier added. The knowledge of these differential effects and the emulsifiers that impart them to emulsion products have mostly been developed within recent years. Such development probably will continue, as it has already resulted in: (1) An expansion of the market for emulsifiers; and (2) some better products. The latter has been recognized by consumers in their preference for some products containing certain emulsifiers over similar products not containing them. Some examples of products to which emulsifiers are added for what the trade considers supplementary effects and the manner of the product's improvement are the following:

In cosmetic emulsions glycerol monostearate (stearic monoglyceride) aids in softening the skin. Triethanolamine (amino-soap emulsifier) improves the cold water lathering and rinsing properties of shaving cream. Lecithin is often added to lipstick bases to improve the spreading properties and the pigment dispersion. Help in preventing shampoo from being rinsed out on the first dash of water can be given by adding emulsifiers which thicken water solutions. In ice cream, certain emulsifiers increase smoothness and permit the incorporation of large quantities of air; in chocolate, the elimination of fat bloom is effected by certain emulsifiers; and in chewing gum, selected emulsifiers add plasticity.

TECHNICAL EFFICIENCY OF EMULSIFIERS

It might be helpful if emulsifiers could be arranged in the order of their efficiency, but there can be no one such fixed array because their efficiencies vary with the materials to which they are added. For instance, the efficiency of an emulsifier varies with the kind of oil in the emulsion. Therefore, the results an emulsifier gives with one oil cannot be translated in terms of any other oil. A number of other conditions also affect relative efficiencies. Among these are temperature, acidity or alkalinity, exposure to air during emulsification, period of time during which stability of emulsion is required, and others. The technical efficiency of emulsifiers obviously has a direct effect on the quantity of emulsifier used, but on the market technical efficiency must give way to economic efficiency as indicated by cost and returns.

EMULSION-PRODUCING CONCENTRATES

There are a large number of products and a great deal of material marketed in the form of emulsion-producing concentrates. These concentrates are composed of the oil for an emulsion and an emulsifier that will act when the product is mixed with water. Large quantities of insecticides and herbicides are marketed in this form. As in so many other parts of the industrial market, the insecticide and herbicide markets are seldom concerned with simple emulsions. Active ingredients toxic to insects or to plants, as the case may be, will usually be dissolved or suspended in the emulsion which acts as a carrier. When a concentrate is employed, it, too, will normally carry the active ingredients.

There are both advantages and disadvantages associated with the marketing of emulsion concentrates. The greatest advantage is in the savings that can be made in container and transportation costs. The biggest saving is in shipping weight, but there is also a large saving in space. Both can be reduced as much as 35 to 50 percent. Other advantages are that the concentrates are not sensitive to freezing temperatures, transportation, or storage. One chief disadvantage is the possibility that when water is added a less satisfactory emulsion may be produced owing to lack of mechanical agitators and consequent insufficient mixing. Another disadvantage is that the usual rules for introducing an emulsifier into the emulsion products have to be modified. There is no universal rule for incorporating emulsifiers, but ordinarily it appears better to mix the emulsifier into: (1) The water for an oil-in-water emulsion; and (2) the oil in a water-in-oil emulsion. In an emulsion concentrate, with no water present, obviously the emulsifier must always be added to the oil. In order to lessen the likelihood of trouble from poor mixing, it is common practice to include emulsifiers in the concentrates in very large doses. Insecticidal concentrates frequently contain 10 percent or more emulsifier.

Emulsion concentrates are marketed in combination with a great variety of other materials. Some of the other materials used are flour, soybean meal, whey, sugar, or the finely ground solids of paint. Usually these blends, containing the emulsion concentrates and emulsifiers, are mixed with still other ingredients to form the final product. The blends usually contain all the emulsifier used in the final product. For example, emulsifiers may be incorporated with flour and sold as a "colloid" for use by bakers in making bread. Not only are these various mixtures of emulsifiers, emulsion concentrates, and other materials made for convenience in use but in some cases they are said to possess advantages to improve the end product.

CHOICE OF EMULSIFIERS

Manufacturers in many fields of industry could well give more consideration to the selection of the best emulsifier in a given situation, or to the use of an emulsifier where none is being used. The rapidly increasing, but very imperfect, knowledge of the field makes marketing and utilization of emulsifiers both an intricate problem and a potentially opportune field of development. The slight proportion of the emulsifier in a product (usually under one-half of 1 percent) is no proper indication of the importance of the emulsifier.

Specific emulsifiers in certain products may be used effectively in proportions of less than 1 part in a thousand. In emulsion concentrates emulsifiers may be present in a higher proportion than 10 percent--the percentage being far lower, however, after the water is added.

The selection of an emulsifier and the strength in which to use it obviously must depend on the user's concept of his long-run market advantage.

A number of factors, both chemical and economic, must serve as guides. For each type emulsion and for each combination of other ingredients certain factors stand out, principal among them being: Stability; texture (including viscosity); color; odor; flavor; toxicity; and cost. With all other influences remaining unchanged, any one of these considerations would be a deciding factor, but it can scarcely be too often repeated that each change in ingredients, conditions, or product characteristics desired has a bearing on the end product. The emulsifier used may have an important influence on any or all of these controlling factors in an emulsion or emulsion product. It must be chosen for its net contribution through all these factors, and others. Even the type emulsifier to produce most readily the type of emulsion desired (oil-in-water or water-in-oil) may have to give way before other requirements of the product.

