alysis. Even sulfate analysis may be improved if published methods are indicative.

Analyses for optical brighteners, corrosion inhibitors, and carboxymethyl cellulose are needed and do not now exist in satisfactory form.

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Surfactant Survey[1]

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SATISFACTORY PAPERS have appeared from time to time on the total production of surface-active agents or on their most important uses. Relatively little data are available however on the types and quantities of surfactants used in specific applications. The principal reason for this is the difficulty of obtaining even reasonably reliable estimates. For some uses, as in household cleaning products, knowledge of the formulations used combined with confidential but available data on the sales of the individual products permit a fairly accurate analysis to be made. In other applications the estimates, guesses, and conjectures of men experienced in the field can be analyzed to provide a fair estimate. In still other applications however, notably those concerned with industrial cleaning, it seems likely that no one anywhere has the answer. For such cases we have provided only guesses.

While this survey is as exhaustive as time would permit, the subject is so vast that it cannot be considered final. It is presented as a start on which others can build, and so our method of calculation is given for those applications where we consider our estimates doubtful.

There are other limitations to be noted. The first of these concerns confidential applications. Many companies have one or two applications tucked away that are unknown to some or all of their competitors. Even where such information is known to us, specific reference has been omitted from this paper though it may be concealed in the totals.

There is also the important question as to which materials should be included as surface-active agents. In general, we used the classification of the U. S. Tariff Commission (18) with two notable exceptions. We omitted both sulfonated oils and the salts of fatty acids since we do not include soaps in this survey. While both classes are undoubtedly surface-active agents and undoubtedly synthetic, it was felt that they require a separate study of their own.

We did include certain materials listed by the U. S. Tariff Commission under "Ore-Flotation Agents" as their function is surface-active. We recognize this to be somewhat inconsistent as there are many such products, notably fatty amines and fatty alcohols, which are also used for surface-active properties but not generally included in the common usage of the term "surface-active agents." We can only plead that time did not permit this more thorough treatment.

Another point to be noted is that the art of application of surface-active agents is still in its adolescence. Changes are constantly being made both in the type of surface-active agents used for given applications and the concentration used. Also it is believed that, in some household products, the type and proportion of surface-active agent in the formula may be varied, depending on the relative costs of the competitive raw materials. Nationally sold household products also seem to vary in composition in various areas of the country, depending on local conditions, such as water hardness, public demand for certain properties, and raw material supply in that area. A survey such as this therefore must be considered, at best, representative of a fleeting instant of time so that greater importance should be placed on the properties required for specific applications rather than the numerical values representing consumption. All figures shown are on an active-agent basis, that is, 100% of organic surfactant.

Principal Product Types

Our method of presenting some of the data requires that abbreviations be used to designate the surfactant types. These abbreviations are shown below.

TABLE I

Principal Surfactant Types

Class name	Typical brand name products	Symbol
Anionic		
Alkylaryl sulfonates	Ultrawet, Nacconal, Nekal	AAS
Alkyl sarcosinate	.....	AS
Condensed aas	Daxad, Tamol	CAS
Dialkyl sulfosuccinates	Aerosol, Decersol	DSS
Fatty alcohol sulfates	Sipex, Dupanol	FAS
Lignin sulfonates	Vinsol, Marasperse	LS
Petroleum sulfonates	Petronate	PS
Secondary alkyl sulfates	Tergitol 08	SAS
Sulfated esters	Alcowet RS	SES
Sulfated ethers	Triton X200	SET
Sulfonated amides	Igepon T	SA
Sulfonated ethers	Alipal	SUE
Sulfonated glycerides	.....	SG
Nonionic		
Alkylolamides	Ninol, Alrosol	AA
Alkylphenol ethers	Triton X100, Igepal CO	APE
Alkyl thioethers	Nonic 218	ATE
Fatty acid esters	Energetic	FES
Fatty alcohol ethers	Brij	FAE
Glycerol monostearate	.....	GM
Polyoxyalkylene ethers	Pluronic	PE
Sorbitan esters and ethers	Span, Tween	SE
Tall oil esters	Renex, Sterox CD	TOE
Cationic—Amine acetates		AM
Quaternary ammonium	Hyamine	QA
Amphoteric	Miranol C2M	A

Total Market

A general analysis of the major trends in the commercial aspect of surface-active agents was published recently (2). For completeness and as a guide to the relative importance of the applications to be discussed Table I lists the production volume of major types of surface-active agents over the past several years.

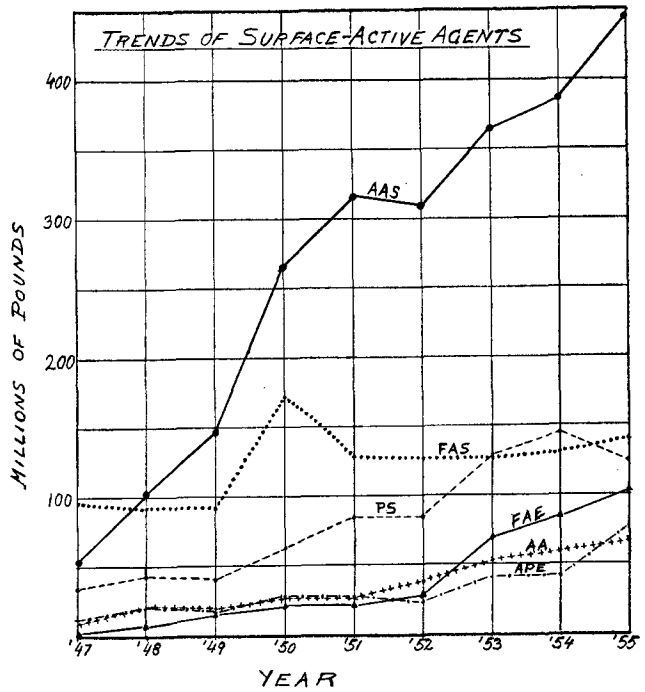

FIG. 1. Production rates for principal surfactants.

