Second place, G. K. Witmer, Battle Laboratories, Montgomery, Ala., with a grade of 99.44.

Again this year certificates will be awarded on the cottonseed and soyabeans series. The results are still too erratic on the peanut series to make the awarding of certificates feasible.

Crude Vegetable Oils

Six samples of crude vegetable oil were distributed by Dr. Richardson and his sub-committee: three each of cottonseed oil and soybean oil. A total of 73 chemists participated in the work, being graded in the case of cottonseed oil on free fatty acid, refining loss and refined color; however the bleached color was reported also. The collaborators were graded on free fatty acid, refining loss, and bleached color on the soybean oils. The results in general were very good, and the following men were awarded certificates this year for proficiency on this work:

First place, Analyst No. 19, C. A. Lathrop of Curtis and Tompkins Ltd., San Francisco, Calif., with a grade of 100.0.

Second place, Analyst No. 20, Edward G. Williams, The Edward G. Williams Laboratory, New Orleans, La., with a grade of 99.367.

In order to eliminate ties in this series a similar method was used to that described in the Oil Seed Series to recalculate the results without tolerances.

Drying Oils

The drying oil series handled by Francis Scofield has been handled on a somewhat more informal basis. There has been no charge to date for the samples, and the organizations participating have taken turns in mailing the samples. Further the analytical determinations made have been varied somewhat.

In all four sets of samples were sent out, and each set consisted of four samples each. Twenty-seven organizations participated, and reports were made on the determination of color, refractive index, specific gravity, acid value, and iodine value. On set No. 4 the Gardner Viscosity and saponification value were added and the specific gravity was deleted.

Tallow and Grease

A new sub-committee was set up in December 1948 to distribute and tabulate the results on check samples of tallow and grease. Due to significant price differentials in the price of these materials a poll of the membership indicated that there would be considerable interest in such a program. W. C. Ault of the Eastern Regional Laboratory acted as chairman of this sub-committee.

Two samples were sent out early in 1949, and the results have been tabulated and mailed to the collaboratories. Thirty-six laboratories participated in the work. Several additional samples were sent outside the country, but on account of custom difficulties the samples evidently were not received. Determinations were made on these samples for free fatty acid, FAC color, titer moisture, insoluble materials, and unsaponifiable. While the results were not too bad, certainly improvement is needed, especially in the reading of color. On sample No. 1, 10 chemists reported FAC 9; 14 chemists reported 7, and 10 reported 5. On sample No. 2, 11 reported FAC 17; 15 reported FAC 11B; 2 reported 19; 3 reported 15; and 1 reported 11A. While it is recognized that few analysts agree too well on FAC colors, these results were extremely varied.

Dr. Ault's report together with the tabulation of results on these two samples are available upon request. It is planned to continue this work next season.

I would like at this time to thank the other members of the Smalley Committee, Mr. Doughtie, Dr. Richardson, Dr. Ault, and Mr. Scofield for their fine cooperation and painstaking effort in handling their phase of the work as well as all of the sub-committee members for their assistance and guidance. T. C. Law and Law and Company in particular have contributed immensely to the success of the oil seed meal and oil seed work through their thorough and careful preparation of samples.

R. T. DOUGHTIE, JR.
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Soap Versus Synthetic Detergents*

FOSTER DEE SNELL, Foster D. Snell, Inc., New York, N. Y.

ON the retailers' shelves synthetic detergents stand side by side with soap in appealing for the consumer's dollar. They similarly compete in the advertising pages. Both appear in flake and bead form. Soap as yet has the bar field in the United States, but one synthetic bar is being test-marketed, another is nearly to that stage, and who can predict how many others are in the laboratory? In England synthetic bars have been sold for some time.

