

SYNTHETIC DETERGENTS

Sixth Edition

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and

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Synthetic Detergents

Preface

This is a work by practical men for practical men. It is not intended to be simply a collection of formulae and recipes, nor does it set out to list all the materials which could conceivably be used as basic ingredients. Excellent books of that kind do exist but, in our view, they are often so comprehensive that it becomes difficult to distinguish between references to literature and practical work. We have purposely confined our text to those details which the practical manufacturing chemist will require and, we hope, will be able to use.

Our intention has been to cover all the operations that a manufacturer is likely to encounter in practice. All of the formulations have been critically selected so as to provide a useful starting-point; each manufacturing chemist can then use his own initiative to develop these formulations to suit his own local, or special, conditions. The reader may notice that we frequently quote from technical brochures issued by raw-material manufacturers. We make no apology for this, for the extensive research and development on which these publications are based often makes them unique as sources of information for workers in this field.

During the past decade the detergent industry has seen a series of upheavals. It has seen a change from hard to soft detergents in the developed countries, and the large-scale introduction of enzymatic powders (and the subsequent problems). It has also had to face the attack on phosphates. In addition, the rate of growth of non-ionic detergents is increasing at the expense of anionic.

The alterations and many additions to this sixth edition reflect the new developments that have taken place as a consequence of these changes. However, the basic structure of the book remains the same, although, since this edition has been completely re-set, the opportunity has been taken to improve layout, to use metric units wherever practical, and to remove some inconsistencies that have crept in over the years.

Although this edition was prepared during a time of economic stagnation, the detergent industry has continued to develop from year to year. We have endeavoured to cover the technical aspects of this healthy trend and we hope that this book will continue to meet the needs of those in or concerned with the detergent industry throughout the world.

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November, 1977*

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* The name ALFOL is a registered trade mark of the Continental Oil Company, Ponca City, Oklahoma, USA.

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1. Development of the Detergent Industry

Although the start of the synthetic detergent industry is not shrouded in the veils of history as were the beginnings of the soap industry, it is nevertheless not easy to pinpoint exactly when the detergent industry, as such, came into being. The primary problem is to decide exactly what is being referred to as a synthetic detergent. The term itself leads to confusion. In the USA the words surfactant or syndet are being used, whilst in Europe the term 'tenside' (for tensio-active material) is coming into fashion.

Many definitions of synthetic detergent have been proposed, all of which are very wide. *The Comité International de Dérivés Tensio Actifs* has after several years of deliberation agreed on the following definitions:

Detergent: Product the formulation of which is specially devised to promote the development of detergency. *Note:* A detergent is a formulation comprising essential constituents (surface active agents) and subsidiary constituents (builders, boosters, fillers and auxiliaries).

Surface Active Agent: Chemical compound which, when dissolved or dispersed in a liquid is preferentially absorbed at an interface, giving rise to a number of physico-chemical or chemical properties of practical interest. The molecule of the compound includes at least one group with an affinity for markedly polar surfaces, ensuring in most cases solubilization in water, and a group which has little affinity for water. *Note:* Compositions in general are usually mixtures of such compounds.

Amphiphilic Product: Product comprising in its molecule, at the same time one or more hydrophilic groups and one or more hydrophobic groups. *Note:* surface active agents are amphiphilic products.

We shall, however, in this book continue to use the term synthetic detergent for a material which cleans (or is used for cleaning), but in this definition we do not include soap.

Even so, this is still a wide definition, because, of course, it can refer to the active ingredient, or the solid, liquid, paste or powder compounded from this active matter. However, this should not lead to confusion, as the industry itself as yet makes no distinction in terminology between the basic material and the ready-for-use product.

The first synthetic detergents which fall into our definition of the term seem to have been developed by the Germans in the First World War

period to allow fats to be utilized for other purposes. These detergents were of the short-chain alkyl naphthalene sulphonate type, made by coupling propyl or butyl alcohols with naphthalene and subsequent sulphonation, and appeared under the general name of Nekal. These products proved to be only fair to moderately good detergents, but good wetting agents and are still being produced in large quantities for use as textile auxiliaries.

In the late 1920s and early 1930s long-chain alcohols were sulphonated and sold as the neutralized sodium salts without any further additions except for sodium sulphate as an extender.

In the early 1930s long-chain alkyl aryl sulphonates with benzene as the aromatic nucleus, and the alkyl portion made from a kerosene fraction, appeared on the market in the USA. Again, these were available as the sodium salts extended with sodium sulphate. Both the alcohol sulphates and the alkyl aryl sulphonates were sold as such as cleaning materials, but did not make any appreciable impression on the total market. At the end of the Second World War alkyl aryl sulphonates had almost completely swamped the sales of alcohol sulphates for the limited uses to which they were applied as general cleaning materials, but the alcohol sulphates were making big inroads into the shampoo field. An exception was Teepol, a secondary alcohol sulphate which remained popular for some years.

