

# Synthetic Detergents in the Soap Industry<sup>1</sup>

H. C. BORGHETTY and C. A. BERGMAN, Organic Chemicals Division,  
General Dyestuff Corporation, New York City

SINCE the successful introduction of synthetic detergents some 20 odd years ago, there has been an ever expanding market for these products, particularly in the post-war years. Although their original development and application was in the textile industry, recently there has been phenomenal growth in many other industries.

One of the largest markets to develop has been the household package field, where these products are consumed in the numerous cleansing jobs in the home. This market has been captured by the large soap manufacturers, who fully realized the value of synthetic detergents, in place of soap, for light household use in hard water areas. They also capitalized fully the superior cleansing and rinsing properties of synthetics for dishwashing and hair shampooing in areas of any water hardness.

The recent introduction of builders such as carboxy methyl cellulose, polyphosphates, and fluorescent optical brightening agents, has permitted the vast development of the "built" synthetic detergent for heavy duty package household products. Our paper is concerned with this field, and the authors will endeavor to show that soap, if correctly built, can also benefit greatly by the use of synthetic detergents. Possibly the pendulum has already swung too much in favor of built synthetics, which often are so heavily built that they are really alkalies disguised as synthetic detergents and as such are often harsh and harmful to the skin and to textile fibers.

From our investigation it appears that there are three main markets divided by the degree of water hardness:

- a) Soft and medium hard water or Atlantic Coast area, where pure soap or slightly modified soap holds its original market excepting for dishwashing where straight neutral synthetic detergents are best.
- b) Extremely hard water, or far Western area, where synthetics easily outperform soap and where there is a tendency evident to use water softening equipment.
- c) An intermediate or Midwestern area, where the water is medium to hard and where there is a field for both built soaps and built synthetics.

A logical desire to make a universal synthetic product that would perform well in all three areas should be somewhat toned down by the economics of the fatty acid market, which would react sharply to a drastic loss of business. One must also consider that any synthetic detergent, in order to clean well, must be heavily built and thus departs too much from the original mildness and neutrality so that the consumer might eventually object.

LET the next consideration be the intermediate market c), where it is felt that the struggle between soap and synthetic detergents will occur. It is felt that combinations of soap, synthetics, and builders, can compete with heavily built alkaline synthetic detergents. Combinations of synthetic detergents with soap have not appeared on the market

and, from all indications, have not been given much consideration.

If one looks back a moment into the textile industry, numerous places are found where soap and synthetic detergents are used, alone and together, effectively and economically. In this industry confusion does not exist as to where each or their combination is best applied. A specific example is the use of non-ionic detergents in continuous raw stock wool scouring. Here soda ash acts as the principal cleansing agent and builder by the partial formation of soap by reaction with wool greases. The synthetic acts as detergent and rinsing agent. In this example it will be noted that the textile industry is not particularly interested in the volume or stability of foam. When we consider products for the retail market however, a different condition exists. Here quantity of foam, persistency of suds, opacity of the bath, and other factors are important.

Soap, when applied under ideal conditions, still seems the best detergent or washing agent for laundry use. It is the cheapest and also offers the best money value. It may be asked, "Why not build soap more extensively and, by so doing, increase its efficiency in hard water areas?" This idea was carried out to a limited degree by the Army and Navy Departments during the war with their salt water bar soaps, which possessed good detergency but poor foam.

The packaged synthetics have been particularly successful in hard water areas where soap fails in the rinsing cycle. When soap is used in sufficient quantity in hard water, it will disperse the lime soaps and curds formed. However when large volumes of hard water are introduced during rinsing, the system breaks down, redepositing lime soaps.

Soap itself is a water softener, and it actually removes the lime salts by forming the insoluble lime soaps. An excess of soap functions by dispersing the precipitation while a further excess of soap is then free to develop a good suds and to clean because it is now in softened water. The presence of the dispersed portion is not a hindrance to cleansing properties. At 20 degrees water hardness it requires 2.5 pounds of soap per 100 gallons water before lasting suds are obtained.

One of the old arguments of soap salesmen against synthetic detergents was based on this fact, that soap was such a good dispersant for its own precipitated metallic salts that a simple excess would eliminate all troubles. While this is quite true, it is offset however once the rinse water is brought into contact with the excess of soap and consumes it, thus redepositing the lime soaps back in the bath on all the fabrics.

Synthetic detergents of the sulfonated type are not actually water softeners. Their lime salts are soluble even in large excesses of metallic salts, and thus they foam well in waters of all hardness. Non-ionic synthetic detergents are not affected in the presence of metallic salts. It naturally follows that these synthetic detergents require no excess when used in hard water areas, thus allowing them to show considerable

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economy over soap. Attempts made to use synthetic detergents as dispersing agents for soap in hard water unfortunately failed because the foaming characteristics of both soap and detergents disappear. This phenomenon is caused by the change in colloidal conditions of the system.