A Thumb-Nail History

The initial step in the development of synthetics was simple; replacement of the sodium carboxylate group of soap, -COONa, with one not so sensitive to hard water, typified by $-OSO_2ONa$. Appreciation of the fact that a polar-non-polar compound of sufficient chain length was needed with a proper degree of polarity on one end led to development of many sources of the polar groups. The difference between sodium stearate, $C_{17}H_{37}COONa$, and octadecane, $C_{18}H_{38}$, is only a carboxyl group. The end carbon of octadecane cannot be commercially oxidized to a carboxyl group. But there are many substitutions which can be made at the end of a hydrocarbon chain, either directly or by roundabout means. Typical of the commercial method is attachment of the aliphatic chain to a benzene ring, itself equivalent to a 4-carbon straight chain, followed by sulfonation. While the aliphatic radical will not sulfonate readily, the aromatic will. From that grew the replacement

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of hydrocarbon chains of fatty origin by those from petroleum sources.

The competitive synthetics may be classified as anion-active agents from petroleum sources, anion-active agents from fat sources, and nonionic agents —which rarely draw on fat stocks.

Petroleum Derivatives

Alkyl Aryl Sulfonates. Of the detergents based on petroleum, the alkyl aryl sulfonates are by far the most important and have now reached more than twice the production of all other synthetic detergents made in this country. Commercial examples are Nacconol—also branded as Swerl— Santomerse, and Oronite. These consist of the sodium salt of keryl benzene sulfonate, $RC_6H_4SO_3Na$, although in some brands toluene made from petroleum replaces benzene. The chain length of the alkyl group, R, should be an average of C_{11}-C_{14} which is about what is present in a close-cut kerosene fraction, hence the coined name of "keryl."

Kerosene may be chlorinated and reacted with benzene in the presence of aluminum chloride as catalyst, or the equivalent reaction may be carried out with an unsaturated hydrocarbon. After distillation of the reaction product *in vacuo,* the distillate is sulfonated to give a monosulfonate, which in turn is neutralized to give the sodium salt. Excess sulfuric acid left from sulfonation is partly separated and the balance neutralized, which gives in many processes a final product containing about 60% of organic detergent and 40% of sodium sulfate. For many uses this is built further to give a final product, usually containing 40% of organic compound and 60% of sodium sulfate, which has nearly the same detergent power as it would have if it were all synthetic organic detergent. When the detergent is intended for domestic sales, further building from the 60% of active agent is often made with other salts. Substantially pure active agent is also produced.

The manufacture of this type of product is not limited to large producers even now, and the trend is away from their doing the whole job. Rather the large manufacturer, usually an oil company, will carry out that step for which it is best equipped, the manufacture of the alkyl-aryl hydrocarbon. Then it will sell this in drum, ton, or carload lots to the sulfonators. The latter will carry out the sulfonation reaction, which parallels the step they have been applying with vegetable oils for years. The sulfonators then finish up the built product for sale. Availability of small drum driers and a small spray-tower unit makes this type of operation more readily feasible. Generally speaking, the final yield of built synthetic is over three times the weight of alkane purchased from the oil company; commonly it is calculated as 3.6 times.

Alkyl Sulfonates. The sodium alkyl sulfonates are an inexpensive type of detergent made from a petroleum fraction by reaction with sulfur dioxide and chlorine, followed by neutralization with sodium hydroxide. The formula may be written RSO_3Na in which R, the alkyl group, varies in chain length, with probably an average of C_{12}-C_{14}. Du Pont controls this field, and their main product of this type is MP 189. Alkyl sulfonates are much like alkyl aryl sulfonates but somewhat poorer detergents.

Economics. Without reciting the detailed costs it is evident that the raw materials are inexpensive; the steps are not unduly numerous and are suited to low-cost operation on a large scale. The raw materials are all available in reasonable supply. Currently the anhydrous active agent is more expensive than soap. When it is considered that building of the organic agent with inorganic salts is feasible to a level far beyond that usually considered for soaps, the cost of production of the consumer product is in the same range as, if not actually lower than, that of soap.

