Synthetic Detergent Raw Materials

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HAD I been called upon to discuss this topic 18 to 24 months ago, our discussion would have centered on one topic, the shortage of almost everything! As I am sure you all know, barring a world-wide conflagration, there is no need to contemplate a shortage of synthetic detergent raw materials during the next five years, assuming that the general pattern of end-product composition remains essentially unchanged.

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Expansion of production capacity has been actively advanced by the basic industries involved, with the result that a rate of sale about 30% over the first six months of 1952, or about 1,100,000 tons a year, could possibly be generally supported at this time. Important materials could actually be provided at about twice the present rate. Let us examine the basic structure of the synthetic detergent industry to determine just what factors are involved.

To appreciate fully the situation regarding raw materials, one should look back about 25 years to the introduction of their line by I. G. Farbenindustrie. Some of these products were derived from fatty acids and amino sulphonic acids. For instance, oleyl chloride and methyl taurine were condensed to yield:

$$CH_3(CH_2)_7CH = CH(CH_2)_7 - CON(CH_3) - CH_2CH_2SO_3Na$$

Another method involved reacting fatty acids with monoethanolamine, followed by sulphation and neutralization. Yet another approach was to condense a fatty amide with ethylene oxide, forming an amide-alcohol, which could be sulphated and neutralized. These products were relatively costly, compared with soap, and it was felt that the only commercial justification for them was in applications of an industrial nature where their superior properties would justify a marked premium.

Following closely upon the introduction of these products came the so-called Gardinols, salts of fatty alcohol sulphates, which exhibited good detergent, foaming, and rinsing properties and seemed well suited for both technical and household applications. However, as introduced, they were unsuited for heavy duty soil removal from cotton fabrics. Nevertheless they were sold at about 35% active concentration, the balance being largely sodium sulphate, in selected areas in the United States, and they met good acceptance in the household field. The principal manufacturing problem was the reduction of coconut oil with metallic sodium. This was costly.

Soon after the Gardinols appeared, the introduction of the Nacconols occurred. These products were based on raw materials, which were then cheap and abundant: benzol, kerosene, chlorine, sulphuric acid, and caustic soda. A so-called keryl benzene was produced by the Friedel-Krafts reaction, the alkylate was sulphonated, and then neutralized with caustic soda. Despite some problems with odor, which were gradually minimized, the new materials found a ready and expanding market, essentially in the industrial field.

Another important development was the so-called Horne-Reed reaction, which is employed for the sulphonation of paraffinic hydrocarbons, such as Fischer-Tropsch distillates (Kogasin) and special kerosene fractions produced from selected crudes by processes assuring aromatic-free products. In the Horne-Reed process long-chain sulphonyl chlorides of random composition are produced by the reaction of SO_2 and Cl_2 in the presence of ultraviolet or other actinic rays. Aliphatic sodium sulphonates are produced by hydrolysis with hot sodium hydroxide or carbonate. The detergent properties of such products are not high. Wetting characteristics are generally good.

POSSIBLY the most important developments in alkylation occurred as the result of the need for high quality aviation gasoline stocks. The result was the introduction of hydrofluoric acid as a catalyst in large-scale manufacturing operations. Under the Tinker patent HF was employed for the production of alkyl aryl hydrocarbons for use as detergent bases. As developed during World War II by the California Research Corporation, this involved the use of polypropylene and benzol. The manufacturing specifications covering the polypropylene were rigid so as to exclude undesirable material. Polypropylene is potentially available from several large sources, provided the installations are operated under the established conditions. No shortage exists, nor is one anticipated.

The pattern of anionic detergent base employment has varied on the basis of both economic and technical considerations. Historically the higher fatty alcohols advanced rapidly in sales, then lost relative position, and once more gained. Present production potential is estimated to be 75,000,000 pounds a year. Monoglycerides were once of considerable importance in household detergents but are seldom found today. Sulphonated paraffins, products of the Horne-Reed reaction, are no longer encountered in the industrial detergent market. Keryl benzols are giving way to polypropylene alkylates. Finally, alkyl naphthalenes, alkyl xylene, and alkyl toluene have been abandoned in favor of polypropylene-benzol alkylates, either on technical grounds or economic considerations, or both. About 85% of the present 500,000,000 pounds a year potential production of detergent alkylate is currently polypropylene-benzol alkylate.

Anionic synthetic detergents comprise the bulk of the market and will therefore be considered first, followed by nonionics. Cationic detergents, while of great technical importance in several fields, are sold in small tonnage and seem destined to remain at the bottom of the list for some time. No attempt will be made to cover all possible variants in each field. Only the important basic items will be mentioned.

