options for the 1980s. Should shortages of petroleum and petroleum-derived chemicals develop during the 1980s, emergency supplements and partial substitutes will be needed in the event that surfactant availability will be limited. In 1978, a laboratory study was conducted on a series of nonphosphate laundry detergents, again using the Terg-O-Tometer, where the effects of expanded concentrations of the detergent enzyme ALCALASE up to 3% in the formulation were evaluated on four of the leading nonphosphate laundry detergent powders (17). The improvement in detergency on protein-soiled EMPA 116 swatches increases with increased enzyme concentration.

Figure 8 summarizes the increased contribution of detergency on a typical enzyme-susceptible soil swatch (EMPA 116).

The performance of all products was favorably enhanced under warm, as well as hot, water wash conditions. Again, it should be noted that these tests were performed without presoaking using the normal 10-min wash period in the Terg-O-Tometer.

Next, studies were made with nonphosphate Tide on the following soil swatches: EMPA 116—blood, milk and ink on cotton; EMPA 101—vegetable oil on cotton; EMPA 104—vegetable oil on polyester/cotton. Again, wash conditions included both hot (50 C) and warm (37 C) water washing (Fig. 9).

The test was repeated at a 2% enzyme level (wt/wt detergent basis) whereas the detergent concentration in the wash water was reduced by 20%. The effect of ALCALASE on protein stain removal at 37 C and 20% less detergent also was significant. Under hot water conditions, detergency was improved at 2% enzyme on oily soil (EMPA 101 and 104). The effect was noted even with the reduced detergent levels (20% less).

Nonphosphate Tide showed improvement in performance on EMPA 116, even at the lower detergent concentrations in the wash water.

This type of study underscores the potential advantages of formulating with high concentrations of enzyme in laundry detergents. Using a lower concentration of surfactant, the alkaline protease offers a partial compensation for the loss in detergency. Should the worst situation happen during the 1980s, e.g., a severe shortage in petroleum does develop, then detergent enzymes may be one of a few alternatives available for consideration by laundry detergent formulators.

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Detergent Builders

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ABSTRACT

A highlight summary of the chemistry of commercial manufacturing processes, relative effectiveness, economic comparison and present uses of the various detergent builders of industrial significance to the soap and detergent industry are presented and reviewed. Builders discussed include the inorganic phosphates, silicates, carbonates, zeolites, and the organic citrates and other polycarboxylate salts (NTA, CMOS and "Builder M").

INTRODUCTION

Detergent builders contribute to improved washing performance in a number of ways (1). They reduce the deleterious activity of hardness ions (Ca^{++} and Mg^{++}) introduced via the wash water and the wash fabric, provide excess basicity to convert sebum fatty acids to effective soaps, which assist in the emulsification and removal of nonpolar components of oily and greasy soils, deflocculate particulate soils, buffer in the optimum detergent pH ranges (9-10.5), and decrease soil redeposition by stabilization of the dispersed soil (adsorption, increased zeta potential).

The complex phosphates became the major builder ingredient in detergents after World War II because of their overall superior ability to perform the functions outlined. By the early 1970s, however, phosphate levels in household laundry products in the USA had been significantly and increasingly reduced because of the eutrophication problem attributed mainly to high levels of phosphates in certain lakes and streams. Legislation in the USA has resulted in many areas of the country allowing essentially no phosphate in household detergent formulations. In Japan, and in Germany more recently, legislation also is resulting in lower phosphate usage.

Considerable research and development activity has been undertaken in the past decade and longer on new organic (2) and inorganic (3,4) builders to replace phosphates in detergent formulations. Of commercial significance, NTA and citrate are the major organic builders, and silicates, carbonates and zeolite A are the major inorganic builders which are now being used increasingly in at least some parts of the world at the expense of the total phosphate usage.

PHOSPHATES

The most common phosphate builder for detergents is sodium tripolyphosphate (STPP) (5), which replaced tetrasodium pyrophosphate (TSPP) in the mid-1960s, as the leading detergent builder. Tetrapotassium pyrophosphate (TKPP) is used mainly in heavy duty liquid detergents, principally because of its relatively higher solubility. Other phosphates used in the soap and detergent industry include trisodium phosphate (TSP) and sodium metaphosphate (SMP).