In common, however, with other chemical developments during this century, progress was not in one direction only. The limiting factor is always the availability of raw materials in a particular country. Concurrently with the above developments, there were developed, both in Germany and the USA, the Igepon type of compounds of which Igepon-T, the sodium salt of oleyl tauride is an example, and in Germany the Mersolates, which are alkane sulphates. In the United Kingdom, Teepol, a secondary olefine sulphate from petrochemical sources, was manufactured in large quantities and is still being produced in England and western Europe to this day.

Each of these basic materials has its advantages and disadvantages, but in considering the feasibility of production the following factors must be taken into account:

- availability of raw materials;
- ease of manufacture;
- cost of raw materials;
- cost of manufacture;
- suitability of finished product.

We have purposely placed suitability last, as it is only too true that not always is the best material made available.

As a result of its ease of manufacture and versatility, the alkyl benzene sulphonate very quickly gained a foothold in the market, and after the last war the existing keryl benzene was very quickly replaced by an alkyl benzene made from propylene tetramer coupled to benzene (PT benzene).

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This PT benzene very quickly displaced all other basic detergents and for the period 1950-65 considerably more than half the detergents used throughout the world were based on this.

To give an idea of the enormous rise in synthetic detergent production, Table I compiled from figures submitted by the American Soap and Detergent Association and the German firm of Henkel & Cie shows both soap and detergent sales in the USA for various years.

TABLE I

US Soap and Detergent Sales		
Year	Soap sales 1000 tons	Synthetic sales 1000 tons
1940	1410	4.5
1950	1340	655
1960	583	1645
1972	587	4448

These figures reveal that immediately after the Second World War synthetics started making inroads into the production of soap, which now seems to have settled down to a constant whereas synthetics have increased enormously.

By 1959 although the US per capita consumption had somewhat levelled out, total production was still rising as shown in Table II which has been compiled from the 1963 Census of Manufacturers by the Bureau of Census of the US Department of Commerce and from the Henkel figures.

TABLE II

Comparative Production Figures for Synthetic Detergents			
	1958 1000 tons	1963 1000 tons	1972 1000 tons
Domestic detergents (solid)	1200	1425	2672
Domestic detergents (liquid)	354	640	1773

The broad picture that appears from Table II is that while solid detergents (among which of course powders are included) are making great strides forward, the liquid detergents are increasing at a much faster rate.

Henkel & Cie have also published world production figures (Table III): recently published data for 1974 and 1975 show insignificant change.

It can be seen that despite a tremendous growth in the past decades, the production of synthetics is still continuing to rise.

No review of the history of the detergent industry can omit mention of the builders, without which the remarkable success outlined above could never have been achieved.

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TABLE III

World Production of Cleaning Agents				
Product	Production 1968 1000 tons	Average annual growth rate 1966-8	Production 1969 1000 tons	Growth rate 1968-9 %
Soaps	6493	— 4.2	6440	— 0.8
Synthetics	7369	+ 11.2	8050	+ 9.2
Others	1015	+ 6.9	1080	+ 6.5

Product	Production 1972 1000 tons	Average annual growth rate 1969-72	Production 1973 1000 tons	Growth rate 1972-3 %
Soaps	6451	+ 0.2	6200	— 3.9
Synthetics	11,095	+ 37.8	12,300	+ 10.9
Others	971	— 10.1	1000	+ 2.9

After the war, when detergents started appearing in appreciable quantities on the retail market, it was noted that white cotton goods were not being washed as white as they should be. This was explained by the fact that although the active material was able to lift the dirt from the cloth it could not keep it in suspension. Hence small spots of dirt were being re-deposited uniformly over the whole surface area of the cloth while in the wash-tub or machine, thus giving the cloth a grey appearance.

The sodium salt of carboxymethylcellulose (CMC) had been known to industry for many years and, in fact, a French patent had been applied for in 1936,¹ using CMC as an additive to washing materials. However, this patent was not developed extensively until the Second World War, when CMC was used in Germany on a moderately large scale, initially as an extender for soap which was in short supply, and then as an additive to the synthetic detergents being produced as a wartime substitute for soaps. When intelligence reports on the German industry were published, the use of CMC as an additive to synthetic detergent powders was noted and investigated and it was found that this addition eliminated the redeposition problem.

