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Discussion of Paper

Mr. M. L. Sheely asked if corrections to the data had been made for the iodine and thiocyanogen values of the unsaponifiable matter in the fats.

Dr. Barbour replied that he had not taken these into account in his analyses.

Mr. Sheely commented that he had found the thiocyanogen and iodine values of the unsaponifiable matter in some soap fats to be rather high.

Dr. Barbour remarked that he had used fats of very low unsaponifiable content and that any such correction would consequently be small.

Some New Detergents

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Soap

THE standard detergent of modern man is soap. In the chemical sense, a soap is a salt of a fatty acid. In the popular sense, the word applies also to any cleansing mixture containing true soap as its most important ingredient. Some authorities would broaden the term further and designate as soaps all organic compounds having soap-like properties. This broad meaning is not yet generally accepted; in the present paper, soap should be understood to refer only to salts of fatty acids or mixtures containing same as their principal ingredient.

The Search for Soap Substitutes

For a long time there have been efforts to modify the essential properties of soap and to find outright substitutes for soap.

There have been many futile efforts to obtain cheaper cleansing agents. For instance, one popular pastime has been to prepare detergents, alleged to be efficient, from cheap cereals or from cheaper earths. Chemically combining true soap with cheap hydrocarbons has been developed at least to the stage of effective work by the press agent. Considering the intrinsic inferiority of most soap substitutes in past experience and allowing for the fact that much of the fat for soap making is essentially a by-product and hence susceptible to wide adjustment in price, one is tempted to predict that the soap business will never be revolutionized merely as the result of the low price of a soap substitute.

More impressive than the search for cheaper detergents has been the search for materials which combine the desirable properties of soap with distinctive properties of their own. Long ago turkey red oil afforded industry a wetting and emulsifying agent which, unlike soap, is soluble in neutral and even acid solutions. Also turkey red oil forms in hard water a precipitate which is less flocculent and has less tendency to adhere to textile fibres than calcium and magnesium soaps. Thus turkey red oil went a long way toward overcoming the two outstanding defects of soap. Along with similar sulfated oils, misnamed sulfonated oils, it found many industrial applications and has even found some favor as a shampoo.

While the sulfated fatty oils are too low in cleansing value to be a serious threat against soap, they have until recently constituted the outstanding class of soap-like materials, and turkey red oil has been the inspiration of the chemist searching for new and better detergents.

Attempts to avoid precipitation of soap in hard water by merely incorporating sulfated oil in the soap were without marked success. Even sulfated oils are appreciably affected by the hardness of the water, due to their soap content. Free fatty acid, even if not present in the original fatty oil, is liberated by the action of sulfuric acid and subsequently converted at least in part to soap when the sulfated oil is neutralized.

Naturally there were attempts to develop sulfated oils free from soaps, both by keeping the carboxyl groups of fatty oils in an esterified state and by using oils containing no fatty acid from which soap could be formed. The search for new wetting, emulsifying, and cleansing agents increased, and within the past five years has become a general scramble. The patent literature already reflects the intensified effort, and is so voluminous that it is altogether impractical to survey any large portion of the field in a brief paper such as the present one. The existence of most of the proposed reagents is still confined to the laboratory or, very likely in some cases, to the printed page. Some of them, developed primarily for use in treatment of textiles, are being exploited commercially. Of these, two groups are of outstanding interest to soap chemists because they can really do the work of soap in addition to some things that soap cannot do.

Alkyl Sulfates

One class of interesting detergents consists of alkyl sulfates, for example, sodium lauryl sulfate. The principal method for making these involves the following three steps.

1. *Reduction.* The fatty acid radical of various fatty materials is reduced, e.g., by high pressure catalytic hydrogenation, with formation of the corresponding normal primary alcohol. For example, lauric acid or its ester yields lauryl alcohol.

2. *Sulfation.* The alcohol is sulfated to yield an alkyl sulfuric acid. For example, lauryl alcohol yields lauryl sulfuric acid, as shown in the equation:

$$C_{12}H_{25}OH+H_2SO_4=(C_{12}H_{25})HSO_4+H_2O$$

3. *Neutralization.* The alkyl sulfuric acid is neutralized to form the sodium or other salt of the alkyl sulfuric acid.

These alkyl sulfates were first developed commercially in Germany by H. Th. Böhme A.-G. A number of patents in the field have been granted in several countries to this company and to Deutsche Hydrierwerke. A still earlier patent application on the hydrogenation step had been filed in Germany by I. G. Farbenindustrie, and these three companies are understood to control jointly in Germany the manufacture and sale of wetting and cleansing agents consisting of the sulfuric acid derivatives of the higher alcohols corresponding to the fatty acids of fats and oils.

In the United States the E. I. du Pont de Nemours

and Company and The Procter and Gamble Company hold licenses from Böhme and Hydrierwerke for manufacture and sale of these same alkyl sulfates. To date, they have been sold mainly in the textile industry in this country as in Europe, but they have been marketed also in a small way to the household.

No one can safely predict how important these alkyl sulfates will become as detergents for general use. It will require years of practical experience to evaluate them accurately in comparison with the available soaps for various uses to which soap is put in the household.