The commercial manufacture of phosphoric acid is done in two ways: (a) the "wet process," which consists of treating ground phosphate rock with sulfuric acid, and (b) the "electric furnace process," which consists of reducing phosphate rock and silica with coke to elemental phosphorus, then burning to phosphorus pentoxide, and absorbing in water to make the acid.

To make STPP, the phosphoric acid is then neutralized with soda ash or caustic soda to a mixture of 1 mol mono- and 2 mol disodium orthophosphate. This is dried, calcined and tempered to give 4 parts by weight of STPP from 1 part by weight of elemental phosphorus.

To make TSPP or TKPP, the acid is treated with sodium or potassium hydroxide, or carbonate, to make disodium or dipotassium orthophosphate, which is converted by heating to the pyrophosphate salt.

TSP is made by completely reacting the phosphoric acid with soda ash or caustic soda, whereas SMP is made by heating and fusion of monosodium phosphate.

SILICATES

The manufacture and use of soluble silicates in soaps and detergents dates to the early 19th Century (6). In addition to the builder functions, sodium and some potassium silicates are used in detergents also to reduce corrosion (by protecting metals and china overglaze), and as a processing aid (in granule binding) (7). Sodium silicate is particularly effective in controlling Mg ion in the wash water (8); it is more effective than either zeolite NaA or NaX in this regard.

Figure 1 outlines the simple chemical reactions of the principal processes used to manufacture the family of materials called soluble silicates. Most of the sodium silicate products manufactured in the world today start with sand and sodium carbonate, which are heated in a furnace or other apparatus to ca. 1,100-1,200 C, as illustrated in Equation 1. This same reaction can be made to occur, essentially in the solid state, for sodium metasilicate products, by heating to ca. 650-850 C, e.g., in a rotary kiln (9) or fluidized bed (10). During the reaction, carbon dioxide is liberated as a gas, and the raw materials are converted into sodium silicate of a given ratio, which is dependent on the relative amounts of the starting materials used. Equation 2 in Figure 1 illustrates another process which, some years ago, had considerable commercial impact in many countries. Sand and sodium sulfate, together with a reducing agent, primarily carbon in the form of finely divided coal, are the raw materials in this reaction. Oxides of sulfur and carbon are by-products. This process can be used when Na_2CO_3 is unavailable or too expensive.

In the pressure reaction (Equation 3), the starting materials are silica flour and alkali hydroxide. The materials are heated to ca. 130-180 C under pressure, to ca. 1200 kPa. An important limitation to the large-scale commercial utility of this process is that only lower ratio products—below ca. 2.5—can be produced economically.

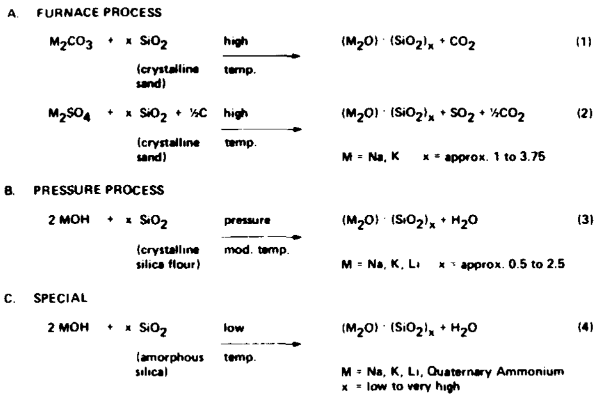

FIG. 1. Chemistry of commercial soluble silicate manufacture.

