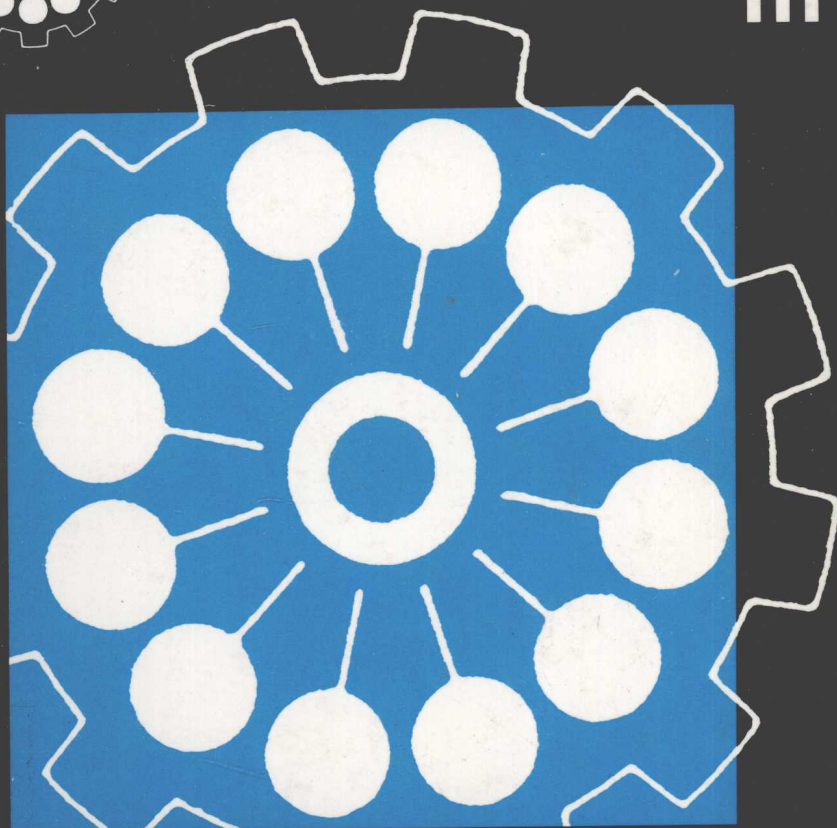
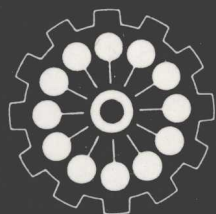


INDUSTRIAL APPLICATIONS OF SURFACTANTS III



Edited by D.R. Karsa

Industrial Applications of Surfactants III

表面活性剂的工业应用 第三版

Edited by

D. R. Karsa

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Preface

This book is a summary of the third Royal Society of Chemistry international symposium on the "Industrial Applications of Surfactants", the previous meetings being held in 1986 and 1989 respectively. Surfactants belong to many chemical classes and are used across the whole spectrum of industry. Hence, any two-day meeting can only provide a snapshot of selected products and application areas. As with the previous two meetings, completely new products and applications are described, the contents of each meeting being complementary to the others.

Where possible, speakers were asked to emphasise the more practical aspects of their products. Once again one or two of the newer more innovative areas, such as polymerisable surfactants and comb surfactants have been highlighted, together with further descriptions of surfactants under their various ionic classifications. Here, likewise, one or two less well-known and newer surfactant types are described, including sarcosinates, sulphobetaines, and alkyloxypropylamines. Finally a limited number of application areas are discussed, including oil field chemicals, emulsifiers for the food industry and new hydrotropes of built liquids.

It is hoped that this volume will prove to be a useful addition to the surfactant bibliography and of interest to those involved in the production, formulation and application of surfactant-based products.

D R KARSA

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Introduction

The Market for Industrial Surfactants in the 1990s — An Overview

Alan H. Turner and Joel H. Houston

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Introduction

My brief is to give an overview of the market for industrial surfactants in the 1990s. This is an enormous subject, and all I can really hope to do is to highlight what seem to me to be some of the main features in West Europe and in North America.

We are all very familiar with the use of surfactants in household detergents. Our television screens remind us of this every evening. The industrial applications are not so obvious; they are much more diverse, but they represent an enormous tonnage.

Perhaps I can bring this home to you in the following way. Many of you will have come here by car. Where is the link between cars and surfactants, apart from the obvious one of the car wash? Think of the manufacturing process: surfactants used in metal cleaning and metal working, in the paint, in the wax polish, in the manufacture and dyeing of the seat and carpet fabrics. The rubber in the tires will probably have been made in an emulsion polymerization process, which depends on surfactants. Let us not forget the detergent additives in the fuel, the lubricants, the grease...

