Soaps and Detergents – The Inorganic Components

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ABSTRACT

The detergent industry uses about $2 billion of inorganic chemicals a year. Two products–sodium tripolyphosphate, with almost $1.5 billion sales, and sodium perborate, with around $0.3 billion sales–dominate the field. They represent some 30% of a detergent powder raw material cost in the U.S. and 55% in Europe. Interest is developing in one new product, the zeolites, which in view of environmental considerations, may find a place in the formulator's pallet but which have still to prove their merits and show an attractiveness to potential manufacturers.

Our generation has seen many changes in the composition of soaps and detergents used for a host of applications, including personal cleansing, dishwashing, clothes and fabric washing, and for many industrial uses, but these changes have been at their most dramatic in the household.

At the turn of the century, natural fibers, predominantly cotton and wool, were washed using soap, soda crystals, considerable manual effort, and in the case of cotton fabrics, boiling or near-boiling water. Wash day was not a happy time!

In the 1920s and early 1930s powder forms of soap, incorporating inorganic materials such as sodium silicate, sodium carbonate, and borax – so-called "builders" – became popular. The latter part of this period saw the introduction of domestic washing machines as well as an increasing use of synthetic fibers alone or blended with natural fibers.

In the late 1930s, and particularly in those countries which were on a war footing, the chemical industry, including the soap industry, was being exhorted to reserve vegetable and animal fats for edible purposes and to substitute products derived from petroleum, coal, and other feedstocks.

In the U.S. the major soap companies realized the potential commercial and performance advantages that could be derived from the use of such materials. From these came the objective to develop products that could:

1. show a performance equivalent to soap in soft water;
2. show improved performance over soap in hard water;
3. cater to the increasing number of domestic washing machines;
4. cater to the growing use of synthetic fabrics.

But for these products to be successful, builders other than the available soda, silicate, and orthophosphates were necessary.

The size of our worldwide industry can be put into perspective by production figures for 1975 which indicate that over 20 million tons of soap and detergent washing and cleaning compounds were produced as shown in Table I. Estimates for 1982 indicate growth to 25 million tons.

While caustic soda and other alkalis are used in the manufacture of soap, and sulfur and alkalis in the manufacture of anionic surfactants, these uses are not covered in this paper, as they are more properly considered as raw materials for intermediates rather than as inorganic components of finished products.

This paper will concentrate on detergents in powder or granular form, the major user of inorganic chemicals. These products comprise a range of different types such as heavy duty, light duty, fine fabric, and presoak products with formulations tailored to meet both end use and individual market habits and requirements.

The heavy duty laundry types are the most important, and in this category formulations vary considerably. For example, in North America, home laundering is normally carried out using preheated domestic water at about 50 C in top-loading automatic machines with high liquor-to-load ratios, with products tailored to meet this requirement without bleaching agents or with chlorine bleach added separately, and without needing to worry too much about the amount of foam generated.

In Western Europe washing machines are usually of the front-loading type, with the water often heated in the machine to a temperature of 90 C and above, and with lower liquor-to-load ratios. This combination of conditions means the continued incorporation of bleaching agents used for many years in many European products is practical. It is necessary to prevent over-foaming by the use of low or controlled-foam products. Formulations and end use patterns are shown in Table II.

SODIUM PERBORATE AND PERCARBONATE

The main use of sodium perborate is as an oxygen bleach in high temperature domestic laundering, the product being incorporated by dry-blending into the finished detergent powder. This bleaching technique, because of the differing washing customs, is essentially a European approach.

Raw materials are natural sodium and calcium borates – the main deposits currently being exploited are in California and Turkey, together accounting for about 85% of world supply and with known reserves sufficient to cover foreseeable requirements.

The enormous difference in the importance of detergent perborate in terms of total borate consumption between the U.S. and Western Europe is shown in Table III.

