Detergents in the Textile Industry*

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THE broad title "Detergents in the Textile Industry," covers both soap and the so-called synthetic detergents. At one time synthetic detergents were of such minor application they were segregated by a special title of their own, but nowadays the improved types warrant a place side by side with soap in the majority of textile scouring operations. The only remaining true differential between soap and synthetic detergents is the stability to hard water, acids, and metallic salts typical of the synthetic detergent category. For scouring under ideal conditions soap is still the best product while synthetic detergents can now be used to supplement soap in all other uses. We are rather in a fortunate position today in that we can trace development of synthetic detergents because we are discussing the textile field which actually first felt the necessity of "improved" or stabilized soaps and developed synthetics to the present highly specialized stage.

In looking back at the original attempts to overcome the shortcomings of soap, it is easy to see the various steps of research and application which led finally to development of all the synthetic surface active agents. The products which were intended originally to replace soap were found to have ideal wetting characteristics that have set some apart as high speed wetting agents; others have become softening agents for textile fibers; others again are used as pasting agents for dyestuffs or as level dyeing assistants. Some are confined to water sequestration, others to dye fixation. The complete gamut of textile products has thus emerged because of the original necessity of overcoming the shortcomings of the soap molecule. This in turn has permitted the correct use of soap in the operations for which it is most fitted, i.e., scouring, and has directed the use of the other surface active agents for the specialty applications for which there is still a growing need.

First attempts to overcome the deficiencies of soap were made by starting from the same fatty acids used in the manufacture of soap itself, reacting with sulfuric acid instead of saponifying. The resultant compounds when neutralized gave water soluble sulfonated oils, exhibiting some soap-like characteristics, but even though they possessed wetting and emulsification properties, they could by no means be termed soaps. When introduced in the market, however, they were actually called soap substitutes because they appeared to have wetting and emulsification properties, which are two of the requisites for a good cleansing agent. Their greater stability to hard water salts opened up a field of application which they have been able to maintain as pasting agents and softening agents.

Today some of these products have been improved to the point where they actually possess stability to most metallic salts and even to acid. One type is stable even in a boiling acid dye bath. Their lack of lubricating and detergent properties caused by the introduction of a polar group, SO_3Na to substitute for the —COONa group of soap, caused investigators to abandon the sulfonation of oils as the ideal medium of making synthetic soap, and it was not until the fatty acid chain was allowed to remain intact by condensation of the fatty acid itself with a sulfonated compound that a true "reinforced" soap was obtained. This material, available commercially under several names and known chemically as oleylmethyl tauride, is still today one of the best of all synthetic detergents and by coincidence is a true synthetic soap differing little chemically from soap itself in that it relies upon the same raw material and possesses only a different polar grouping. Its stability to hard water, metallic salts, acids, and high temperatures is outstanding. Its sudsing properties are comparable to those of soap, but its solubility is considerably superior even in the presence of salt.

To emphasize this point it is sufficient to consider that dyeing of direct colors on fabrics, carried out in a soap bath, gives excellent brightness of shade, and level dyeing properties are obtainable, but at the sacrifice of a great deal of color value as it is not possible to utilize Glauber's salt or common salt in the soap bath fully to exhaust the dyes themselves. The advent of this synthetic "soap," stable and soluble in salt solutions, has replaced soap to a considerable extent for such applications.

A FEW decades ago textile mills purchased soap as the only surface active agent used. In recent years the writer has not seen one single textile mill that does not use at least one synthetic surface active agent, nor has he seen a textile mill that does not use soap.

The controversy, soap vs. synthetic detergent, goes on unabated in other industrial fields where detergents other than soap are still, relatively speaking, new, but in the textile industry the variety of applications has necessitated the quick rearrangement of the specific surface active agent for each use.

In considering soil removal from textile fibers, oils, waxes, greases, etc. are thought of in direct association with mechanical dirt. Such a combination is readily removable by soap or by synthetic detergents. This soil combination is not the same as the mechanically adhered dry dirt type that must be removed in laundry practice. The synthetic detergent types will not remove this latter type of soil, and this is one of the reasons that ardent soap enthusiasts condemn the synthetics, and rightly so. Unfortunately their rejection of synthetics is extended to fields where such soil conditions are no longer typical.

There are many points to be carefully considered in the evaluations of detergency besides the emulsification properties, decrease in interfacial tension, dispersion effect, and redeposition factor, and these are:

Nature of soil
Type of material to be scoured
Water (mineral salt content)
Type of detergent (ionization)
pH of solution
Solvent action of detergent solution
Selective removal of some mineral oils by oil soluble detergents.

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Elimination of one of these points or the excessive emphasis on one or two of them only, can lead to a great deal of false information or erroneous conclusions.