Oil and Fat Derivatives

Alkyl Sulfates. The alkyl sulfates were among the first synthetics made on a large scale and paved the way for the great broadening of the detergent field which has occurred since. These, sometimes termed fatty alcohol sulfates, reached commercial success in the 1930s. In the formula, $ROSO_3Na$, R represents an alkyl group having a chain length averaging about C_{12}, connected to an oxygen atom of the sulfate group rather than to sulfur as in the sulfonates. Coconut oil is the fat source most used, as having the desired average chain length. Examples are Orvus WA, Duponol, and Dreft. The oil is reduced to the fatty alcohol either by high-pressure hydrogenation with a catalyst, or by sodium reduction, the Bouveault-Blanc process. The alcohol is then esterified with sulfuric acid which in turn is neutralized with caustic soda, giving the final sodium alkyl sulfate. As with the alkyl aryl sulfonate, some sodium sulfate is normally produced as a by-product of manufacture. These synthetics not only can be built with inorganic salt in the way described for the alkyl aryl sulfonates, but they will tolerate even higher building. Thus usual practice builds to about 25% of active agent.

There is some preliminary indication that petroleum sources may in time supply part of this market by furnishing fatty alcohols. A Shell subsidiary in Britain produces secondary alcohol sulfates from petroleum, the end product being inferior to the U. S. fatty alcohol sulfates. In Germany both fatty alcohols and fatty acids have been produced from hydrocarbons, but at high cost. The hydrocarbons themselves are made by polymerizing the lower gaseous olefins, or from water gas by the Fischer-Tropsch synthesis. American refiners are in the process of building plants to produce such olefins, but fatty alcohols from this source will probably not be available for some years.

Sulfated Monoglycerides. One company has produced the sodium sulfated monoglycerides for commercial sale. They are somewhat similar to the alkyl sulfates in character and properties. The general structure is $RCOOCH_2CH(OH)CH_2OSO_3Na$, in which R is an alkyl group with an average chain length of about C_{12}. An example is Arctic Syntex M, present in Vel. The triglyceride is converted to monoglyceride by technics familiar to the food industries and then the sulfuric ester is formed. Again the fat stock used is normally coconut oil. Building is much like that with the alkyl sulfates. Instability in strongly acid or alkaline solutions results from the ester linkage.

Amide Sulfonates. An early type of synthetic detergent which has gone along steadily but not spectacularly is typified by the product of condensation of oleyl chloride with methyl taurine. The sodium salt, called Igepon T, has the formula $C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$. This type of product is in some properties a better detergent than the alkyl sulfates, but it is expensive both in terms of raw materials and in processing. Although various fatty materials may be used, oleic acid is most suitable to give a detergent for the textile industry where this class of products has found its major application.

Economics. The starting material is a fat in each case. The number of steps is greater than in production of soap and the anhydrous yield a little greater. Roughly the same materials are used. So the cost of the organic synthetic from fat is higher than for soap, if only because it is usually produced on a smaller scale. The higher tolerance to inorganic builders permits these to compete with the petroleum-derived synthetics.

Nonionic Detergents

These are either derived from a polyhydroxy alcohol or from ethylene oxide. The former are mannitol or sorbitol derivatives, usually esters with a fatty acid. They are relatively unimportant as detergents. The latter are obtained by addition of ethylene oxide to a long chain alcohol, phenol, mercaptan, amine, or fatty acid. Typical ethylene oxide derivatives are Triton X-100 and Glim. One which does not draw on fat stocks as raw material is even being used in commercial laundries on cotton goods. Incidentally one anion-active material is also making a splurge in that field.

The economics of nonionic detergents are briefly stated. They cannot be built with conventional builders. Ordinarily, at least half the finished weight is from ethylene oxide, which is currently valued at 15-16c per pound. The addition is made catalytically at low pressure to avoid explosive effects. Therefore they have to be efficient to compete.

Production

The following two condensed tables show production of limited classes of synthetic detergents. The 1945 figures are official, the 1947 were obtained from a canvass of the trade. Soap production, as reported from about 90% of soap manufacturers, was obtained from the Soap and Glycerine Producers' Association and is included for comparison.