The total U.S. production of sodium perborate in 1975

TABLE I

Production of Soaps and Detergents in 1975[a]

	Million tons
Household soap	3.055
Toilet soap	1.596
Soap flakes	0.343
Soap powders	0.276
Solid synthetic detergents	8.652
Liquids	3.494
Scouring cleaners	0.597
Other cleaning compounds including fabric softeners, detergent paste, and similar products	0.839

[a] Henkel KGA, Dusseldorf, March 1977.

TABLE II

Detergent Formulations and Use Patterns

		Europe		U.S.
Anionic active	%	5	15	15-20
Nonionic active	%	5	2-3	1-2
Soap	%	5	---	---
STPP	%	30-40	35	0 / 24 / 35
Sodium silicate	%	5	5	6-10
Sodium perborate	%	20-25	20-25	0-6 (some products)
Grams/liter		4-6		2-3
Liquor: load ratio		6-8:1		15-20:1
Temperature	°C	60-100		38-55

TABLE III

Borate Consumption[a]

	U.S. (1975)	Western Europe (1974)
	(Thousands of short tons B_2O_3)	
Glass and ceramics uses	135	180
Sodium perborate	14	130
Others	121	90
Total	270	400

[a] *Chemical Economics Handbook*, SRI International, Menlo Park, CA; sections 717.1001A and 717.1008G, Boron Minerals and Chemicals.

was about 60,000 short tons supplemented by about 20,000 short tons of imported material. Of this total almost half was used in dry bleaches and some 30% in formulated detergent powders. In contrast, the consumption of sodium perborate in Western Europe for detergents is of the order of 570,000 short tons.

Total world consumption of sodium perborate in detergents is estimated at ca. 650,000 short tons, or about 15% of the world borate demand – this places detergent sodium perborate second only to the glass and ceramics industry as a consumer of borate.

An essential in the manufacture of sodium perborate is the rigorous exclusion of impurities, particularly heavy metals, to avoid catalytic decomposition of the finished product. Stabilizers are added during the manufacturing process.

An alternative to sodium perborate for detergent applications is provided by sodium percarbonate, manufactured similarly to sodium perborate but starting from soda ash instead of from borax.

Sodium percarbonate offers two advantages over sodium perborate; the obvious economic advantage from replacing borax by soda ash and the removal of problems connected with the toxicological hazard of the use of perborate in areas where water is subsequently used to irrigate certain crops.

Current U.K. annual consumption of percarbonate is estimated to be ca. 18,000 tons.

SILICATE

Sodium silicate, used as a corrosion inhibitor and as an intermediate to make magnesium silicate as a perborate stabilizer, has also been used to the extent of 10-20% as a builder in some U.S. nonphosphate detergent powders for use in areas where phosphates are prohibited by law.

Silicate consumption in detergent powders is estimated at ca. 130,000 tons in the U.S., 170,000 tons in Western Europe, and ca. 400,000 tons worldwide. Total estimated world consumption of silicate is about 2 million tons.

The main use of sodium silicate is in the manufacture of silica gels and silicate catalyst supports; other important end uses include pigment and adhesive manufacture.

Sodium silicates are manufactured by fusing soda ash with high grade silica sand. By varying the reaction ratio and conditions, a range of silicates can be prepared with different degrees of alkalinity and other properties. For detergent applications the ratio $SiO_2:Na_2O$ is normally around 2:1.

Raw materials are readily available and cheap, the main cost is the energy required for fusion. High grade silica sand is in demand for glass manufacture, and some material is obtained by acid washing of lower quality sands.

A recent development in the silicate field has been the suggestion that certain grades of synthetic zeolites (sodium aluminosilicates) could partially replace sodium tripolyphosphate in detergent powders on the basis of their ability to remove calcium ions from wash liquors by ion exchange.

The manufacture of such zeolites involves crystallization, under controlled conditions, from an aqueous solution containing sodium aluminate, sodium silicate, and caustic soda in defined ratios. Since these products contain roughly one third of their finished weight of sodium silicate, development of major zeolite markets would be of interest to silicate producers.