Although figures of the Tariff Commission are used as a guide, there is little doubt that the values given are not correct for all categories on account of errors and omissions of the companies reporting, perhaps because some of the material is used captively. For example, for petroleum sulfonates, where large quantities are used by the manufacturing company itself, our figures are substantially higher than those reported by the Tariff Commission.

Properties Required

There are a large number of surface-active agents; several hundred different trade products were listed in recent surveys. Although many of these are duplicates offered by different manufacturers, there are still a large number of different chemical types represented. Each type has its own set of physical and surface-active properties. The prospective user is faced with the enormous task of differentiating among these to select the one best suited for his application. Often he can do this only with the intelligent cooperation of the supplier.

But the supplier too has his problems. There are an equally large number of applications which require surfactants; to which should he devote his efforts? To help answer this problem we have collected data both on the total volume of surfactants required in the more important applications and the physical and surface-active properties that the surfactant must have in order to be considered for each use.

The physical and chemical properties required in major uses are shown in Table II. These are the properties provided by the products presently used by the major users for each application. Often however there are specialty applications within each major use where somewhat different properties are required. It should also be noted that while the absence of a desired property can sometimes be overcome by blending with an additive, the presence of an undesirable property usually eliminates a chemical type from further consideration. Thus foam stabilizers can be added to products of moderate foaming properties where high foam is required, but products developing high foam are seldom considered in those metal-cleaning applications where low foam is required.

Volume of Use

Table III shows our estimate of the volume of surfactants used in major applications in 1955. The principal types of products used, in estimated order of importance by volume, are also shown. The chemical types represented by the symbols are shown in Table I.

In some applications there is a sharp difference in the volumes of each type of surfactant used. One or a few surfactant types have most of the market while other types have a much more limited use. This is shown in Table III by capital letters for the former, lower case for the latter.

There are many more applications for surfactants, some requiring only a few pounds a year, others probably requiring millions of pounds. Some of the more important of these are shown in Table IV. Most of these applications use between 100,000 and 500,000 lbs. per year, but a few are larger. These latter are included as more detailed information was not available to us. The volume represented by these applications in Table V was at least 10 million pounds in 1955.

Since general break-downs are sometimes of interest, a summary of Table III is given in Table V.

Applications

It is not possible to discuss each of these applications in detail, but a few clarifying comments are offered:

TABLE 11

Properties of Surfactants Required for Each Use

	Anti-static	Deterg. fabric	Deterg. hard surf.	Dispersing	Dust-laying	Emul. hydrocarbons	Emul. min. oils	Emul. nat. oils	Effective high salt	Effective high temp.	Effective low temp.	High foam	Lubricating	Lime soap disp.	Non-corrosive	Non-substantive	Non-toxic or irr.	Oil-soluble	Rinsibility	Softening	Stable to acids	Stable to alkali	Stable to heat	Stable to hard water	Stable to metal ions	Stable to ox agents	Stable to red agents	Substantive	Suspending	Solubilizing	Thickening	Very low foam	Wetting	Rewetting	Remarks
Carwash and cleaners	—	—	**	*	—	—	—	**	—	—	—	—	—	—	**	—	**	—	**	—	—	—	—	*	—	—	—	—	*	—	—	—	*	—	Must not remove or emulsify wax
Concrete, air entraining	—	—	—	—	—	—	—	—	*	—	*	**	—	—	—	—	—	—	—	—	—	—	—	**	—	—	—	—	—	—	—	—	—	—	Low cost, critical factor
Cosmetics and pharmaceuticals																																		
Creams	—	—	—	—	—	—	**	—	—	—	—	—	—	—	—	—	**	*	—	*	—	—	*	—	—	—	—	—	—	—	—	*	—	—	Must not defat skin excessively
Shampoos	—	*	—	—	—	—	—	*	—	—	*	**	—	—	—	—	**	—	—	*	—	—	—	**	—	—	—	*	*	—	*	—	—	—	Pleasant feeling on skin
Toothpaste	—	—	—	—	—	—	—	—	*	—	*	**	—	—	*	—	**	—	—	—	—	—	—	*	—	—	—	—	—	—	—	—	—	—	Absence of taste essential
Dry cleaning	**	*	—	—	—	—	—	—	—	—	—	—	—	—	*	—	*	**	—	—	—	—	—	—	—	—	—	—	**	—	—	*	*	—	Must not affect colors
Dye dispersing	—	—	—	**	—	—	—	—	—	—	—	—	—	—	—	—	*	—	—	—	**	*	—	**	—	**	—	—	**	—	—	*	*	—	Must solubilize water in cleaning solvent
Fire-fighting	—	—	—	—	—	—	—	—	—	—	**	—	—	—	**	—	*	—	—	—	—	**	—	**	—	**	—	—	—	—	—	*	**	—	
Food	—	—	—	—	—	—	**	—	—	—	*	—	—	—	*	—	**	—	—	—	—	—	*	—	—	—	—	—	—	—	—	**	—	—	Absence of taste
Formulated cleaning compounds																																		
Dairy cleaners	—	—	**	*	*	—	—	**	*	*	*	*	—	*	**	—	**	—	**	—	**	**	—	**	—	—	—	—	*	—	—	—	—	—	Variety of compounds involved
Detergent-sanitizers																																		
(Cationic ingred.)	—	—	—	—	—	—	—	—	*	—	**	—	—	—	*	—	—	—	**	—	*	—	—	*	*	—	—	—	—	—	—	—	—	—	Good germicidal power required
(Nonionic ingred.)	—	—	**	*	*	—	—	—	—	—	*	—	—	—	**	*	—	—	—	—	*	—	—	*	*	—	—	—	—	—	—	—	—	—	No reduction of germicidal power
Dishwashing, comm., hand	—	—	**	*	—	—	—	**	—	—	—	**	—	—	—	—	**	—	**	—	—	**	—	**	—	—	—	—	**	—	—	—	—	—	
Dishwashing, comm., mach	—	—	**	*	*	—	—	—	—	—	—	—	—	—	—	—	—	—	**	—	—	**	*	**	—	*	—	—	—	—	—	—	—	—	—	
Floor cleaners	—	—	**	*	—	*	—	**	—	—	—	*	—	—	**	—	*	—	*	—	—	*	—	**	—	—	—	—	*	—	—	—	—	—	—	
Iodophors	—	—	**	—	—	—	—	—	—	—	*	—	—	—	—	—	—	—	*	—	—	—	—	**	—	**	—	—	—	**	—	—	—	—	
Laundry, commercial	—	**	—	*	—	—	—	**	—	—	**	—	*	—	*	—	*	—	*	*	—	**	—	*	—	**	—	—	**	—	—	—	*	—	Good solubilizing of iodine
Rug cleaners	*	**	—	*	—	—	—	**	—	—	—	**	*	—	*	—	*	—	**	**	—	—	—	**	—	—	—	—	—	—	—	—	*	—	
Household products																																		
Bars, synthetic	—	*	*	—	—	—	—	**	—	—	*	**	**	—	—	—	**	—	—	**	—	—	—	**	—	—	—	—	—	—	—	—	—	—	Limited solubility, low density
Bleaches, powdered	—	*	*	**	—	—	—	—	*	—	—	*	—	—	—	—	*	—	*	—	—	—	—	—	*	**	—	—	—	**	—	—	*	—	Non-hygroscopic
Dishwashing, powders	—	—	**	*	—	—	**	—	—	—	—	**	—	—	—	—	**	—	**	—	—	*	—	**	—	—	—	—	**	—	—	—	—	—	
Dishwashing, liquid	—	—	**	*	—	—	—	—	—	—	—	**	—	—	**	—	**	—	**	—	—	*	—	**	—	—	—	—	**	—	*	—	—	—	
Laundry, high foam	—	**	—	*	—	—	—	**	—	—	—	**	—	—	*	—	*	—	*	—	—	**	—	**	—	—	—	—	**	—	—	—	*	—	
Laundry, low foam	—	**	—	*	—	—	—	**	—	—	—	—	—	—	*	—	*	—	*	—	—	**	—	**	—	—	—	—	**	—	—	**	*	—	
Scouring powder	—	—	**	**	*	—	*	*	*	—	*	**	—	—	**	—	**	—	*	—	—	**	—	*	—	—	—	—	**	—	—	—	*	—	
Woodwork and wall	—	—	**	**	—	—	—	**	—	—	—	*	—	—	**	—	**	—	*	—	—	**	—	*	—	—	—	—	**	—	—	—	*	—	
Metal cleaning																																		
Alkaline cleaners	—	—	**	*	—	—	**	—	**	*	—	—	—	—	**	—	—	—	*	—	—	**	—	*	**	—	—	—	*	—	—	*	*	—	
Emulsion cleaners	—	—	**	—	—	**	*	—	—	—	—	—	—	—	**	—	—	*	*	—	—	—	—	*	**	—	—	—	—	—	—	**	—	—	
Acid cleaners	—	—	**	*	—	*	*	—	—	—	—	—	—	—	—	—	—	—	—	—	**	—	—	—	**	**	—	—	*	—	—	**	*	—	
Metal cutting	—	—	—	—	—	—	—	—	—	**	—	*	—	—	**	—	**	**	—	—	—	—	**	—	—	—	—	—	—	—	—	—	—	—	
Ore flotation	—	—	—	—	—	—	—	—	—	—	*	*	—	—	—	—	—	—	—	—	—	—	—	—	*	**	—	**	—	—	—	—	—	—	Selective absorption most important
Paint																																		
Latex emulsifier	—	—	—	—	**	—	—	—	—	—	**	—	—	—	**	—	**	—	—	—	—	—	—	**	—	—	—	—	*	—	—	**	—	—	Absence of odor desirable
Pigment dispersant	—	—	—	**	—	—	—	—	—	—	*	—	—	—	*	—	*	—	—	—	—	—	—	—	**	—	—	—	**	—	—	**	*	—	
Paper and pulp																																		
Felt washing	*	**	—	*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	**	*	*	—	*	—	—	—	—	*	—	—	—	—	—	
Pulp additive	**	—	—	—	—	—	—	—	**	—	—	—	**	—	—	—	—	—	—	—	*	*	—	—	*	—	—	—	—	—	—	**	—	—	
Pitch dispersant	—	—	—	**	—	*	*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	**	—	—	—	—	**	—	—	*	—	—	
Rewetting absorbent paper	—	—	—	—	—	—	—	—	—	—	**	—	—	—	—	—	**	—	—	—	—	—	—	*	—	—	—	**	—	—	—	—	*	**	Must retain rewetting
Slimicide	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	**	—	—	—	—	—	—	—	—	*	—	Germicidal properties
Pesticides																																		
Emulsifiers	—	—	—	—	—	**	—	—	—	—	*	—	—	—	*	—	*	—	—	—	—	—	—	**	—	—	—	—	—	—	—	**	*	—	
Wettable powders	*	—	—	**	—	—	—	—	—	—	—	—	—	—	—	—	*	—	—	—	—	—	—	**	—	—	—	—	—	**	—	*	**	—	
Petroleum																																		
Acidizing	—	—	—	*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	**	—	—	—	—	—	**	—	**	—	—	—	*	—	
Demulsifier	—	—	—	—	—	—	—	—	**	—	—	—	—	—	—	—	—	—	—	—	—	—	—	*	—	—	—	—	—	—	—	**	—	—	
Gasoline additive	—	—	—	*	—	—	—	—	—	—	—	—	—	—	*	—	—	**	—	—	—	—	—	—	—	—	—	—	**	—	—	*	—	—	
Lube-oil additive	—	—	**	*	—	—	—	—	**	—	—	—	—	—	**	—	—	**	—	—	—	—	**	—	—	—	—	—	**	—	—	*	—	—	Absence of ash desirable
Secondary recovery	—	—	—	—	**	—	—	—	—	—	—	—	—	—	—	**	—	—	—	—	—	—	—	**	—	—	—	—	—	—	—	*	*	—	Effective in very low concentration
Transmission oil additive	—	—	**	*	—	—	—	—	—	**	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	**	—	—	*	—	—	
Plastics and resin emulsifier	—	—	—	—	—	**	—	—	—	—	—	—	—	—	*	—	*	—	—	—	—	—	—	—	—	—	—	—	**	**	—	*	—	—	Low salt content
Textiles																																		
Waxes and polishes	—	—	—	—	—	**	—	—	—	—	—	—	—	—	**	—	**	—	—	—	—	—	—	—	—	—	—	—	**	—	—	**	*	—	
Wallboard	—	—	—	—	—	—	—	—	**	—	—	**	—	—	—	—	—	—	—	—	—	—	—	**	—	—	—	—	*	—	—	—	—	—	Dense, strong foam required