Product	Production in lb.	
	1945	1947
Soap	2,859,000,000	2,792,000,000
Alkyl sulfates and sulfated monoglycerides	29,000,000	49,000,000
Sulfonated amides and sulfuric esters of amides	9,000,000	12,000,000
Total	2,897,000,000	2,841,000,000
Total synthetics	38,000,000	61,000,000

Detergents Based on Oils and Fats

Product	Production in lb.	
	1945	1947
Alkyl aryl sulfonates	65,000,000	150,000,000
Alkyl sulfonates	11,000,000	30,000,000
Total	76,000,000	180,000,000

Detergents Based on Petroleum

Figures show that soap production is tremendous in comparison with synthetic-detergent production, but that the latter is increasing rapidly, particularly for petroleum-based detergents. And in two years, while synthetics from fat sources increased 60%, those from petroleum increased at over double that rate. Information about nonionics is less definite. Total 1945 production reported was under two million pounds. It is believed that either of two plants will produce that much in 1948. But it is necessarily small as compared with the anion-active detergents.

As recently as 1940, the sales of synthetic detergents to the public could be considered as negligible. In the war years some products sold as synthetic detergents contained an amount of true detergent comparable to the amount of pepper and salt one puts on a steak. In 1948 for every five pounds of soap sold to the public there will be one pound of synthetic sold. And the peak has not been reached. Each of the three major soap companies has two brands which it pushes in competition with soap. Only two brands are believed to be currently based entirely on fat stocks for the organic detergent molecule.

Efficiency and Building

Generally speaking, the synthetic anion-active detergents built with sodium sulfate are good on all types of work except cottons. In hard water their increased efficiency is in sharp contrast to the decrease in effectiveness of soap. Actually in distilled water such a sulfate-built synthetic detergent is not as good as soap. The following table gives an idea of comparative effectiveness. Dispersing power is a linear measure of power to suspend oiled umber, which is to be published in detail later. Interfacial tension is against benzene containing 0.5% of oleic acid.

Detergent	Dispersing power	Surface tension dynes/cm.	Interfacial tension dynes/cm.
Tallow-coconut oil soap flakes	91	25.7	4.7
Sodium alkyl aryl sulfonate	9	31.9	2.6
Sodium alkyl sulfate	7	32.7	2.9

Comparative Properties of Soap and Synthetics, at 0.2% Concentration

Thus it appears that the striking difference is in dispersing power which can be translated as ability to deflocculate and suspend soil, to prevent redeposition.

The building with molecularly dehydrated phosphates and the addition of carboxyl methyl cellulose go a long way toward overcoming this deficiency of the synthetics for washing cotton goods. When properly built, synthetics can wash better than soap. Such building—initiated recently—is spreading rapidly, but is limited by the available supplies of the builders mentioned.

The Future

The first synthetic detergents were those based on fats and oils. Those which have appeared on the market in the largest volume are based on petroleum because the raw materials are low in cost as compared with fats and oils, and the supply is constant and dependable. At some future date it seems probable that most synthetics will draw on petroleum fractions and condensed gaseous olefins for hydrocarbon radicals.

The growth of use of synthetic detergents is not apt to diminish the soap market radically in the foreseeable future. It is apt to hold it static. In its field soap is low in cost and efficient. For example, it is improbable that any substantial part of the commercial laundry market will be lost to synthetics.

The first call on the fats and oils is for edible purposes. A short world supply appears probable for a few years ahead—how far ahead ties in with political problems and hoped-for improvements in standards of living, not nationally but internationally. These are beyond chemistry.

The present trend is to supplement our normal supply of soap with synthetics and to accompany that with the development of more and more applications for all kinds of surface-active agents. Synthetic detergents themselves are being studied with a view to bringing their general cleansing ability up to that of soap in soft water. This apparently can be done by special building. Combinations of anion-active agents with nonionics also show greater detergent ability than either one alone; the combination is not merely additive but is more—it is synergistic. Research activity in this field is still intense.