Stability of an emulsion is a must, although the degree of stability required varies tremendously. If the emulsifier exhibits an electrical charge it usually cannot well be used in contact with materials bearing an opposite charge. Similarly, the emulsifier needs to be selected for its performance in conjunction with the acidity or alkalinity of accompanying materials. Closely related in practice to stability of emulsion are texture and viscosity. Texture can be impaired either by instability of an emulsion or by a stable emulsion made with a wrong emulsifier. Viscosity of the emulsifier usually affects both stability of the emulsion and texture of product.

Odor, flavor, and color are of utmost importance in some products and are insignificant in others. In paint mixtures, color must exactly meet the customer's desire, whereas flavor is outside the field of interest. In the same product, odor has an importance most difficult to evaluate. In cosmetics and lotions, odors may be of extreme significance from a sales standpoint.

Toxicity obviously is a vital factor in food products, and it requires consideration in any product that will come in contact with man, animals, or plants. For example, paint materials have received continuing research and have been subjected to numerous regulations not only because of dangers associated with making and using toxic paints, but also because of possible ill effects resulting from contact with, or abrasion of, painted surfaces.

An example of an emulsifier requirement important enough in terms of the Federal Food, Drug, and Cosmetic Act to be given extended formal consideration and legal status is that included in the standards for white bread. In an order proposed in 1943 but never put into effect, the only emulsifiers mentioned were lecithin and monoglycerides and diglycerides of fatty acids. By 1952, when the latest order was issued, several additional emulsifiers had come into rather widespread use in bakery products. They included diacetyl tartaric acid esters of monoglycerides and diglycerides, sorbitan esters of fatty acids, and polyoxyethylene glycol esters of fatty acids.

The subparagraph in the 1952 order that covers shortening and emulsifiers permitted in white bread reads as follows: "Shortening, in which or in conjunction with which may be used lecithin, mono- and diglycerides of fat-forming fatty acids (except lauric acid), or diacetyl tartaric acid esters of mono- and diglycerides of fat-forming fatty acids (except lauric acid), or a combination of two or more. The total weight of mono- and diglycerides, including diacetyl tartaric acid esters of mono- or diglycerides of fat-forming fatty acids, used does not exceed 20 percent by weight of the combination of such a preparation and the shortening, and the total amount of monoglyceride in such mixture does not exceed 8 percent by weight of the combination; but if purified or concentrated monoglyceride is used the amount of such a preparation does not exceed 10 percent by weight of the combination of such preparation and the shortening. For the purposes of this section the lecithin may include related phosphatides derived from the corn or soya-bean oil from which the lecithin was obtained."

From the findings of fact published with the standards, it appears that three points largely determined the permission to include any given types of emulsifiers, as follows: (1) Proved nontoxicity; (2) embodiment of no characteristics that would permit a reduction in nutritional constituents, such as shortening or eggs, without materially changing the readily perceptible properties of the finished product; and (3) no action that would prolong the softness of the product apart from characteristics of freshness that the consumer usually connects with softness. One of the three points was included as a safeguard of the consumer's health, one as a safeguard for nutrition, and one to avoid misrepresentation on the market.

Three principal changes relative to emulsifiers were made between the proposed order in 1943 and the order of 1952. The latter order: (1) Permits the use of diacetyl tartaric acid esters of monoglycerides and diglycerides; (2) permits the use of lecithin made from corn oil, as well as lecithin from soybean oil, as previously allowed; and (3) limits the concentration of monoglycerides and diglycerides, including diacetyl tartaric acid esters, to 20 percent of all emulsifiers and shortening for customary commercial monoglycerides and diglycerides and to 10 percent for distilled monoglycerides. This limitation has the purpose of avoiding the misleading softening effect that higher concentrations might impart.

In view of the innumerable product requirements and potential product qualities and the many possible emulsifiers and ways of using them, it is not surprising that extensive product differentiation is seen in the market for emulsion products, with many of the variations protected by patents or secret processes. An example is in the resin field, where the use of a specific emulsifier in the polymerization process may directly improve the resin performance.

POTENTIAL MARKET DEVELOPMENT FOR EMULSIFIERS

Summarizing all the variables in terms of market outlets for fats and oils, a larger market can be expected in numerous circumstances where improved emulsifiers either improve a product moving to consumers or lower its cost. Quality influence and cost must be the final determinants. It might possibly happen that the emulsifier that gave the greatest product improvement also resulted in the least product cost per unit.

Undoubtedly, an enormous amount of technical research remains to be done on the use of emulsifiers in industry. Basic concepts have been developed, however, to indicate that imaginative continuation of research and engineering already done, plus imaginative customer service and sales policies on the part of the fats and oils derivatives industries, offer opportunities for market expansion in numerous directions. The concerted effort given to maintaining or improving quality under the conditions of World War II furnished a remarkable impetus. An example is the substitution of emulsifiers for scarce alcohol to disperse essential oils in cosmetics. No one potential use, however, can be expected to assure a satisfactory market for fats and oils. Although judgments differ greatly, some informed opinions in the emulsifier industry indicate that increases as great as tenfold are probable within 5 years in several important segments of the market. Prominent mention is made of paints, insecticides, fungicides, weed killers, textile processing, ice cream, and bake goods.

There appears to be an increasingly widespread realization that the innumerable variations among emulsifiers hold the key to market expansion. Almost wherever one turns in modern industry, the ingredients for some product will include oil-like and water-like substances. Their combination may become simpler, the results may become better, or both, if an improved emulsifier can be found. The fats and oils industry has an important interest in furnishing raw materials for better and less expensive products that progressively improving emulsifiers should make possible.

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