** Major requirement. * Secondary requirement.

Car Wash. As with everything else concerning automobiles, the volume is much larger than a casual estimate might indicate. The Chilton Company estimates that there were about 236 million washes of private automobiles (19). In addition, based on a McGraw-Hill estimate of the frequency of washing trucks and tractors, there are approximately 200 million washes of this larger equipment. This would indicate a total volume of synthetics of about 10 million pounds. Although this is a price-conscious market, the ratio of cost of labor to cost of materials is so high that performance is the more important consideration in selecting a surfactant.

Chemical Intermediate. Some of the nonionic produced is eventually sulfated to produce products like Alipal and fatty ether sulfates. There is probably additional nonionic converted to other forms for use in petroleum demulsifying, but this is not included in the figure given.

Concrete. Surface-active agents are incorporated in concrete to entrain air, creating voids when the concrete sets. This provides space for expansion of any residual water on freezing, thus preventing cracking of the concrete. The proportion of surfactant used is only 0.02–0.04%, but the volume of concrete (300 million barrels of cement in 1955) (21) is so large that this would represent a market of 50–100 million pounds per year. The market will undoubtedly increase both as the total volume of concrete increases and as a higher proportion of concrete than the present 60% uses such air-entraining agents. Price is the determining factor for the bulk of the volume, but special requirements permit the sale of some materials at their normally higher prices. (NOTE: Just before publication a communication was received which indicated that the volume of use may be 20 million pounds per year.)

Cosmetics. An analysis of surfactants used in shampoo formulations appeared recently (11). This has been adjusted to account for the increase in shampoo sales from $117 million in 1954 to $122 million in 1955. While no important new trends have appeared, amphoteric surfactants have attained some major volume primarily because of the absence of eye and skin irritation.

For those of us brought up in the industrial field, the volume of sales in the cosmetic industry at first seem surprising. For example, in 1955 the sales of various creams and lotions to enhance or substitute for milady's beauty amounted to about $250 million (10). This is about 80 million pounds of products containing 6 million pounds of surface-active agents. To all this must be added about 2 million pounds of surfactants contained in products like salve and ointments, some of which would normally be classed as pharmaceutical products.

After many years of having a relatively unchanged product, the toothpaste industry in the last few years has undergone a series of changes of formulation which are not yet over. Nevertheless there has been little recent change in either the types or quantities of surfactants used by the industry. The most important consideration is the absence of taste and toxicity.

Dispersing Dyes, Carbon, and Pigments. Surfactants are commonly added to dyes by the manufacturers of these materials to aid in their dispersal. Dispersing agents are also added to carbon black and various pigments. The figure presented is an educated guess.