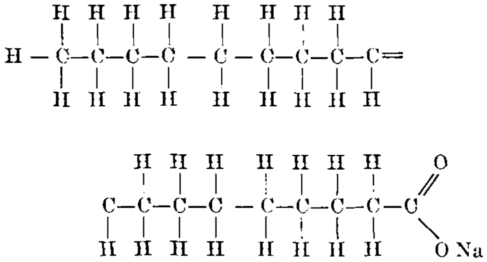
The success of many of the better synthetics in one field should not prove that any synthetic will outperform soap. The recent highly publicized campaign surrounding the addition of carboxy methyl cellulose to synthetics in order to outperform soap is the definite admission that soap alone is superior to synthetics in the laundry field. This is a point which was controversial for years, and its settlement has not added luster to the synthetic detergent claims. From recent work it appears that carboxy methyl cellulose improves the detergency mainly of the alkyl aryl and alkyl sulfonates which were always known to be among the poorest of the detergents in the laundry field. The lack of a suitable method of laboratory standard evaluation of detergency contributes greatly to the confusion that exists in the entire field of detergency. The improvements available for use in soap by incorporating builders or water softening agents possessing, if not true detergency, at least synergistic effects are often overlooked by synthetic detergent manufacturers. The use of fluorescent dyes which increase the whiteness effect of fabrics seems to offer more advantage to the synthetics. The soap industry has given a great impetus to these new products.

Fortunately in the textile field we are dealing with materials, soils, water, and processes that are well defined and, if not exactly controllable, at least well investigated. Certainly over a period of 20 years there has been ample opportunity to make the necessary practical textile mill trials and compile a vast amount of information on all fibers (wool, cotton, and synthetic cellulosic) in all stages of processing whether fiber, yarn, or fabric. The short scouring operations for rayon contrast to the long scouring times for cotton and to the strong alkali absorbing characteristics of wool above the iso-electric point or of acid below; different scouring techniques are thus employed.

Structure of Detergent Molecules

Detergent molecules possess the general characteristic of all surface active agents and are composed of a hydrocarbon chain which is the hydrophobic, non-polar portion and a solubilizing polar grouping. The balance between these two opposites determines the behavior and solubility of the resultant product. The hydrophobic or water-repelling portion is free to attach itself to other hydrophobic products while the hydrophilic or water-friendly part will always tend to be attracted to water. The concentration at the surface of water or the interface of water and oil explains the wetting and emulsion properties of the final surface active agent. Soaps typify all such products of the detergent type; they possess a long hydrocarbon chain (C_{12}-C_{18}) with one terminal —COONa— water soluble group. For instance, the non-polar chain attaches itself to oil, and the total is floated away or emulsified in the water because of the polar group. The longer the fatty chain, the higher the detergency.

Typical of soaps used in the textile industry is sodium oleate. Its molecular structure is



which can be considered to concentrate at the water surface or orient at an interface of water-oil.

Unsaturated fatty acids have better solubility than saturated types and are used mainly on rayon yarns and fabrics. The titer of oleate soaps 3°-10°C. is considered advantageous for delicate fibers.

The longer the chain, the higher the degree of saturation, the greater the degree of absence of hydroxyl groups all mean lower solubility and in the textile industry are interpreted correctly as better scouring, better fulling, and greater economy as well, hence the popularity of the higher titer tallow soaps (41.5°C.). Synthetic detergents derived from fats, such as the true sulfonate oleylmethyl tauride

$$C_{17}H_{33}CO\ N(CH_3)\text{—}CH_2CH_2SO_3Na$$

and the sulfated alcohol

$$CH_3(CH_2)_{10}\ CH_2\ OSO_3Na$$

are, chemically speaking, no more synthetic than soap and differ from the latter solely in the substitution of the stable polar group —SO_3Na for the —COONa. Their lime salts are soluble and effective in contrast to those of soap. These synthetics possess all the properties of soap under normal conditions and function well in hard water, acid, salt, or dyeing liquors.

Perhaps more truly synthetic are the alkyl aryl sulfonates typified by dodecyl benzene sodium sulfonate,

$$C_{12}H_{25}(C_6H_4)\ SO_3Na$$

derived from petroleum, and possessing excellent stability to acid, alkali, and hard water. They are actually a chemical modification of the well established plain wetting agents of the alkyl naphthalene sulfonate series, but the longer alkyl chain (dodecyl in place of butyl) imparts the high scouring properties while the wetting character is well maintained. The necessity of adding large quantities of organic salts as electrolytes in order to obtain full detergency can be obviated by using tetrasodium pyrophosphate, which is very effective where alkali addition is permissible. All the above types including the sulphated alkyl aryl poly ethers and several other sulphonics are anionic, as in soap, and are used extensively alone or in conjunction with soap throughout the textile, dyeing, and finishing industry. They are satisfactory in kier boiling of cotton, neutral and alkaline dyebaths, acid dyeing of wool, and to aid penetration and leveling. In continuous open boil-off baths for spun rayon these can be used in hard water without scum or stains developing on fibers. They represent the largest group of detergent other than soap, and the multitude of products and trade names on the market actually create difficulty of selection.