Despite the considerable advances made in the production of the active detergent matter, by the end of the Second World War progress in the use of detergents for heavy-duty (cotton) washing was still relatively slow, although they had already displaced soaps to a considerable extent in the field of fine laundering and dish-washing. To improve the heavy-duty washing properties, manufacturers turned for analogies to the soap industry. Soap for cotton washing had for many years been 'built' with alkaline materials such as carbonates, silicates, borax, and orthophosphates. All of these singly and in combination were tried with moderate success. Condensed phosphates had started appearing on the market in increasing quantities and from 1947 onwards heavy-duty detergent formu-

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lations were introduced, initially with tetra sodium pyrophosphate and then with sodium tripolyphosphate with startling success.

With the advent of CMC and tripolyphosphate builders the detergent industry established itself and has never looked back. The action of the condensed phosphates will be discussed later, but, to look at production figures again, the production of tripolyphosphate in the USA is enlightening.

TABLE IV

Production of Sodium Tripolyphosphate	
Year	Tons
1947	102,000
1950	280,000
1959	700,000
1964	80,000,000
1967	95,000,000
1970	109,000,000
1972	94,000,000
1974	82,000,000

Taken from the US Department of Commerce figures

It will be noted that there is a falling off after 1970. The reason is a combination of restrictions on and opposition to the use of phosphates, and also international shortages of raw materials.

Propylene tetramer benzene sulphonate held almost undisputed sway as the major ingredient used in washing operations till the early 1960s. Around this time it was noted, however, that sewage treatment problems were arising. The amount of foam on rivers was increasing and where water was being drawn from wells located close to household discharge points, the water tended to foam when coming out of the tap. This was attributed to the fact that propylene-based alkyl benzene sulphonates are not completely degraded by the bacteria naturally present in effluents, and was further narrowed down to the fact that it is the branched-chain formation of the alkyl benzene which hinders the attack by the bacteria. However, fatty acid sulphates were found to degrade very easily, and since all naturally occurring fatty acids from which fatty alcohols are produced are of the straight-chain variety (as also are the Ziegler alcohols which started appearing in commercial quantities at about this time), it seemed possible that a straight-chain alkyl benzene might be degradable.

Methods of test were developed and it was, in fact, proved that linear alkyl benzene is biodegradable. Germany introduced legislation prohibiting the discharge of non-biologically degradable material into sewer systems. In the USA detergent manufacturers agreed voluntarily to switch over from PT benzene to linear alkyl benzene by June 1965. In the United Kingdom a similar type of 'gentleman's agreement' was entered into.

The change to linear alkyl benzene (which can be considered as a return

to a purified form of the keryl benzene in use twenty years previously) gave some rather surprising results. It was found that the detergency in a heavy-duty formulation using linear alkyl benzene sulphonate was approximately 10 per cent better than when using PT benzene sulphonate, solutions of the neutralized sulphonic acid had a lower cloud point, and pastes and slurries had a lower viscosity. The first two results were obviously advantageous and a lower viscosity in slurries had an advantage when the product was spray-dried to a powder, but when the LAS was sold as a liquid or paste detergent, this lower viscosity had to be overcome as sales appeal was lost. The manufacture of powders based on LAS posed some problems, however. Powders became sticky and lost their free-flowing characteristics, whether made by spray-drying or one of the other methods. Mausner and Rainer² have indicated that the actual isomer distribution of the linear alkylate has an effect on the stickiness of the powder, with the 2-phenyl isomer giving the greatest tendency to stickiness and the 5- or 6-phenyl isomer the least. Additives to overcome this tendency have therefore been developed (p 66).

The switch to linear alkyl benzene is not, however, complete. In many parts of the world where the problem of sewage treatment is not serious, the PT benzene is still being used in ever-growing quantities. Also the Ziegler alcohols are now competitively priced with the linear alkyl benzenes, and alkane sulphonates are reappearing.

Having successfully coped with the problem of biodegradation the industry faced a new attack. It appeared that in certain lakes and ponds algae started reproducing at an unprecedented rate. This was blamed on the extensive use of phosphates which are a food for these organisms, and again the detergent industry became the whipping boy, because tremendous amounts of sodium tripolyphosphate are used and then discharged down the sewer. (The term eutrophication, meaning nutrition by chemical means, has been applied to this phenomenon.) It is not clear whether the blame should be taken solely by the detergent industry, as concurrently with the increase in the use of detergent phosphates there was an increase in the use of phosphate fertilizers, which also find their way into natural water systems. However, with the big international preoccupation with ecology the detergent industry is searching for an efficient substitute for sodium tripolyphosphate. To date a complete replacement has not been found but in the Scandinavian countries particularly, formulations of household powders are beginning to appear with appreciable portions of the phosphate replaced by NTA (nitrilo triacetic acid) which is a better sequestering agent than tripolyphosphate but has none of the other properties exhibited by the phosphate. We are inclined to fear that in time the extended use of NTA might bring new problems of this sort, as it contains nitrogen which is again a good fertilizer and nutrient for algae. We quote from an editorial comment in *Chemical Week* on this subject:³

'We caution the legislations and administrations against shooting from the hip. They may blast phosphate out of detergents, but they may not be very proud of their victory when the facts are finally in.'