Dry Cleaning. This is one industry where the development of a new method, the charge system, has somewhat reduced the total volume of surfactants required. The charge system permits filtering of the used, dry-cleaning solution for re-use and so has helped the acceptance of synthetics in this field (23). Based on the quantities of solvent used, reported to be about 110 million gallons of Stoddard solvent and 100–127 million pounds of perchlorethylene in 1953, an estimate of 12 million pounds of surfactants for 1955 is obtained (12). This checks reasonably well with independent estimates of men experienced in this field. The use of nonionics is increasing steadily and may now approach 30% of the total. This is primarily because of their ability to solubilize the correct amount of water in the solvents, making an important contribution to the removal of water-based soil (34).

Surface-active agents are also used for "wet cleaning" in dry-cleaning plants (34).

Fertilizer. There is still some controversy on the usefulness of adding surfactants to fertilizer. Since some companies do find the products useful, it seems likely that acceptance depends on conditions existing in each plant. The figure given is an estimate that may be somewhat low.

Fire-fighting. Sales for this use have been slow because of the difficulty of obtaining acceptance by each municipality. The market will undoubtedly grow from the present size, guessed at 0.5 million pounds.

TABLE III

Estimated Use of Surfactants in 1955
(100% active basis)

Application	Principal products used	Approx. volume (millions of pounds)
Carwash	AAS, ape, fas, sas	10
Chemical intermediate	APE	20
Concrete	Resins, ls, cas	75
Cosmetics, pharmaceuticals		
Creams	GM, se, ape	8
Germicides	QA	1
Shampoos	FAS, sg, aa, a	8
Toothpaste	AS, FAS	1
Dry cleaning	PS, aas, ape, se, aa, sa, fas	12
Dispersing dyes, pigments, carbon	CAS, LS, APE	2
Fertilizers	AAS	0.5
Fire-fighting	DSS	0.5
Food	GM, se	25
Formulated cleaners		
Dairy cleaners	AAS, APE	6
Detergent-sanitizers	QA, APE	6
Dishwashing, hand	AAS	13
Dishwashing, machine	APE. pe	1
Floor cleaners	APE, AA, AAS	5
Laundry, commercial	FAS, aas, ape	4
Rug cleaners	FAS, AAS	2
Maintenance and misc.	AAS, ape	9
Household products		
Bars, synthetic	SG, fas, sa	3
Bleaches, powder	AAS	0.5
Dishwashing, powder	AAS, fas	50
Dishwashing, liquid	AAS, FAS, AA, SUE, ape	65
Laundry, high foam	AAS, fas, aa	350
Laundry, low foam	TOE, aas, ape, pe	55
Scouring powder	AAS	20
Softening agents	QA	1.5
Woodwork and wall	AAS	2
Wool washing	AAS, FAS	1
Leather and fur	APE, FAS, SA, TOE	4
Metal cleaning	APE, aas, pe, fes, ps, fas, ls	4
Metal cutting	PS, aa, sa	21
Ore flotation	AM, ps, aas, ls, fas	12
Paint	AAS, cas, ape, toe, aas, sas	9
Paper	CAS, ape, aas, pe, qa	6
Pesticides		
Emulsifiers	SE, AAS, ape, fes, toe	12
Wettable powder	LS, sa	4
Petroleum		
Acidizing	APE	0.5
Demulsifying	Special Nonionics, ps, aas	30
Gasoline additive	.....	2
Lube-oil additive	PS, aas	145
Secondary oil recovery	QA	2
Transmission oil additive	PS	2.5
Plastics and resins	FAS, aas, set, fes	4
Rubber	CAS	2
Textiles	APE, AAS, SES, sa, fae, aa, fas, qa	30
Wallboard	AAS	1
Waxes and polishes	SE	5
Miscellaneous (Table IV)	.....	10
		1,063

Food. This market requires a separate, detailed study. Primary requirement is acceptance by the Food and Drug Administration. The figure given is an estimate by men experienced in the field. Fatty glycerides and fatty esters of various glycols are the principal products used. Their addition to bread and cakes increases the homogeneity and smoothness of the products and permits incorporation of larger amounts of sugar and shortening. They are also incorporated in ice cream, chocolates, and various "candies" as emulsifiers.

Formulated Detergents. There are a wide variety of cleaning compounds made by companies of all sizes from giants to individuals operating in garages. Data on most such compounds are not published, but reasonable estimates can be compiled based on sales of the raw materials.

Dairy Cleaners. Dairy cleaners include both products used primarily for cleaning and those which are expected to sanitize as well as clean. A recent publication (3) estimated that about 3 million pounds of cationic are used for this purpose, indicating that approximately an equal quantity of nonionic would be used. Since other estimates (6) indicate a total volume of approximately 12 million pounds of surfactant in dairy cleaning, this would indicate an additional 6 million pounds not expected to sanitize. In addition, surfactants are finding a new and growing market as solubilizers for iodine.

Dishwashing, Commercial. Large quantities of alkylaryl sulfonates are used in commercial hand dishwashing compounds. A principal consideration is the low cost at which good performance can be obtained. Very large quantities of products are used in commercial dishwashing machines, but only small quantities of surfactants are incorporated as wetting and rinsing aids. Low foam is a major consideration.