If it is a luxury car, there will be some leather in it - more surfactants used here. Is there a foam fire extinguisher?

But let's get out of the car. The asphalt of the car park makes us think of bitumen emulsions, and the concrete of super-plasticizers and foamed concrete. The weeds are kept under control with agrochemicals, perhaps supplied as an emulsion concentrate?

If like me you had a sandwich and a glass of beer for your

lunch, you may have thought of the food emulsifiers used in bread manufacture, the surfactants used for glass and bottle washing, and then the bill - the paper industry uses surfactants too. I could go on, but I am sure you get my point. Is there any major manufacturing industry which does NOT use any surfactants somewhere, disguised as a process aid? Can anyone think of one?

Something else that may strike you: most of these applications have been with us for many years. Emulsion polymerization was developed during World War II, and the use of synthetic surfactants in the textile industry goes back to the 1930s. Metal cleaning and working, leather and paper manufacture, food, paint - these are long-established industries with long-established processes. In most cases (though not quite all), the types of surfactants they are using today are the same ones they have been using for many years. This is often because of the sheer amount of work (and, of course, associated cost) of evaluating alternative surfactants. Where are the new applications? What is the incentive for a surfactant manufacturer to look towards the industrial applications sector? What are the prospects for novel surfactants?

This is the third, well-attended, Salford conference on industrial surfactants, so clearly there is a lot of interest and activity in this subject. I am sure that we shall hear interesting things about novel surfactants and novel applications in the course of this symposium. Let us remember that today's novel surfactant application may - in favorable circumstances - grow into tomorrow's commodity business.

Industrial Surfactants 1990 - West Europe and U.S.

But let us return to 1991. I shall give some figures to show the size of the industrial surfactant market in W. Europe and the most important types of surfactants used.¹ I shall also show for comparison some corresponding data for the U.S., taken from a study which our company issued in July this year.²

We have to be careful here with our definitions. What do we include as an industrial use? Does it mean all non-domestic applications, including institutional cleaning? What do we include as a surfactant? Do we include soap or not? Some writers do not consider lignosulfonates to be true surfactants. What about detergent additives for lubricating oil, or frothing agents for ore flotation? These are matters of judgment, but they need to be borne in mind when comparing figures from different sources. Figure 1 shows the consumption of surfactants (including soap) in industrial applications in West Europe and the U.S. in 1990, and the main types of surfactants involved.