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The search is still going on for a phosphate substitute. NTA on its own will only partially replace phosphates. A mixture of NTA and borax has been suggested as a complete replacement but here again the borax might produce more problems than the phosphate is alleged to produce. Some of the hydroxy-polycarboxylic acids (see p 77) not containing nitrogen are also being considered. A recent development in the search for acceptable phosphate substitutes was reported in the *Stuttgarter Nachrichten* on 25 February 1976.

'It appears that the firm of Henkel are running a year's experiment with the housewives of the Stuttgart district. The washing powders used by the housewives contain a partial substitution of the phosphate by a zeolite (identified as aluminium silicate). This field test is checking both the quality of the clothes washed in the district of Busnau and also the effect on the local sewage plant. At the time of going to press it is of course early to comment on this development, but we have been given to understand that Henkel have patented the use of aluminium silicate as an additive to washing powders in Europe, and also that Procter & Gamble have similar patent protection in the USA.'

The chemistry and structure of these types of zeolites is discussed fully by Anthony C. Savitsky in *Soap* of March 1977 (p 29).

In December 1970 the US Surgeon General released a report stating that it had been found that NTA causes birth defects in rats when their drinking water is contaminated both with NTA and mercury or cadmium salts. As a result the use of NTA in the United States is now gradually being phased out from detergents and several very large plants that were being built for the manufacture of NTA are being converted to other uses. The report had specifically indicated that there is no health hazard at the present use levels. Despite this, some firms are still continuing with the use of NTA, as they consider that heavy metals of the above types are not a source of contamination in their areas.

Two important reviews have appeared on this subject. In *European Chemical News* (19 November 1976), under the title 'No case for a European ban on detergent phosphates', it is pointed out that, in parts of the USA, although the phosphate ban is in effect, deterioration in washing quality is being experienced with no appreciable improvement in quality of water in lakes and slow-flowing rivers. The Swedish/Swiss policy of treating sewage water—which is anyway inevitable—is recommended.

Phosphorus and Potassium (No. 90, July/August 1977) concludes that there are no reasonable grounds for banning NTA.

Despite all this, it appears that the pressure on detergent manufacturers will ensure a gradual diminution of the P content of detergent products.

The biggest single revolutionary trend in the detergent industry in recent years has been the use of enzyme additives. Enzymes as aids to washing are not new to the industry. Proteolytic enzymes had been tried as additives to washing powders in Germany in the 1920s with only moderate success and again in Switzerland in the 1930s. Enzymes, which can be called organic catalysts, tend to hasten reactions and the proteolytic enzymes convert or

'break down' proteins wholly or partially into amino acids. The action is rather slow and the production costs high, but with improved methods of production and purification, strains of enzymes, usually in admixture with a proportion of amylase which breaks down starches, were developed which were relatively fast acting. These were added initially to 'pre-soak' detergents and found immediate acceptance in the European countries where washing habits were such that washing was normally soaked for a period prior to the wash proper. Better and better strains of enzymes were developed, with stability to a wider pH spectrum, stability against perborate and quicker action. In the United States detergent manufacturers resisted the incorporation of enzymes into their powders for some years after this type of powder had almost completely swept the board in Europe but in 1968 enzymatic powders started appearing there as well. The position at present is that enzymatic powders are now holding a large proportion of the household detergent market and formulations appeared made for machine washing. Some washing-machine manufacturers are now producing automatic washing machines with a 'Bio' programme which allows the washing to remain in contact with the detergent solution for an extended period of time at a relatively low temperature before beginning the washing and heating cycle. The future of enzymes is at the moment obscure as the production of enzymatic powders has raised its own problems (see p 83), and one Scandinavian firm has already decided to withdraw its powder containing enzymes from the market, but other large firms are taking enzymes out of some of their powders while forging ahead with others.

No problems have as yet been encountered at the consumer level but it is wise to be cautious. The basic enzyme itself is a mixture of organic material, some 6 per cent true protease, the balance being unidentified organic matter. It must be mentioned that producers of proteolytic enzymes are now bringing on to the market highly refined, practically dust-free, encapsulated enzymes, which do not contain so much undefined organic material deriving from the fermentation process. It is possible that some side effects might still be discovered, but at the present moment after ten years of continuous use in Europe, this has not occurred.

These, then, are the main trends in the development of detergents, but one must not lose sight of the fact that many other types of detergent were produced in large or small quantities concurrently with the few mentioned above. Each has a definite place and use of its own, but the vast majority are modifications of the few types mentioned above.

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