TABLE IV

Miscellaneous Applications

Wetting agent in radiator cleaners, windshield cleaners, shave cream, coal mines, foundries, waterless hand cleaners, window cleaners, adhesives, bottle washing, rubber bonding, de-inking paper
Detergents in tire cleaners, pet shampoos, railroad car cleaners, washing fruits and vegetables, and in mechanics hand soap
Dispersant in boiler water, inks, drilling muds, and polishing and buffing compounds
Foaming agent in bubble bath and electroplating baths
Lubricant in wire drawing
Conditioner in hair rinses
Solubilizing agent for perfumes and pharmaceuticals
Clouding agent for ammonia

Floor Cleaners. It is reported that approximately 5.5 million gallons of these products were made in 1954, with approximately 4% growth for 1955. Assuming 10% active-agent, this would indicate about 5 million pounds of surfactant.

Laundries, Commercial. Data in this field are particularly hard to obtain both because the practice varies considerably in institutional, home, and linen supply laundries, and because there is considerable variation, even from laundry to laundry of the same type. It is certain that all laundries have long resisted the use of synthetic materials. Though progress has been slow, the gain of these products has been definite. It is essential that the product selected be low in cost and perform successfully at the higher temperatures normally used in commercial laundries. In addition however, it requires patient, laundry-by-laundry sale by men skilled in this field. A very large market remains untapped. A product formulated around tallow sulfate now has most of the present market.

Rug Cleaning. The National Institute of Rug Cleaning Inc. reports that rug-cleaning value is about 80–90 million dollars per year. It is estimated that 11.5–13 million standard-size rugs are cleaned annually (36). This would indicate that about two million pounds of active agents are required.

Maintenance and Miscellaneous Cleaners. There is a relatively large volume of products known as "janitor's supplies." As they are made by a variety of companies of all sizes and locations, an accurate estimate is not available. An arbitrary guess is that approximately 7 million pounds of active agent are used for this purpose.

Household Products. Relatively new, only 4 million pounds of synthetic and soap-synthetic bars were produced in 1954 (15). It seems positive however that synthetic bars will capture an increasing share of the market. Their principal competitor for attention will probably be soap-synthetic combinations. As soap has practically all desired properties for a bar with the exception of resistance to hard water, a concentrated attempt to overcome this deficiency will no doubt be made.

As the market for powdered chlorine bleaches increases, a modest market for surfactants increases also. The surfactant used to improve wetting and provide foam is in addition to sodium toluene sulfonate used primarily as a solubilizing agent. Resistance to oxidation is an obvious major requirement.

The market for "light-duty" powdered compounds, which were used primarily for dishwashing, is held almost exclusively by alkylaryl sulfonates. The survey for 1955 included some lauryl sulfate which has now been displaced.

Liquid detergents are making rapid strides in this field, creating a market for different types of surfactants, notably lauryl sulfates, sulfated nonionics, and alkylolamides. Price is a most important consideration to success.

As to laundry, home, and high foam, this market is so large that considerations other than performance enter into the selection of these products. For example, there must be assurance of an adequate supply. Relatively few products share an enormous market. The philosophy appears to be that of concentrating on alkylaryl sulfonate or tallow sulfate and using minor quantities of modifiers to offset any deficiency in properties.

The figures given are accurate for U. S. requirements but assume exports of 100 million pounds of finished product in 1955. This figure for exports is an educated guess.

For laundry, home, and low foam, there is still a considerable juggling of formulations in this field. Everything is being tried from combinations of surfactants with soap, to the use of higher foaming materials combined with defoamers, to formulations based on very low-foaming nonionics.

The volume of these products will probably continue to increase, but attention has been taken from them by the introduction of liquid, heavy-duty detergents. These products have not been included in this survey as they were not a factor in 1955. It might be noted however that they are based on surface-active agents similar to materials currently used so that it is not likely that there will be any cataclysmic demise of present products or the creation of major new products unless we extend the terms surface-active agents to hydrotropic agents, such as sodium toluene sulfonate, the use of which will jump to millions of pounds. This product is presently also being used in some powdered formulations as a dispersant and anti-caking agent.

A fairly reliable estimate of scouring powders is obtained since the total volume sold is known, and the concentration of 4% can be assumed for the active agent.

Cationic softeners are now being sold for addition to the washer to fluff up clothes and give them a softer feel.

Actually the household market has not been a giant market for suppliers of finished surfactants for some years. Practically all of the anionic used (about 510 million pounds) are made by the companies that use them, so at most only 50 million, or about 10% of the market, are available to suppliers of finished surfactants.

Leather and Fur. Data were particularly difficult for us to get so the figures given are largely guess. In addition to the surfactant uses given, the condensed alkylarylsulfonates find use as synthetic tanning agents.

There is a moderate volume of surfactant used in the cleaning of furs before they are made into clothing. As this use is relatively unknown, the volume and surfactant types are combined in the figures given for leather.

Metal Cleaning. The field is so complex that it undoubtedly requires a separate report of its own. Because of the many different types of cleaners for many different types of metals in many different operations, data are particularly difficult to obtain. The data can only be considered an educated guess.

Metal Cutting. Surfactants have been used for some time as emulsifiers for the oils used for cutting metals. A newer and growing application is their use in soluble, cutting fluids. Their purpose is that of increasing contact between the fluids and the metal in order to conduct away heat more quickly. An important consideration is the absence of corrosion of the newly cut surface. At present, performance is a more important consideration than price. There are about 200 million pounds of cutting fluids, using about 15% of surfactant (65% active) (13).