Zeolites, being insoluble solids, may cause problems by settling out in some washing machines and will affect urban water treatment plants – in terms of sludge volume and character if the zeolites are retained and in terms of effluent suspended solids if they are not. In addition, there is the question of the effect on sewage pipes if large quantities of zeolites are used in detergent powders.

These latter factors are being investigated on a small scale at a sewage works in Western Germany with a view to testing the environmental acceptability of zeolites. A report on this investigation will be given at this conference. Zeolite-containing products are being tested in some areas of Germany, Holland, and Switzerland, and by a major detergent manufacturer in certain areas of the U.S.

At this time too little is known, we feel, about their long term environmental effects, their eventual price, availability, and cost performance characteristics for an objective assessment of their role as future inorganic detergent powder raw materials.

SODIUM TRIPOLYPHOSPHATE (STPP)

When chemists were looking for the optimum builder for the new synthetic detergents, they initially chose an already existing commercial product, sodium pyrophosphate. They then found that another complex phosphate, sodium tripolyphosphate, was ideal because of its performance characteristics, nontoxicity, ease of incorporation, cost effectiveness, and ready and growing availability.

STPP became a vital product for the modern synthetic powder detergent industry, which has fundamentally been built up on a combination of organic active matter – derived from both petroleum and natural sources – and STPP, based on the rough and ready equation:

Soap + soda = detergent + sodium tripolyphosphate

The annual world use of STPP today is approaching 3 million tons.

In view of the vital role of STPP, it is appropriate here to trace some of the changes that have taken place in its use in the 1970s. For almost 10 years some environmentalists and pressure groups have expressed concern about eutrophication, the occurrence of excessive algal growth in some slow-moving waters, naming phosphates as a major identifiable cause. No doubt this subject will be discussed in considerable detail in this conference, including the other nutritional elements necessary for eutrophication as well as the difficult and unresolved problem of providing a substitute with STPP's unique properties in terms of cost performance, nontoxicity, availability, and overall usefulness to the formulator and detergent manufacturers. Here it is sufficient to record that, generally speaking, it is technically agreed that if it is thought necessary or desirable in some localized eutrophication areas to limit phosphates introduced into water by way of sewage from human sources and from detergents – some 35-50% depending on the location – the preferred way is to remove them by already available means at sewage works (such as is practiced in Sweden).

As is well known, legislation restricts the use of phosphates in domestic detergent powders in the areas around the U.S. Great Lakes, depriving some 20% of the U.S. population of efficient phosphate-containing domestic detergents, with pressures to increase this percentage. An additional 10% of the U.S. population is subject to legislation setting 35% as a maximum phosphate content, leaving 70% of the U.S. population not subject to phosphate-controlling legislation. Severe restrictions are also imposed on phosphate levels in detergents by Canadian authorities.

In the U.K. the Secretary of State for the Environment's Standing Technical Committee on Synthetic Detergents, which was formed in 1957, is charged to: "Keep under review the difficulties, or risks of difficulty, arising in sewage works, river and water supply as a result of the use of synthetic detergents and related products." It reports annually to the Secretary of State on its findings.

This committee does not "regard the presence of phosphates in detergents as constituting any significant environmental problems." In Germany and Switzerland legislation covering labeling of packets with agreed dosage recommendations is in force. In Scandinavia and Japan soapers voluntarily have accepted limitations on phosphate in detergents to 22-30%.

It is interesting to note the 1970 and 1976 production figures for STPP shown in Table IV.

TABLE IV

Production of STPP

	1970	1976
	(Million tons)	
U.S.	1.09	0.66
Western Europe	0.94	1.29
Other	0.67	0.85
Total	2.70	2.80

The decrease in U.S. consumption has, of course, been brought about as a result of legislation and by a gradual reduction in phosphate levels of some domestic fabric washing detergents. However, the reduction in North American consumption has been more than made up by other countries increasing their consumption.