Considered as soap substitutes, the most interesting property of the alkyl sulfates is their resistance to precipitation in hard water, a property particularly marked in the case of the derivatives of the unsaturated alcohols and of the saturated alcohols of 10 or 12 carbon content. Some of the heavy metal alkyl sulfates are more soluble than the corresponding sodium compounds, which, oddly enough, are in turn more soluble than the corresponding potassium compounds.

Magnesium lauryl sulfate, for instance, is very soluble in water, much more so than the freely soluble sodium salt. Also calcium lauryl sulfate is appreciably soluble. Consequently the hardest water has little or no adverse effect on sodium lauryl sulfate, which lathers and cleanses in sea water at least as well as in distilled water. This is truly a spectacular property.

Variations in the type of the normal primary alcohol produce about the variation in properties of the alkyl sulfates as would be predicted from a knowledge of the soaps of the corresponding fatty acids. Sodium octadecyl sulfate and sodium cetyl sulfate, corresponding to sodium stearate and sodium palmitate perform very well in hot water, but not so well in cold water. The sodium alkyl sulfates derived from the lower alcohols, corresponding to coconut oil soap, are much more soluble. Likewise the sulfates derived from unsaturated alcohols are quite soluble, like sodium oleate. All these types are being developed commercially, as well as mixed types. The unsaturated alcohols may be prepared by the reducing action of alkali metals and lower alcohols on fatty esters.

At present relatively little is known of the alkyl sulfate detergents from the higher alcohols other than the normal primary alcohols. Doubtlessly many investigators have tried to prepare the addition products of sulfuric acid and unsaturated petroleum hydrocarbons in the hope of obtaining valuable wetting and cleansing agents. Such a reaction might be expected to yield a considerable proportion of secondary alkyl sulfates. The rather scarce literature on this obvious idea is testimony of the difficulty involved, and perhaps an indication of some degree of honesty on the part of even the seekers of paper patents. Sulfation of wax alcohols has received considerable study but the available tonnage is not likely to make this source of any great commercial importance. At different times over a period of years it has been proposed to sulfate oxidized petroleum products, and several I.G. patents have proposed sulfating the unsaponifiable fraction of oxidized paraffin, which might be expected to yield a considerable proportion of secondary alkyl sulfates. At present commercial exploitation of the alkyl sulfates as detergents is practically limited to those derived from the higher alcohols obtained by reducing the corresponding fatty acids or their esters.

Acylated Sulfonates

Another class of new wetting and cleansing agents of more than average interest may, for lack of a better class name, be called acylated sulfonates. One type consists of the fatty acid esters of hydroxy sulfonates of low molecular weight, e.g., the oleic acid ester of sodium isethionate, the molecular formula of which is:

$C_{17}H_{33}—CO—O—CH_2—CH_2—SO_3Na$

Another type consists of the corresponding acid amides, in which the oxygen involved in the ester linkage is replaced by —NH— or —NR—. One of the simplest possible formulas for a compound of this type is the condensation product of oleic acid and a salt of amino isethionic acid or taurine, as follows:

$C_{17}H_{33}—CO—NH—CH_2—CH_2—SO_3Na$

Commercial wetting agents of both these types have been developed by I. G. Farbenindustrie. They have cleansing and sudsing power similar in a general way to those of soap or of the alkyl sulfates, and resemble the latter in resistance to precipitation by hardness. The molecular formula is capable of variations similar to those of the alkyl sulfates and many more besides. Years of research may be required to determine the effect of these variations in structure on the properties of the compounds, and also to determine their practical value as substitutes for soap in household and laundry use. At least the acylated sulfonates are a very interesting development in the detergent field.

Discussion of Paper

Mr. Richardson passed around some of the new detergents in bar form. On inquiry as to the retail price of the bars, Mr. Richardson stated that he was not sure of the price but thought it would be rather high. A 4-oz. package of Drift retails at 15c, he stated, a price sufficient to ensure that the new detergents will cause no dislocation of the soap business. On inquiry as to whether the new products are most efficient when used alone or in conjunction with fatty acid soaps, Mr. Richardson stated that when used with fatty acid soaps, their action is similar to Turkey red oil. They do not completely overcome the incompatibility of soap and hard water and so do not entirely prevent precipitation of curd. His conclusion was that the new detergents are more efficient when used alone than with fatty acid soaps.

British Guiana—Import Duties Increased on Certain Edible Oils; Modified on Copra

Ordinances approved by the Governor of British Guiana and published in the Official Gazette on November 17, 1933, increased the duty on edible oils of all kinds, except mustard oil and olive oil, imported into British Guiana, from $0.26 to $1.20 per imperial gallon, under the general tariff (from $0.13 to $0.60 per imperial gallon, British preferential tariff), and replaced the existing ad valorem duty of 33⅓ per cent, general tariff (16⅔ per cent, British preferential), on copra by a specific rate of $4 per 100 pounds, general, and $2 per 100 pounds, preferential tariff. A surtax of 30 per cent of the duty is collected in addition to the rates given above.

Louisville, Ky.—The Interstate Commerce Commission on Dec. 29 ruled that specifically labeled vegetable oil, including cottonseed oil, can be shipped on a transit freight rate basis.

The decision was made after several railroads operating in the South asked for a ruling on the vegetable oil rates at Atlanta, Chattanooga, Louisville, Memphis, Chicago, Cincinnati and Columbus.