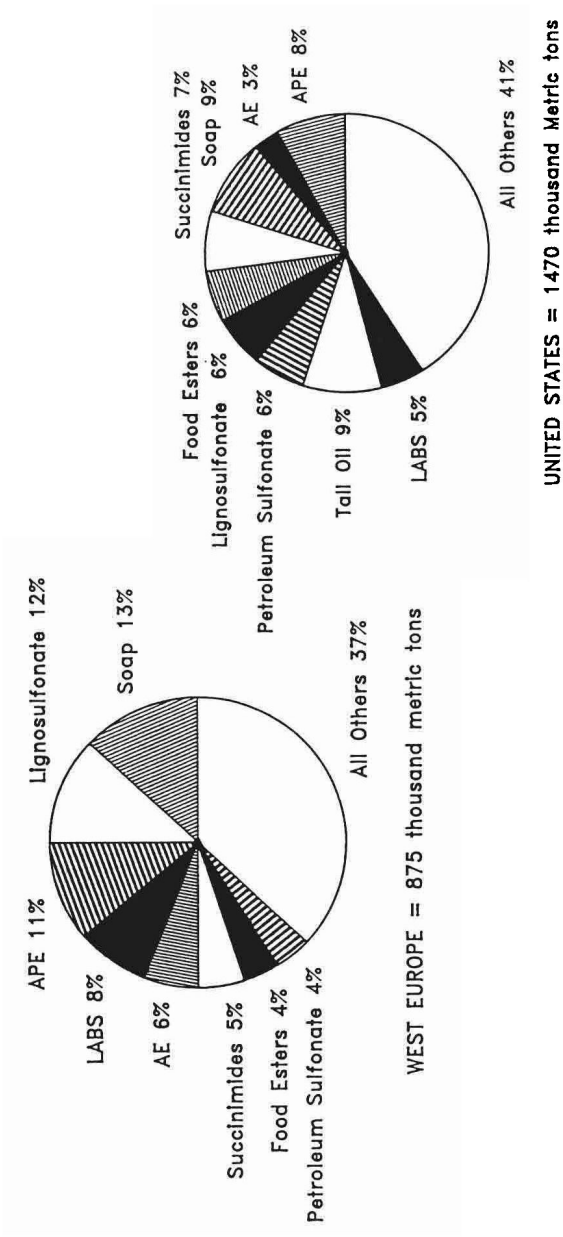


Figure 1 SURFACTANTS IN INDUSTRIAL APPLICATIONS, 1990

When we look at the types of surfactants being used in West Europe, we have a total surfactant consumption of 875 thousand tons, with soaps, lignosulfonates and APE as the most important materials, followed by LABS, AE, succinimides (entirely for petroleum additives), glycerol and glycol esters, and petroleum sulfonates.

In the U.S., the total is much larger at 1470 thousand tons. Soaps, lignosulfonates and APE are all important but we also have tall oil derivatives which make up nearly 10% of the total, but which are negligible in Europe. The "Others" category includes just about every type of surfactant commercially available.

Figure 2 shows the relative importance of industrial applications in the total consumption of surfactants in West Europe and the U.S. These figures relate to 1990 and do NOT include soaps. In volume terms, the total consumption of surfactants in household applications and in personal care products is approximately the same in West Europe and in the U.S. However, industrial outlets in the U.S. take a significantly bigger share of the pie (and it is a large pie) than they do in West Europe. For other parts of the world, household outlets would take an even larger share, and industrial outlets a smaller share, than in West Europe.³

As an approximation, about half the total surfactant consumption in the U.S., or more than 1 million tons, goes into industrial outlets. For West Europe, industrial outlets account for around one-third of the total surfactant consumption (excluding soap).

It is not too difficult to understand why the industrial use of surfactants in the U.S. should be so high. After I&I cleaning, the largest single use sector is in the petroleum industry. Figure 3 shows the various ways in which surfactants are used in the petroleum industry. In terms of volume, lube oil additives are dominant; we find here large volumes of specialty surfactants which have little or no use in other applications, e.g. the polybutene succinimides, alkyl phenates and salicylates. With the highly developed state of the petroleum industry and dependence on the automobile, it is not surprising that nearly a quarter of a million tons of surfactants are consumed each year in the U.S. as lubricating oil additives, making this the largest single industrial outlet for surfactants. Significant quantities of surface-active materials are also used in petroleum exploration and production activities⁴.

Petroleum additives are not quite so important in West Europe, where they account for about 11% of the total industrial surfactants consumption, as against 17% in the U.S. (Figure 4). On the other hand, the plastics and elastomers industry takes a

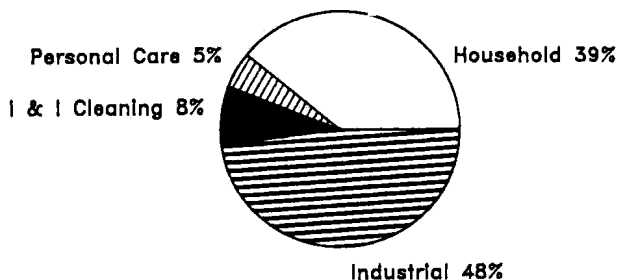
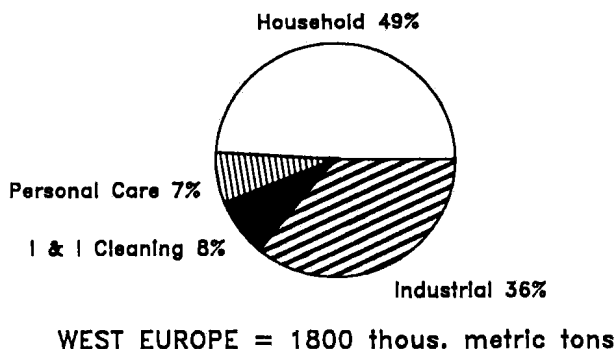


Figure 2 SURFACTANT* OUTLETS IN WEST EUROPE & U.S.

* Does not include soap.

- Lube Oil Additives
- Fuel Additives
- Grease Additives
- Emulsifiers/Demulsifiers
- Biocides
- Drilling Mud Additives
- Corrosion Inhibitors
- Enhanced Oil Recovery
- Others

Figure 3 USES OF SURFACTANTS IN THE PETROLEUM INDUSTRY

rather larger share of the total industrial surfactants consumption in West Europe (14%), than it does in the U.S. (8%). The main application here is emulsion polymerization, although use as antistatic additives in a finished polymer is of some importance. Various types of soaps are important here.