Ore Flotation. This is a relatively new and growing market of great size. The surfactant is used to change the nature of the surface of one or more components of the mixture. This difference is the basis for separating the components of the mixture. It seems obvious that long and complex applications research remains to be done to win the market. The volumes involved are so large however that this could certainly become one of the larger users of surface-active agents. The figure given in this report is primarily a guess. Products other than those listed are being used in special cases, but most of this information is still confidential. The 1954 Tariff Commission lists 4.35 million pounds of cyclic and 20,335 million pounds of acyclic flotation reagents for a total of 24.7 million pounds. While all ore-flotation reagents can be termed "surface-active," materials such as fatty acids, xanthates and other organics are used, which are probably not included in Tariff Commission figures on surface-active agents. It is estimated that about 8 million pounds of the 24.7 million pounds listed as flotation agents should be listed as surface-active agents, in addition to at least 2 million pounds of standard types.

Paints. Approximately 45 million gallons of latex paint were used in 1955 (14). Such paints require surface-active agents as emulsifiers in the manufacture of the latex, as

TABLE V

Distribution by Application—1955

Application	Millions of pounds	%
Household cleaning	548	51.5
Petroleum	182	17
Concrete	75	7
Formulated cleaners	46	4.5
Textiles	30	3
Food	25	2.5
Other aqueous cleaning	25	2.5
Metal cutting	21	2
Chemical intermediate	20	2
Cosmetics	18	2
Agriculture	16.5	1
Dry cleaning	10	1
Other	42.5	4
	1,059	100

dispersants for the pigment, and as stabilizers for the paint. The estimate given is based on calculations assuming the 2% emulsifiers required for the latex, which is approximately 60% of the paint. The pigment dispersants are calculated at 0.5% of the total paint with stabilizers an additional 0.3%. It is expected that the amount of emulsifier used will decrease as polyvinyl acetate paints replace the butadiene-styrene types.

Paper Industry. The data we have been able to obtain in this field are probably low as it seems incredible that so little surfactant can be used for so huge a volume of material. A promising application appears to be the dispersing of pitch from certain types of wood. A large market would also exist for a surfactant which could retain its rewetting properties over long periods of time for incorporation into absorbent papers and towels. Small quantities are used as additives to the pulp that will be used in the manufacture of rayon.

Pesticides. The use of emulsifiers for insecticides, herbicides, and fungicides is growing steadily (7, 16). This field requires a variety of surfactant compositions, often a combination of anionic and nonionic types. Price is usually secondary to performance as special properties are normally needed.

Additional quantities of surfactants are used as dispersing agents in wettable powders. Small amounts are also used for reducing the dusting of some of the more toxic materials.

Petroleum. The petroleum industry uses large quantities of surfactants both in processing and in its finished product. The largest use is that of detergent additives to lubricating oils. Petroleum sulfonates have a large part of this volume, much of it captive production, but the variation in their composition has opened some market for the bottoms from alkylaryl sulfonate production. For some reason published figures vary widely (17, 1).

An interesting and growing application is demulsifying, which is the use of specialty nonionics to remove water in the crude oil brought up from the ground. Our figure for this application is a guess.

A new application of great promise is the introduction of suitable surfactants into producing wells in order to increase the rate of production. Also surfactants are being used in the water flooding, or secondary oil recovery, operation in an attempt to recover some of the two-thirds of the total volume of oils which remain in the field. The volumes of water used are so huge that even though the surfactant is used at the concentration of about 10 parts per million, the total requirements will be many millions of pounds if wide acceptance is obtained. At present cationics are used to break up formations caused by bacteria.

Plastics, Resins, and Rubber. This field was not studied adequately for accurate data. Surfactants are used as emulsifiers of polyvinyl chloride, but only a small proportion of polyvinyl chloride is produced by this process. Smaller quantities of synthetics are used for polyvinyl acetate. Most of the large volume plastics do not require surfactants in their production. There is a small volume of surfactants used as specialty plasticizers.

The rubber industry uses about 90 million pounds of emulsifiers, but this is almost entirely soap. This is not only for the lower price but for the ease of breaking the emulsion when it is desired to coagulate the emulsion solids.

Textiles. This is another large and complex field requiring a special study. The present figures were obtained by taking a study published previously (15) and modifying the volumes of surfactants by the ratio of each type of material processed in 1952, the basis for the previous study, and 1954, the latest figures available (9). This was then modified by an estimate of the change caused by the principal trend, that of replacement of fatty alcohol sulfates by nonionics.

Wallboard. Foaming agents are incorporated to make the wallboard more porous. Price is an important consideration so that lower-cost soaps will retain somewhat more than half of the market. The estimate is based on user's requirements.

A relatively small quantity of surface agent also goes into the manufacture of light-weight foamed plaster and concrete slabs.

Waxes and Polishes. The volume of industrial and household waxes and polishes is now approximately 500 million pounds per year. This requires large volumes of emulsifiers, but most of this is amine soap or soap formed *in situ.* As the preparation of these emulsions is an art, most present products are still based on historical formulations. This is a fertile field for research for formulations based on synthetics.