STPP is manufactured by converting at high temperatures the correct grade of sodium orthophosphate which, in turn, is made by the neutralization of phosphoric acid with soda ash or caustic soda.

There are two methods used to manufacture phosphoric acid – the thermal and wet routes. Thermal acid is derived from phosphorus which is manufactured by smelting phosphate rock in the presence of coke and silica in a closed electric furnace. The majority of the world's phosphorus has and is being produced in the U.S. where, generally speaking, the phosphate rock available is of low/medium quality and energy costs historically have been low.

The wet route, reaction of sulfuric acid with phosphate rock, produces a less pure form of phosphoric acid, known as "merchant" grade, which is used in major quantities by the fertilizer industry, but there are technologies available whereby this acid is used to manufacture STPP on a fully economic basis.

SODIUM CARBONATE

The use of soda ash as a buffer and water softener in the laundering operation has virtually disappeared in markets where tripolyphosphate, which performs both functions more effectively, is used. Soda ash is still employed for these purposes in other markets, however.

Soda ash has been used in some U.S. nonphosphate detergent powders at levels of up to 20% in areas where the use of phosphates is restricted by law. The annual use of soda ash for this purpose is ca. 100,000 tons.

Of much greater significance is the use of soda ash in manufacturing STPP and sodium silicate.

Based on our estimated annual world usage of these two materials in detergent powder manufacture, the soda ash requirement is of the order of 2.4 million tons.

It is evident that total soda ash consumption in detergent powders (both as a formulation component and as a raw material in the manufacture of other ingredients) is over 10% of the total world soda ash production, estimated at 27 million tons per year.

Over half the total world output is used in the glass industry, other major outlets being miscellaneous chemical manufacture and as a processing aid in many other industries such as pulp and paper, but our industry

TABLE V

Production of Soda Ash[a]

	Natural	Synthetic	Total
		(Millions of short tons)	
1970	2.678	4.393	7.071
1976	5.216	2.242	7.458

[a] *Chemical Economics Handbook*, SRI International, Menlo Park, CA; section 733.6000B, Sodium Carbonate (Manual of Current Indicators).

TABLE VI

Sodium Sulfate Consumption in Detergents[a]

	1968	1969	1973	1974
	(Thousands of short tons)			
U.S.	202	—	400	—
Canada	—	8	—	35

[a]*Chemical Economics Handbook,* SRI International, Menlo Park, CA; sections 770.4000E and 770.4020C, Sodium Sulfate.

consumes a very considerable share.

The basic manufacturing route for soda ash is the "Solvay" (Ammonia Soda) process starting from brine and limestone. Since 1970, the increasing production of "natural" soda ash, which has almost doubled in the U.S. while output of "Solvay" synthetic material has fallen by about 50%, is significant. In 1976 "natural" material accounted for over two thirds of total U.S. output as shown in Table V.

SODIUM SULFATE

Sodium sulfate is another inorganic raw material which has benefited in recent years from the enforced reduction in detergent phosphate contents in North America. While most of the tripolyphosphate eliminated has been replaced by soda ash and sodium silicate, sodium sulfate has also played a part, as shown by data for sodium sulfate consumption in detergents for these markets (Table VI).

Industry estimates of total world sodium sulfate indicate ca. 20% is used in detergents, a distant second behind the pulp/paper industry, which consumes almost 70% of production (Table VII).

TABLE VII

World Supply/Demand by End Use – Sodium Sulfate (1973/74)

	(Thousands of tons)
Total world production	4,000
Consumption in:	
Pulp/paper	2,750
Detergents	750
Glass	350
Others	150

Manufacture has traditionally been mainly by the Mannheim furnace by the reaction of salt and sulfuric acid. In the U.S., this process has been largely superseded by natural material from lake brines, together with important tonnages of by-product material arising from the manufacture of viscose rayon, chromic acid, dichromate, and other products.