The I&I cleaning markets are important both in the U.S. (15%) and in Europe (18%).

The second largest industrial outlet for surfactants in the U.S. is ore flotation, which is understandably more important in the U.S. (11%) than it is in Europe. The function of surfactants in ore flotation is to separate unwanted material from desirable ore components. The desirable minerals are captured by surfactant froth bubbles and so rise to the top of the bath. Chemicals which assist by increasing the volume of foam ("frothers") include methylisobutyl carbinol, linear alcohols and polypropylene glycol, none of which is normally regarded as a surfactant. Agents which promote incorporation of the desired mineral in the froth bubbles are called "collectors," and include tall oil fatty acids, amines and xanthates.

In the U.S., the food industry accounts for around 7% of the total industrial consumption. Surfactant additives are used in foods both as emulsifiers (to modify starch, protein or fatty products) and to improve texture and reduce "staling," as well as improving finished product quality. Needless to say, only a very restricted range of surfactants, particularly glycerides, are approved for use in food. Perhaps in Europe we are not so fond of having our food improved: surfactant use in the food industry is relatively modest at around 5% (Figure 4).

One sector where Europe is ahead of the U.S. is the textile industry (12% of industrial surfactants in W. Europe, only 6% in the U.S.)

Textiles is really a group of industries, including natural fibers such as cotton and wool as well as the production and processing of synthetic fibers (rayon, polyester, polyolefin, etc.) Virtually every type of surfactant finds some use in the textile industry. Uses include the scouring of raw cotton and wool, aids for applying and removing other process chemicals, and in synthetics as fiber lubricants, scouring, weaving, dyeing and printing aids, as well as assistants for the application of antistatic, permanent press and other finishes.

Another industry where surfactant consumption is more important in Europe than in the U.S. is cement and concrete, where surfactants are used as air-entraining agents and as components of