The relative cost of carbonate vs hydroxide plays a major part in determining overall economics of the furnace or kiln vs autoclave processes. In some locations, Na_2CO_3 is ca. 0.7 as expensive as NaOH on an active Na_2O basis. On the other hand, energy requirements for a 2.4 ratio silicate made in an autoclave are only 0.3 of the cost of the same ratio silicate made in a furnace, neglecting the energy used in grinding sand to silica flour. This difference in energy cost is likely to become even more significant in the future, although there is still room for considerable energy efficiency improvement in the furnace process. Up to 3 times the theoretical energy can be consumed, depending on furnace production rates, in many typical open-hearth furnace plants. Versatility of product ratios and economics of scale and operation still favor the furnace over other processes, except for special, lower volume requirements in certain locations, or for special products.

Equation 4 in Figure 1 illustrates that essentially the same chemistry is involved in the pressure reaction, except that specialty silicates, such as quaternary ammonium silicates, can be made simply; the limit of 2.5 does not apply to the ratio of the silicate products made in the process, when the much more expensive amorphous forms of silica are used as one of the starting raw materials in place of crystalline sand. Temperature can range from ambient to 100 C in this process.

The most important factors determining which process is used to manufacture silicate products in volume, in any specific location in the world, are the availability, cost and purity of the starting raw materials, i.e., sodium vs potassium carbonate, alkali sulfate vs carbonate vs hydroxide, and crystalline sand vs amorphous silica, as well as the kind and purity of the silicate product desired. It appears that, for the near future, overall production economics will continue to favor the furnace route, as a general rule, for large-volume silicate manufacture.

CARBONATES

Sodium carbonate (5) is used in some nonphosphate detergent formulations, principally along with silicates. Although the carbonates are the least expensive builders, some questions have been raised concerning the use of carbonates because of higher corrosivity, and build-up of insoluble deposits on fabric and machinery. Substantial detergent usage of sodium carbonate has been in alkaline metal cleaners, tank car cleaners, food and dairy cleaners and other hard-surface cleaning applications.

In the U.S., the detergent industry is almost entirely reliant on naturally produced soda ash, which is derived from Trona ore. The Solvay process route to synthetic sodium carbonate is now generally more expensive than the naturally derived ash process used in the U.S.

ZEOLITES

Certain crystalline aluminosilicates are called zeolites (11), or alternatively, molecular sieves. These materials have a 3-dimensional framework structure in which silicon and aluminum atoms are tetrahedrally coordinated to oxygen atoms. The framework structure enfolds cavities containing water molecules and cations that are capable of undergoing desorption and cation exchange. The presence of aluminum atoms in the framework results in negative charges—1 unit of negative charge for each aluminum atom. The charges are neutralized by exchangeable cations that are in the cativites within the zeolite structure.

Of the various known zeolites, Procter and Gamble (3), and Henkel (4), have selected and developed zeolite NaA because of the high capacity and rapid ion exchange of its sodium ions for calcium and its other desirable properties for use in detergents.

The chemistry (7) of the two major manufacturing methods for making zeolite NaA is illustrated in Figure 2. One method (12-17) uses sodium silicate and sodium aluminate, which is made from alumina trihydrate and NaOH, as shown in Figure 2A. The other method (18-21) uses a kaolin type of clay which is calcined, and NaOH, as shown in Figure 2B.

Silicate Process

In a continuous process (22) for making zeolite NaA from alumina trihydrate and sodium silicate (Fig. 3), sodium aluminate is first made from alumina trihydrate and NaOH. When this solution is mixed with aqueous sodium silicate, the amorphous product that forms is mixed well. When this is heated to 77-110 C, zeolite NaA crystallizes from the reaction mixture in 1-8 hr. The crystals are separated from the mother liquor, and the wet filter cake product is dried. The mother liquor contains NaOH, which is concentrated by evaporation and recycled to make more sodium aluminate. Sources of silica other than liquid sodium silicate can be used in this reaction, e.g., any amorphous silica may be used, but only at a major economic disadvantage.

Clay Process

The process for making zeolite NaA from clay and NaOH (18-19) is outlined in Figure 4. It is necessary to calcine the kaolin type of clay at ca. 500-600 C in order to convert it to a more reactive form, called metakaolin. Metakaolin is amorphous to X-rays and no longer has the kaolin crystal structure. If the clay is not calcined, hydroxy-sodalite crystallizes during the process. Digestion of the calcined clay with aqueous NaOH results in the formation of amorphous sodium aluminosilicate, from which zeolite NaA is crystallized in a few hours at 90-110 C. The rest of the process is similar to that previously described for the sodium silicate process, when the excess NaOH required in the clay process is recovered.