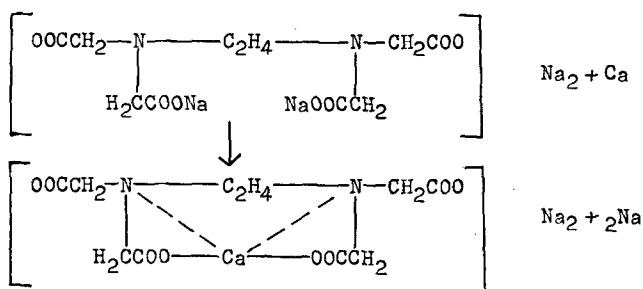
THE use of soap and polyphosphates in combination would appear to be a better approach to the problem, but such is not actually so because the water softening phosphates protect the soap only when there is no excess of hardness. The moment the rinsing cycle commences, the entire system precipitates in like manner to where an excess of soap has been used to redisperse precipitated soap. One advantage of this polyphosphate method however is that it makes possible a clear soap solution in hard water and an initial good cleansing. It is important of course to choose a polyphosphate that is heat stable, so that sequestering properties are not lost during dissolving of the soap solution.

The primary function of a synthetic detergent, when used in soap, is its ability to disperse lime soaps. Synthetic detergents vary greatly in this respect. A simple, reliable, and efficient method for evaluating lime soap dispersing properties is known. This test is based upon measuring the amount of synthetic detergent necessary completely to disperse a given amount of an insoluble calcium soap. A detailed description of this test is appended to this paper. Suffice it to say here that the smaller the quantity of synthetic detergent needed to disperse the calcium soap, the more efficient the agent.

We would like to cite a few typical figures for various well-known synthetic detergents. A 32% active Sodium Salt of Oleyl Methyl Tauride requires 15-20% on the weight of soap. A 100% active Polyethylene Oxide Condensate requires 3-5% on the weight of soap. A 40% active Sodium Alkyl Aryl Sulfonate requires 80-85% on the weight of the soap. An 85% active Alkyl Benzene Sulfonate requires 40-45% on the weight of soap.

The secondary functions of synthetics that have to be considered are the solubilizing effect on the soap itself and on the soil, aid in emulsification, and the stability to minerals in the water. An example of soap solubilization is evidenced when non-ionic detergents are added to high-titer type soaps to give the effect of low titer.

The question often comes up about the difference between lime soap dispersing power and sequestration. Agents like the Sodium Salt of Ethylene Diamine Tetra Acetic Acid are sequestering agents. They function on a molecular ratio basis, forming a chelate (ring structure) with calcium or other divalent ions.



Chelate Formation

When present in sufficient quantities, they soften water. The polyphosphates, which have the advantage of low price, function in a similar manner forming linear complexes. However, these complexes are not as stable as the ring structures and tend to hydrolyze and break down.

The lime soap dispersing agent does not soften water. It suspends and deflocculates insoluble soaps, keeping them in fine dispersion and in a rinsable condition. Its action is not governed by the degree of hardness of the water, and therefore, if present in soap during the rinsing, it will continue to function whereas the polyphosphate system breaks down. With the above information as a background, our laboratory conducted a considerable amount of work, based upon ternary systems consisting of soap, synthetic detergent, and complex phosphate, to learn whether soap could be built to be more effective in water of low and medium hardness. Tetra Sodium Pyro Phosphate was selected as the water correcting phosphate because of its desirable properties for admixture with soap. The soap used was a neutral pure tallow soap type. Synthetic detergents used were:

- 32% active Sodium Salt of Oleyl Methyl Tauride
- 100% active Polyethylene Oxide Condensate
- 85% active Alkyl Benzene Sulfonate

Detergency and foaming characteristics were the principal observations, and our studies were conducted in water of 150 and 250 p.p.m. hardness. Previous experience has shown the built synthetic detergent to be more satisfactory than built soap in water of over 250 p.p.m. This becomes evident when it is considered that the amount of polyphosphate to be incorporated in the soap becomes very large (over 25%) to correct higher degrees of water hardness. Detergency tests were made on Soil Cloth (G.D.C. No. 26) and were run in a Tergometer (at 140°F. for 20 minutes, at a speed of 60 r.p.m.). Foam tests were made by the Ross-Miles procedure.

Persistency of suds was observed during the detergency tests. It is felt that persistency of suds is more important than volume of initial foam since this is the indicator to the layman that the bath is still active. All ternary mixtures contained 25% Tetra Sodium Pyro Phosphate as this quantity was needed to correct the water hardness during the washing cycle. The balance of the mixture consisted of soap and synthetic detergent. For example:

- 25% Tetra Sodium Pyro Phosphate (or other polyphosphate)
- 15% Synthetic Detergent
- 60% Soap

100

#### Detergency Observations

*In Water 150 p.p.m. (0.25% Total Solids Concentration).* Oleyl Methyl Tauride mixtures produced between 30-40% increase in detergency efficiency over straight soap.

Alkyl Benzene Sulfonate mixtures produced between 0-15% increase in detergency efficiency over straight soap.

Polyethylene Oxide Condensate mixtures produced 20-40% increase in detergency efficiency over straight soap.