Anionic detergents are, in general, composed of an active ingredient, so-called builders, a soil redeposition controller, and an optical bleach. The composition varies rather widely, and no attempt will be made to indicate formulae. For general consideration we have employed the following basis:

Active ingredient	25% by weight
Tripoly and/or tetrasodium pyrophosphate	50% by weight
Sodium sulphate and sodium chloride	5% by weight
Sodium silicate	8% by weight
Sodium carboxymethyl cellulose	3% by weight
Optical bleach	Trace
Water	9% by weight

The active ingredient in the large tonnage items may be sodium alkyl aryl sulphonate or a sodium fatty alcohol sulphate or mixtures thereof. Sulphated ethylene oxide-amide adducts or similar materials are encountered in the smaller tonnage field. The principal basic products required for active ingredient production are:

Animal fats	Hydrogen
Benzol	Paraffinic kerosene
Caustic soda	Propylene polymer
Catalysts (HF, $AlCl_3$, H_2SO_4, copper chromite)	Sodium metal
Ethylene oxide	Sulphuric acid
	Vegetable oils

Of the above, all are in good supply, except sulphuric acid and possibly benzol and metallic sodium. In fact, we believe that the needs for the next five years may be considered as assured.

Benzol has not been freely available for some time. When the present emergency arose, some interruptions occurred in benzol supplies, and production of synthetic detergents was affected. However the requirements for synthetic detergents are quite small and only represent about 6% of the total available. Now that plants for the production of benzol from petroleum have been activated, future supplies should be adequate.

Sulphur and sulphuric acid have been the source of much discussion, and the fact is that they may not be in free supply for some years. The synthetic detergent industry requires only about 200,000 tons of sulphuric acid a year, or about 1.25% of the national production. Up to 50% of this acid may be returned for further use in other industries. No shortages are anticipated for detergent production.

Sodium metal was in short supply for several years and adversely affected the production of higher fatty alcohols. A change in process has reduced the need for this item, and the supply seems adequate.

The so-called builders are inorganic chemicals, which include sodium chloride, sodium silicates, sodium sulphate, sodium tripolyphosphate (TPP), tetra sodium pyrophosphate (TSPP), and trisodium phosphate (TSP).

PHOSPHATES are the most important and largest class of true builders. They impart great improvement in detergency to synthetics, possibly by preventing soil redeposition. This mechanism is not clear however and is subject to question. They also act as sequestering agents for calcium and magnesium ions in hard water. Of the three phosphates listed above, tripoly is generally considered to be the best performer, followed closely by tetrasodium pyrophosphate. Trisodium phosphate is not particularly outstanding as a detergency builder and has the disadvantage of a high pH (10.6-11.0). The other two phosphates have pH's in the range of 9-10. Those latter materials are used as builders in most of the heavy duty detergents, and they are incorporated in spray or drum-dried products in percentages varying from 10-60.

The supply of all of the above chemicals is adequate and well in excess of current needs. There was a pressing need for more phosphate production, particularly tripolyphosphate. This has been overcome by plant completions, with some additional production yet to come in. About 550,000 tons a year of TPP or TSPP will be available by the end of 1952. Sodium carboxymethyl cellulose (CMC) and optical bleaches are readily available, and no shortages are anticipated.

Nonionic detergents vary widely in composition, but much of the tonnage is based upon adducts of ethylene oxide and alkylphenols, fatty acids, or fatty amides. There has been some shortage of these chemicals, but it would appear to be over. Ethylene oxide production capacity was about 540,000,000 pounds in 1950, is now estimated to be 585,000,000 pounds, and is expected to reach 860,000,000 pounds in 1955. Detergent and surfactant consumption of ethylene oxide is low just now (about 30,000,000 pounds a year) due to the textile recession. The past consumption has been about 35,000,000 pounds a year, and it has been estimated that 70,000,000 pounds, or 8% of the available, may be required in 1955. This figure seems high.

Alkylphenols, such as nonyl phenol, have been scarce at times. Present expansion of manufacturing capacity has eased the situation, and production of about 12,000,000 pounds a year is now available. Fatty acids and amides are in good supply.

Cationic detergents are actually employed for many applications where detergency is only of passing importance: algicides, bacteristats, textile fibre processing, etc. The tonnage is relatively small and does not seem destined to grow rapidly. Raw materials of principal importance for the manufacture of cationics are alkyl chlorides (C_{12}-C_{16}); alkyl benzyl chlorides; fatty amides; and tertiary amines. There are no important raw material shortages in this field.