Analysis by Product Classification

The U. S. Tariff Commission's annually published data on the production and sales of surface-active agents is grouped to avoid disclosure of the production of any one company so the data are sometimes difficult to interpret. In Table VI we have listed our analysis of the 1955 report on surfactants, covering only those classes considered in our study. For comparison we have listed the totals obtained from the figures we used in Table IV.

TABLE VI

Analysis by Tariff Commission Classifications
(Millions of pounds)

Class	Tariff totals	Identified	Not accounted for
Cyclic			
Esters and ethers, non-sulf.	71.8	58.1	13.7
N-containing, non-sulf.	10.1	9.7	0.4
Sulfated and sulfonated			
Alkylaryl sulfonates	455.7	440.6	15.1
Lignin derivatives	79.6	78.7	0.9
Petroleum derivatives	124.5	176.5	....
Other	22.0	13.0	9.0
Acyclic			
Esters and ethers, non-sulf.	101.2	97.6	3.6
N-containing, non-sulf.	65.4	42.4	23.0
Alcohols and esters, sulf.	137.0	113.4	23.6
N-containing, sulfated	....	4.0	0.2
Other or unknown	4.2	29.0	....
	1,071.5	1,063.0	89.5

It must be noted that the amount identified includes surfactants not included in the Tariff Commission totals. Our work indicates a production of at least 1,152 million pounds.

As shown, we have accounted for over 91% of the total production. While this is a high percentage, it still leaves a substantial 89.5 million pounds unidentified. Some of this is material sold to the U. S. and local government units. Sales of finished products reported in the census of manufacturers to such units are included in our survey, but raw materials for direct use or for formulation are not included.

Similarly all exports are not included. We have not accounted for the export of any surfactants as produced. In addition, we have included a guess for the exports of the largest producer of laundry detergents but no estimates for other producers or other household products. Since calculations for household products are based on consumption figures rather than production, a significant portion of the 93.5 million pounds unaccounted for may be found here.

A third volume of use not included are the many applications requiring less than 100,000 pounds per year. Although each of these is relatively small, there are so many such applications that the total volume is undoubtedly several million pounds per year.

These three additional markets for surfactants probably account for practically all of the difference in most classifications except that of acyclic, N-containing, and nonsulfated. This difference is believed to be principally that of materials used as corrosion inhibition.

End-Use Distribution

It may be of interest to note the very different end-use patterns of some major types of surfactants. The figures used are taken from Table III and so do not include the modifications just discussed. Only major uses are shown.

TABLE VII

End-Use Patterns of Selected Surfactants

	AAS	FAS	APE	PS
Commercial laundry	....	4	....	....
Cosmetics	....	6	....	....
Formulated detergents	6	....	19	....
Household	(85)	(80)	(14)	....
Laundry	64	65	14	....
Dishwashing	16	20	....[a]	....
Scouring powder	5	....	35	....
Intermediate	....	....	....[a]	....
Metal cutting	....	....	....	11
Petroleum	2	....	....	82
Textile	....	....	13	....
Miscellaneous	7	5	19	7

[a] Combined as the uses are alternate.

Conclusions

This study emphasizes the differences in properties required of surfactants for various application, the large and growing number of uses requiring more than 500,000 pounds per year, and the constantly changing pattern of use, making most of the recent estimates of volume distribution obsolete.

For some time it has been customary to estimate the household market as 75–80% of the total. This study shows that this estimate is certainly high as household use is now probably only 50–55% of the total. This fact may be important in releasing our energies for the creative development of markets in the industrial fields. There is a rich potential market in such applications as ore flotation, agriculture, road building, and petroleum processing.

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Evaluation of Surfactants for Oil Field Flooding

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CRUDE OIL IN PETROLEUM RESERVOIRS occurs as a liquid distributed in the pore spaces of fine-grained sedimentary rock. Water is always present in the pores as a second liquid phase. On the average the pores are from 10 to 20 microns in diameter. Oil contained in an undeveloped field is usually saturated with hydrocarbon gas and is under considerable pressure. The first production obtained from wells in a new field is therefore the result of the release and expansion of dissolved gas. When this natural source of energy is depleted, flow of oil into the producing wells declines to a low rate or ceases altogether until finally continued operation becomes uneconomical. At this point in many fields it is not uncommon to find more than two-thirds of the original oil content still remaining within the pores of the reservoir rock. Unless some external source of energy is applied, this oil will remain uncovered.

One of the most common and most efficient external sources of energy used to supplement the natural reservoir energy and prolong oil production is water under pressure. Water may be injected into part of the existing wells, and the oil driven ahead of it may be collected in those remaining. The process of applying energy from external sources to increase oil production is known as secondary recovery. When water under pressure is the external source, the process is called water-flooding. Under ideal conditions, water flooding can about double the volume of oil produced. Nevertheless about one-third of the original oil in place still remains within the reservoir, unrecoverable by presently practical methods. It is estimated (1) that there are 194 billion barrels of oil in U. S. reservoirs which is not now economically recoverable. This is about five times the known recoverable reserves.

Surfactant Flooding

Aside from occasional gross inhomogeneities in oil reservoir rocks, the failure of water flooding to displace a larger fraction of the oil present can be blamed on capillary forces operating within the rock pores. These capillary forces are generally described in terms of the energies of the phase boundaries present, *e.g.*, the oil-water, rock-water, and rock-oil interfaces. The relationship between these energies controls such important factors as the degree to which water tends to displace oil from the rock surface and