*In Water 250 p.p.m. (0.25% Total Solids Concentration).* The deterative action of the straight soap fell off considerably (45%) whereas the ternary mix-

ture maintained about equal detergency efficiency (range -5% to +40% increase). When the total solid concentration was raised 0.4%, the general pattern remained the same except that the detergency action of the straight soap increased in the 250 p.p.m. water. This was to be expected. However when one considers that in actual use the rinsability would be very poor and lime soap deposits would form on fabric and machine, it loses its value.

#### Foaming Observations (Ross-Miles Procedure)

*Water 150 p.p.m. (0.25% Total Solid Concentration).* Foam tests of the initial foaming solutions show, on the average, one-half the amount of foam as the straight soap. If we consider this for the various classes of detergents, we find that the alkyl aryl was best, followed by the ethylene oxide condensate, and then the oleyl methyl tauride.

*Water 250 p.p.m. (0.25% Total Solid Concentration).* Here the same general pattern exists for the combination of soap, synthetics, and polyphosphates. However the foaming ability of the soap in waters of 250 p.p.m. was greatly reduced, being only 30% as efficient as when tested in waters of 150 p.p.m., a decided drop.

When tested at 0.40% concentrations, the straight soap regained its foaming properties in water of 250 p.p.m. However, as mentioned previously, the rinsing properties under practical conditions would be poor in water of this hardness. Likewise the foaming properties of the mixtures of soap, synthetic, and polyphosphates increased at the 0.40% concentration.

Persistency of suds was observed during *all the detergency tests* and was rated good to very good, with the exception of two concentrations of polyethylene oxide condensates. This was in water of 250 p.p.m. at 0.25% concentration (total solids), and in this case it was rated fair.

In formulations such as have been discussed soap has been depended upon to do the major share of the cleaning job. The complex phosphate has the role of a water-softening agent and controls the foam and allows the soap to function at full efficiency in the hard water. The synthetic detergent functions as a lime soap dispersing agent, particularly during the rinsing cycle, to prevent deposits of insoluble soap from forming on the fabric.

Looking at the problem from this point of view, it becomes apparent that there is a limitation on the amount of complex phosphate and synthetic detergent that can be incorporated in the soap if there is going to be sufficient soap present to maintain good detergency action. In these tests 25% Tetra Sodium Pyro Phosphate was used as this much is needed for correction of the hard water. The amount of synthetic detergent necessary depends on its efficiency as a limesoap dispersing agent. If only 5% synthetic is needed, on the weight of the calcium soap, to disperse it, this amount should be incorporated in the product. If tests show 15% is needed, proportionately more will have to be used.

#### Conclusion

It is the opinion of the authors that much can be done to improve the efficiency of soap in hard water

by building it on a ternary system, which will make it more competitive against built synthetic detergents in areas of low and medium hard water. This appears to be particularly advantageous because of the present low prices of fat and greases and the large stocks that are available today.

#### Lime Soap Dispersion Test

The lime soap dispersion test measures the ability of auxiliaries to disperse insoluble metallic soaps.

*Object:* To find the minimum amount of the auxiliary necessary to disperse completely the insoluble metallic soap, calcium oleate.

*Reagents:* Distilled water is used throughout. U.S.P. sodium oleate 0.5 g./100 ml. of solution. Auxiliary to be tested 0.25 g./100 ml. of solution. Hard water 60% hardness from calcium and 40% hardness from magnesium, the total of the two being 1 g./l.—calculated as  $\text{CaCO}_3$  [= 70° English hardness (Clark)].

*Procedure:* (Carried out at approximately 77°F.) Five ml. of the sodium oleate is pipetted into a test tube and an arbitrary amount of dispersing agent (5 ml. is a convenient starting point) is pipetted into the test tube followed by 10 ml. of the hard water and enough distilled water to bring the total volume to 30 ml. The test tube is then stoppered and inverted 20 times, being returned to the starting position each time. After the test tube has been allowed to stand for 30 seconds, the condition of the lime soap particles is observed.

If a coagulated precipitate appears with clear solution between the clumps, it is obvious that there is not enough dispersing agent present to disperse the lime soap. As increasing amounts of dispersing agent are employed, the coagulum will become distributed throughout the tube. Just before the end point contents of the tube become translucent and at the end point there are no longer any large clumps present.

*Calculation:* The amount of dispersing agent is expressed as percentage of the weight of sodium oleate employed in the test.

Therefore by dividing the weight of dispersing agent required to disperse the lime soap by weight of the sodium oleate used and multiplying the answer by 100, the percentage of lime soap dispersing power is obtained.

NOTE: The weight of the sodium oleate used is constant, i.e., 5 ml. of a solution containing 0.5 g./100 ml. which equals 0.025 gram of sodium oleate is used in every case.

$$\% \text{ Lime Soap Dispersing Power} = \frac{\text{(grams of dispersing agent to disperse lime soap)}}{0.025 \text{ (weight of sodium oleate)}} \times 100$$

e.g. It requires 6 ml. of an auxiliary to reach a satisfactory end point in the test.

1. Six ml. of the 0.25% solution of the auxiliary = 0.015 gram.
2. The weight of sodium oleate used = 0.025 gram.
3. Therefore:

$$\frac{0.015}{0.025} \times 100 = 60\% \text{ lime soap dispersing power.}$$

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