There seems to be little doubt that the percentage of the total detergent market retained by soap will decrease further. How much further is beyond guess, the rash guesses of a few years ago have already been exceeded. The trend away from natural products of agriculture or animal husbandry has been going on for decades. This competition of soap and synthetic detergents is but one small part of it. But in an expanding economy that does not predict that the soap industry will go into a decline. It merely suggests that in the economist's terms, it is becoming a mature industry.

Biological Synthesis of Fatty Acids[1]

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ALTHOUGH little is yet known of the details of the mechanism of the conversion of carbohydrate to fat, the problem has engaged the attention of investigators since about 1850 and is thus one of the oldest of biochemical studies. Previous to this date it had been assumed that body fat was simply derived from dietary fat. Impressed by the large amounts of milk fat continually secreted by the lactating cow on ordinary pasture, Liebig was led to believe that this fat must have been formed from carbohydrate in the diet. Soon after (1860) Lawes and Gilbert (1) performed their classical experiments at Rothamsted with oxen, sheep, and pigs in which careful balance studies of carbohydrate, protein, and fat left no doubt that body fat can be synthesized from dietary carbohydrate. Later studies by several investigators with many animal species thoroughly confirmed their conclusion. In shorter term experiments with the dog Morgulis and Pratt (2) observed, under appropriate feeding conditions, respiratory quotients much greater than unity, which would be required for the carbohydrate to fat conversion. In plants also there is abundant evidence for fat formation from carbohydrate. Seeds during ripening undergo a change from high-carbohydrate, low-fat content to high-fat levels. Studies with seeds included not only those which were still attached to the plant but also separated seeds in which there could be no doubt about the carbohydrate to fat transformation occurring within the seed. Respiratory quotients of 1.5 or greater have been noted during active oil formation.

The formation of fat in various microorganisms would seem to offer ideal test systems for study since the composition of the medium can be so readily controlled and since evidence for the precursor of fat synthesis might be obtained. Many yeasts and fungi synthesize large quantities of fat from relatively simple media. The many contributions in this field cannot be reviewed here, but classical among these investigations has been that of Haehn and Kintoff (3) with *Endomyces vernalis* in which it was shown that acetaldehyde, lactic acid, pyruvic acid, glycerol, aldol, and ethyl alcohol could serve as fat precursors. A strict comparison of their relative efficiency as precursors was difficult however because of different toxicities of the substances tested. A review of subsequent investigations with different microorganisms seems to show that in addition to glucose itself, pyruvate, alcohol, and acetate were the most active as fat precursors. There is little doubt however that the limitations of toxicity and permeability differences make this type of experimentation dubious for the selection of the probable immediate precursor.

Older Theories of Fatty Acid Synthesis

Hexose Condensation Theory: An early and obvious suggestion for the mechanism of fatty acid synthesis was that hexose units combined directly to form a C_{18} precursor of stearic and oleic acids. Emil Fischer (4) first proposed this theory and also postulated the mixed condensation of hexoses and pentoses to explain the occurrence of such acids as palmitic. The predominant occurrence of C_{12}, C_{18}, and C_{24} in nature has been offered as evidence for condensation of hexose units, but more direct evidence was lacking. Reichel and Schmid (5) and Embde (6) found that fructose was more readily converted to fat than other monosaccharides, and this has been offered in support of hexose condensation.

In considering biochemical reactions analogous to the type of reaction leading to carbon-to-carbon linking of hexose molecules, the reverse aldolase reaction comes to mind (see Figure 1). There is no experimental evidence for this reaction involving hexoses rather than trioses, nor for the existence of the highly hydroxylated intermediates which would result. The latter cannot constitute evidence against the hypothesis since intermediates are notoriously missing for the support of any theory of fatty acid synthesis or

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[1] Presented at 22nd fall meeting, American Oil Chemists' Society, New York City, Nov. 15-17, 1948.