A. SILICATE PROCESS

$$2\,\mathrm{NaOH} + \mathrm{Al_2O_3}\cdot 3\,\mathrm{H_2O} \xrightarrow[\text{temp.}]{\text{moderate}} \underset{\text{Sodium Aluminate}}{2\,\mathrm{NaAl\,(OH)_4}}$$

$$12\,\mathrm{NaAl\,(OH)_4} + 4\,(\mathrm{Na_2O})\cdot(\mathrm{SiO_2})_3 + 7\,\mathrm{H_2O} \xrightarrow[\text{temp.}]{\text{moderate}} \underset{\text{Zeolite NaA}}{\mathrm{Na_{12}\,[(AlO_2)\,(SiO_2)]_{12}\cdot 27\,H_2O}} + 8\,\mathrm{NaOH}$$

B. CLAY PROCESS

$$\underset{\text{Kaolin}}{2\,\mathrm{Al_2Si_2O_5\,(OH)_4}} \xrightarrow[\text{calcine}]{500\text{-}600\text{ C}} \underset{\text{Metakaolin}}{2\,\mathrm{Al_2Si_2O_7}} + 4\,\mathrm{H_2O}$$

$$21\,\mathrm{H_2O} + \underset{\text{Metakaolin}}{6\,\mathrm{Al_2Si_2O_7}} + 12\,\mathrm{NaOH} \xrightarrow[\text{temp.}]{\text{moderate}} \underset{\text{Zeolite NaA}}{\mathrm{Na_{12}\,[(AlO_2)\,(SiO_2)]_{12}\cdot 27\,H_2O}}$$

FIG. 2. Chemistry of commercial zeolite NaA manufacture.

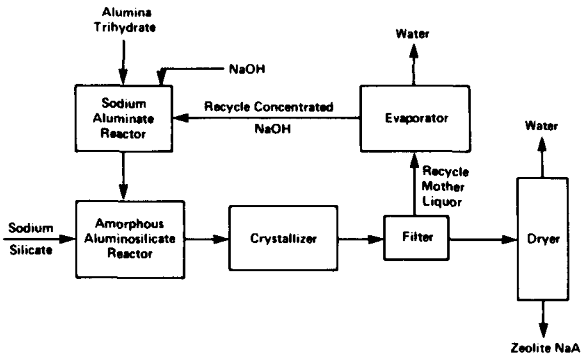

FIG. 3. Process for manufacture of zeolite NaA using sodium silicate and alumina trihydrate.

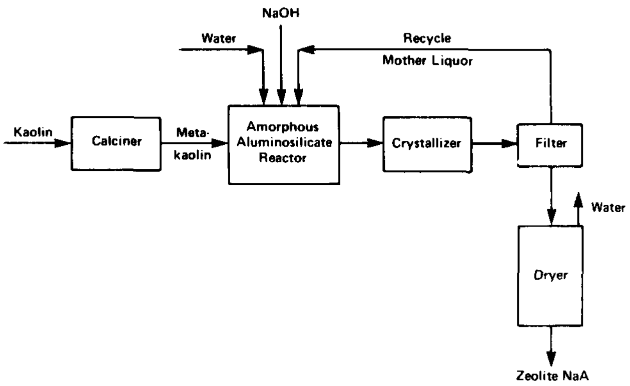

FIG. 4. Process for manufacture of zeolite NaA using kaolin clay and sodium hydroxide.

CITRATES

The sodium or potassium salts of citric acid are used in some heavy-duty liquid detergents and in some general purpose cleaners, for example, in "Wisk" (Lever Bros.) (23) and "Mr. Clean" (Procter & Gamble). Citrates are the prime example of safe, biodegradable organic detergent builders. Although effective as builders, they are not as good at sequestering Ca ions as STPP, NTA, or zeolite A.