THE reverse charged soaps or cationic detergents based usually on quaternary ammonium compounds are increasing in importance and although soap-like in appearance are, generally speaking, of poor detergency, but have found use as softening agents on cellulosic fibers because of the monomolecular layer of large cation oriented on the negatively charged cellulose. An example of a quaternary is the alkyl ($R=C_8-C_{18}$) dimethyl benzyl ammonium chloride which ionizes as reverse charged material having the large part of the molecule in the cation. These products will precipitate in the presence of soap and the other anionic detergents mentioned above and, furthermore, cannot be used during dyeing. Their application is confined to aftertreatment of yarns and fabrics. Some of the better scouring types are used in acid scouring bath of wool under certain special conditions.

Far more important as detergents and of growing supply are the new non-ionics which have all of the advantages of the true detergents coupled with stability under all textile conditions. They furthermore possess very low affinity for fibers and therefore have remarkable rinsability and high economy. The alkyl aryl polyglycol ethers

$$R\,C_6H_4O(CH_2CH_2O)_xH$$

resemble the soap molecule in long chain structure and also the alkyl aryl types, but there is no terminal polar grouping. The low cost of these types and the high scouring efficiency permit actual money value at today's market against the best tallow soaps in wool scouring, where curtailment of alkali in the rinse is important. Their action in peroxide bleaching baths, where they act as wetting agents and later as detergents, is of real value in continuous bleaching of fabrics. The same advantage is noted when they are used as wetting agents in desizing baths; they show no harmful action on the enzyme and later are present to perform the scouring function.

The use of non-ionic detergents in sulfuric acid carbonizing of wool, where wetting at low temperatures of cellulosic materials and minimum substantivity for wool are important factors, has been well established. The high stability of non-ionics in sulfuric acid also permits use in the popular parchmentizing finish for cotton fabrics known as the Heberlein process. The compatibility of non-ionics with cationic compounds opens the field to combination products possessing detergency and other specific uses such as mildew-proofing and mothproofing.

Another excellent example of non-ionic-cationic combinations is in urea-formaldehyde resin impregnation baths where the cationic softening agent acts as a lubricant and plasticizing agent for the resin and the detergent functions as a penetrant and later acts as a scouring agent for the uncured resin and catalyst.

Soap and synthetic detergents may be amalgamated into one group as far as the textile industry is concerned, and the correct selection of synthetic or soap will be made more readily once the exact facts are recognized.

☆ ☆ ☆ ABSTRACTS ☆ ☆ ☆

Oils and Fats

Edited by
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THE COMPONENT FATTY ACIDS AND GLYCERIDES OF DHUPA FAT. M. N. Baliga and M. L. Meara (The Univ. Liverpool). *J. Soc. Chem. Ind. 68,* 52-4(1949).

THE COMPONENT ACIDS OF SOME SEAL BLUBBER AND LIVER FATS. T. P. Hilditch and S. P. Pathak (Univ. Liverpool). *Biochem. J. 44,* 218-24(1949).

DEFATTING BONE LIQUOR FOR PREPARATION OF STANDARD GLUE. V. Smirnova and L. Zueva-Vniemp. *Myasanaya Industriya 1948,* No. 2, 85-7. Glue liquor contg. 0.02% fat, or 3.5% on the dry basis, was defatted by means of a dairy type centrifuge. Significant fat removal occurred when the speed was over 2,800 r.p.m. When the temp. of the liquor was 80°, 79.5% of the fat was removed, at 55-60°, 59.6% was removed. A system for processing bone glue-liquors was presented.

DETERMINATION OF C^{14} IN FATTY ACIDS BY DIRECT MOUNT TECHNIC. C. Entenman, S. R. Lerner, I. L. Chaikoff, and W. G. Dauben (Univ. California, Berkeley). *Proc. Soc. Exptl. Biol. Med. 70,* 364-8(1949).

BELLIER VALUE. A. Lacerda. *Rev. soc. Brasil. quim. 16,* 153-63(1947). The method is modified so that methanol is substituted for ethanol in the saponifying solution.

CANADIAN ERUCIC ACID OILS. III. SHORTENINGS FROM RAPE AND MUSTARD SEED OILS. H. J. Lips, N. H. Grace, and S. Jegard. *Can. J. Res. 27F.* 28-34(1949). Processed rape and mustard seed oils were hydrogenated at 50-lb. pressure and 284°F., using a commercial nickel formate catalyst, and were deodorized for one hour at 464°F. The stability of the hardened oils compared favorably with that of a standard commercial vegetable shortening. Taste panel tests indicated that both the rape and mustard shortenings were as satisfactory as the commercial reference material for the preparation of pastry and doughnuts. Special study of the rape product showed that it could be plasticized, and it gave good results in baking volume experiments.

MECHANISM OF FAT SPLITTING. L. Lascaray (Vitoria, Spain). *Ind. Eng. Chem. 41,* 786-90(1949). Comparison of experimental results obtained by fat splitting in an autoclave and by the Twitchell process shows the similarity of the reaction mechanism in both. The reaction rate increases with temperature and with amount of reagent, and changes with its nature, and the reaction is limited only by the ratio of fat to water. Fat hydrolysis is mainly homogeneous because an appreciable amount of water is dissolved in the oil phase. The splitting reagents increase the solubility of water in the oil phase and make this water more active by liberating hydrogen ions in it. Action of splitting reagents is due to their highly hydrated and ionizing functional groups.