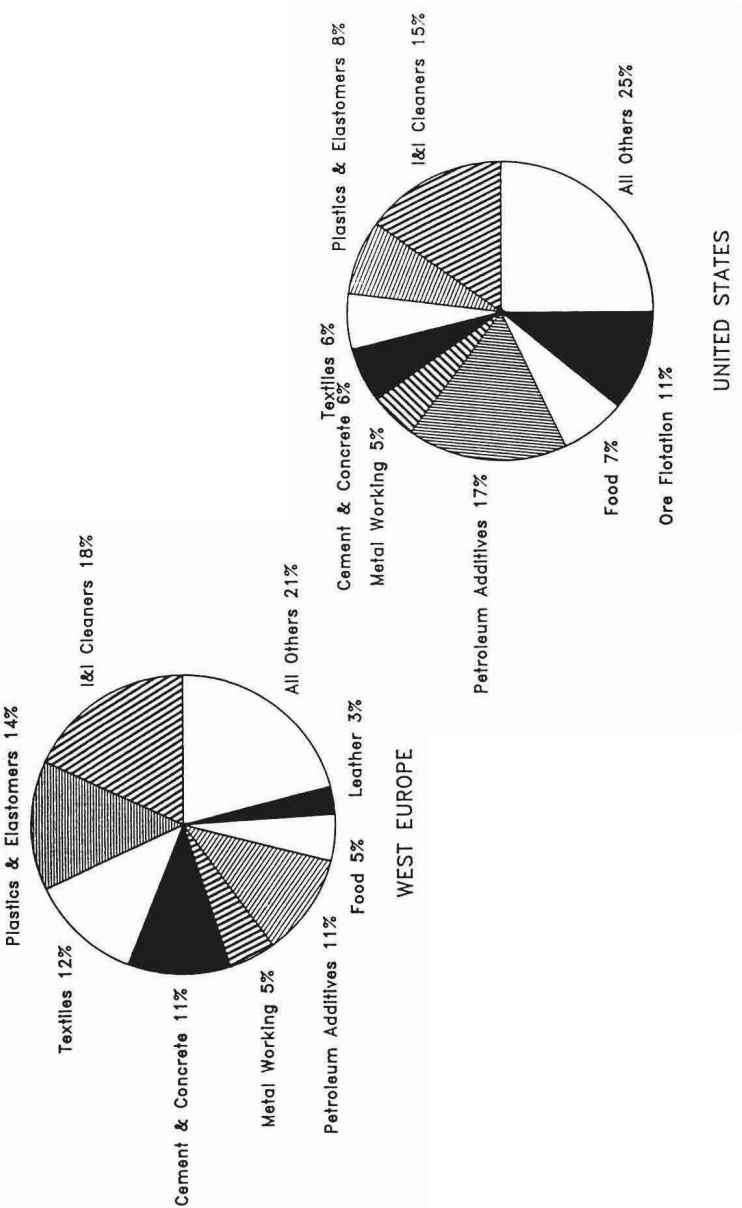


Figure 4 MAJOR INDUSTRIAL OUTLETS FOR SURFACTANTS, 1990

admixtures (superplasticizers, water reducing agents, etc.) (11% in W. Europe, only 6% in U.S.)

A lot of lignosulfonates are used, but synthetic sulfonates based on naphthalene/formaldehyde or melamine/formaldehyde condensates are becoming increasingly popular.

The metalworking industry uses a lot of surfactants, not as foaming agents, but in cutting fluids, rolling oils, drawing compounds and forging lubricants. The surfactants act as emulsifiers, lubricants and corrosion inhibitors, (5% in both W. Europe and the U.S.).

Time does not allow me to comment on all the industrial uses, and I would remind you that there are many interesting applications hidden in the "Others" category of Figure 4.

Why are surfactants used in these various applications? In general, the role of the surfactant in these various processes derives from its ability to undergo adsorption at an interface. This can result in the lowering of a surface or interfacial tension, and/or a stabilization of one or more interfaces (as for example in a foam or an emulsion). Solubilization can also be important. It is perhaps easy to understand in a qualitative way how a surfactant can generate or stabilize a foam, and lubricate or wet a surface, but the question of why one type of surfactant functions better than another type in a specific application is much more complex. Indeed, it is commonly held that the selection of a surfactant for an application such as emulsion polymerization is more of an art than a science.

For a surfactant producer, the household sector and the industrial sector call for very different approaches. In the household sector, you have to deal in the main with a handful of multinational customers who tell their suppliers in broad terms what they want, how much (or usually how little!) they are prepared to pay, but not how they intend to use the product. In the industrial sector, the customer is often not an expert in surfactants, and is looking for an "effect." The cost of the surfactant is not unimportant, but often it is a minor item in the total process cost. The customer does expect the surfactant producer to know all about his product, and also to be expert in the customer's own application and be able to assist in sorting out any problems. The supplier has to be service-oriented. While, as noted a moment ago, the cost of the surfactant may be relatively unimportant, if the overall process is upset, the operating cost can be enormous.

No surfactant supplier can be expert in all industrial application areas, so we have seen the development of companies

which specialize in supplying a range of auxiliaries (not only surfactants but also other chemicals) to a specific industry. Figures 5-9 show some examples of companies which engage in this type of activity in the plastics and elastomers, petroleum, textile, cement and concrete, and food industries. These are a representative selection and not intended to be comprehensive; we apologize to any companies which have been left out.

Some of the largest industrial users of surfactants are themselves surfactant producers, who can develop processes and applications based on their own surfactant range. Figure 10 gives some examples and again, this list does not pretend to be complete.

Although these producers do not necessarily all make a complete range of surfactants, a company such as ICI would have little need to look beyond their own product range for their surfactant requirements.

Future Prospects for Industrial Surfactants

So much for the industrial surfactant market as it stands today. Where do we go from here? Many of the applications I have mentioned have been around now for a good many years. How is industry going to respond to the challenge to come up with some new applications and some new surfactants? We can consider the future outlook under three headings: the overall surfactant requirements of individual industries, the replacement of current surfactants by others, and novel applications.

a) Overall requirements by individual industries

We have seen in recent times a period of low economic growth which has had a major impact on industries such as textiles, metal, construction etc. This has of necessity been reflected in the consumption of surfactants by these industries. There is some hope that things are beginning to improve slowly, but the overall prospects are far from exciting. The textile industry is vulnerable to imports, while the leather industry continues a slow decline. Industries such as cement and concrete, metalworking, or asphalt tend to run parallel with the national economy of the country.

b) Replacement of current surfactants by others?

One of the driving forces for change is of course the regulatory issue, and, in particular, concern about effluents. When an aqueous effluent has to be disposed of via municipal waste water treatment plants, there is natural concern about biodegradability, foaming and aquatic toxicity. Not all industrial uses of surfactants generate an aqueous effluent, but those which do (e.g. textiles, paper, leather) are under increasing pressure to reduce and clean up their effluents.