Citric acid is produced by biological organisms as part of the tricarboxylic acid (Krebs) cycle. It is made commercially by fermentation of sugar (cane, beet, corn) using *Aspergillus niger*.

OTHER POLYCARBOXYLATE SALTS

Two organic compounds similar to sodium citrate that have been extensively researched are the ether polycarboxylate salts "CMOS" and "Builder M" (2). They have not yet been produced and used in substantial commercial volume. However, they have potential for use in built liquid detergents if manufacturing costs were to prove competitive.

Another organic polycarboxylate chelating agent that is in use commercially in detergents in some parts of the world (particularly Canada, also Sweden) is NTA.

TABLE I

Mid-1980 Prices of Detergent Builders

Builder	Price ($/lb) (100% solids basis)
Citric acid (50% LIQ-W)	0.56
Sodium citrate (white powder)	0.685
NTA	0.385
STPP	0.30
TSPP	0.31
Zeolite NaA	0.22
Sodium silicate 2.0 ratio (44% solids)	0.123
Sodium silicate 2.4 ratio (47% solids)	0.126
Sodium carbonate	0.040-0.043

Nitrilotriacetic Acid (NTA)

NTA, sodium salt, is an excellent Ca and Mg ion chelating agent, in fact, better than STPP. In the late 1960s, NTA was beginning to appear in some U.S. detergents, but a voluntary cessation of large-scale use in detergents in the U.S. occurred in late-1970 at the urging of the U.S. Surgeon General, when concerns arose over the material's safety, based on some animal testing. In May 1980, in a letter from EPA Assistant Administrator Steven Jellinek to the Procter and Gamble Company, EPA announced that it saw no reason, based on present information, to regulate the use of NTA in detergents. This was not an endorsement, Jellineck said, and did not preclude future action in the event of new findings (23).

NTA is made commercially from the reaction of hydrogen cyanide, ammonia, and formaldehyde, and is used in detergents in the form of the sodium salt.

1980 VOLUMES AND PRICES

The detergent builder business is expected to take ca. 2.5 billion lb/year of products for 1980 in the U.S. Industry estimates (23) that phosphates (primarily STPP) have ca. 60% of the market, or ca. 1.5 billion lb/year; silicates (primarily 2.0-to-2.4 ratio products) are a distant second in volume with ca. 400 million lb/year; zeolite A and carbonates roughly are at 300 million lb/year each; and relatively little citrate and NTA are presently used. Major growth is expected in the use of zeolite A, in the USA and on a worldwide basis (3,4,7,24).

Industry sources in mid-1980 gave approximate prices for these builders as shown in Table I. These are bulk prices, F.O.B., point of manufacturing.

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Update on Surfactants:
What Do We Have to Work with?

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ABSTRACT

The number of commercially available surfactants continues to grow, but at a slower pace than in the past decade. Low-cost raw material continues to guide the market. Several surfactants, such as AOS, have yet to reach their potential volumes. The class, structure and chemistry of the major and developing surfactants are reviewed and some unique application examples are described.

INTRODUCTION

To answer the rhetorical question posed by the title of this paper, at the present time, the surfactant chemist or formulator can "work with" over 600 surface-active agents manufactured by about 160 producers in the U.S. These 600-plus surfactants represent a production volume of ca. 5 billion lb of products (1). The major portion is consumed as packaged soaps and detergents (i.e., cleaning products) for household and industrial use. The balance is used in such diverse applications as agricultural sprays, cosmetics, ore flotation, foods, lubricants, pharmaceuticals, textile processing, oil well drilling, leather manufacture, inks, synthetic elastomer production, and oil recovery operations.

The three primary sources of raw materials for surfactants are natural fats and oils (2-4), silvichemicals, such as lignin and tall oil, and coal tar and petrochemical stocks. The first two sources are renewable whereas the petroleum and coal chemical stocks are in a relatively limited supply. The issue of renewability, though obviously important, is not discussed in this paper. Surfactants generally are