Detergent Manufacture Including Zeolite Builders and Other New Materials

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Marshall Sittig

NOYES DATA CORPORATION
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DETERGENT MANUFACTURE INCLUDING ZEOLITE BUILDERS AND OTHER NEW MATERIALS

Foreword

This book is a continuation and up-dating of our 1976 volume on *Detergent Manufacture* which enjoyed a ready, universal acceptance by the industry. Much progress has been made in the meantime, and detergents may no longer be accused of causing eutrophication, as phosphates are being replaced by natural and synthetic zeolites. Zeolites may be regarded as a type of inorganic exchange "resin" since their usefulness depends on the cationic exchange of the sodium in the zeolite for the calcium or magnesium of hard water.

Based on the patent literature, this book describes processes from 609 patents.

This book serves a double purpose in that is supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of the manufacture and technology of detergents.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of

this book is to describe the number of technical possibilities available, which may open up profitable areas to research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring our new durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

15 Reasons Why the U.S. Patent Office Literature Is Important to You

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.
2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.
5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
10. Obtain licenses — many U.S. chemical patents have not been developed commercially.
11. Patents provide an excellent starting point for the next investigator.
12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.
15. It is a creative source of ideas for those with imagination.

Contents and Subject Index

Introduction

The overall detergent market is relatively stable, growing at only about 2% per year. However, it is a huge market of several billion pounds per year and composition shifts in response to environmental quality demands are imposing new requirements on detergent product ingredients.

The most recent development, which is discussed in some detail in this volume, involves the use of zeolitic ion exchange materials as builders to replace environmentally harmful phosphates in sequestering hard water ions and aiding detergent action.

HISTORY AND PRODUCT EVOLUTION

The first synthetic detergents were produced in Germany in World War I when animal fats were diverted to other wartime uses and were unavailable for soap manufacture. The first synthetics were short chain alkyl naphthalene sulfonates. They were only fair as detergents but are good wetting agents and are still used as textile auxiliaries.

In the late 1920s and early 1930s long chain alcohol sulfates were sold as the sodium salts together with sodium sulfate extender as the only other constituent. In the 1930s long chain alkyl aryl sulfonates were also introduced and by the end of World War II in 1945 had largely supplanted alcohol sulfates as detergents. From 1950 to 1965 detergents made by reacting propylene tetramer with benzene and sulfonating the product were predominant and had the major portion of the market the world over. Also in 1950 to 1955 the art of detergent formulation advanced and explosive growth occurred in the use of phosphate (tetrasodium pyrophosphate and sodium tripolyphosphate) builders.

Starting in the early 1960s a wave of ecological consciousness spread and this resulted in four major changes in detergent compositions: (1) Tetrapropylene, a branched chain material was replaced with linear chains attached to the benzene nucleus. Also long chain alcohols regained popularity but the key point was that the long chain had to be linear and hence degradable. This change is complete in most developed countries where pollution control laws are highly developed, although some underdeveloped countries still use non-degradable materials.

(2) Algae growth and eutrophication in lakes caused fingers to be pointed at phosphates as the culprits. The influence of phosphates has been disputed but, in any event, searches for nonphosphate builder materials have gone on and are still going on. NTA (nitrilotriacetic acid) was once hailed as the perfect replacement for phosphates but health hazard fears have stunted its growth altogether. Polycarboxylic acids and similar materials have found the most favor as phosphate replacements in building detergents.

(3) A third major change in detergent formulations was in the introduction of enzyme additives to such formulations. These materials serve as catalysts to break down protein materials which may stain clothes. They are often used in a prewashing step to break down materials which are then loosened and removed in the washing cycle. These materials were first introduced in Europe and found wide acceptance there but only entered the U.S. market in the late 1960s, where they are now widely used.

(4) The fourth and latest change in detergent formulations has been the use of zeolite builders, as noted above and as described in detail in a separate section later in this volume. Alternative scenarios for various levels of zeolite use have been presented by H.F. Whalen, Jr., Director of Corporate Development of PQ Corp., Valley Forge, Pa. in a paper presented before the Chemical Marketing Research Association in New York City in May 1978.

DEFINITION OF TERMS

Soaps and detergents are performance products. (By dictionary definition a detergent is a cleaning agent and includes ordinary bar soap, which is classically based on natural fat. In popular usage, however, the term detergent excludes soap, being restricted to the family of cleaning compounds derived largely from petrochemicals. This volume follows popular usage.) Literally thousands of chemical compositions can be formulated which clean a surface. Detergents can be formulated with entirely different organic and inorganic chemicals to exhibit the same cleaning power or have the same biodegradability. They also can be formulated to:

(1) Maximize cleaning power
(2) Maximize biodegradability
(3) Minimize eutrophication potential in a specific receiving water

(4) Maximize cleaning power/unit cost
(5) Minimize air or water pollutants and solid wastes arising from the manufacturing processes.

The primary reason for the success of detergents is their ability to overcome the hard water behavior of soaps. Even though the detergents also react with hard water minerals, the resulting compounds are themselves soluble, or remain colloidally dispersed in the water system. There are four main groups of detergents: anionics, cationics, amphoterics and nonionics.

Anionics comprise the most important group of detergents. They are usually the sodium salts of an organic sulfate or sulfonate. Sulfates are made from long chain fatty alcohols (of animal or petroleum origin). Sulfonates generally are made from alkyl aryl precursors.

Cationic detergents are known as inverted soaps because the long chain ion is of the opposite charge to that of a true soap when dispersed in water. This class of detergents is made in quite small volumes. They are relatively expensive and somewhat harsh on the skin. They make excellent bacteriostats and fabric softeners and are used for this purpose.

Nonionic detergents are increasingly popular active ingredients of automatic washing machine formulations. These products are unaffected by hard water (they do not form ions) and are very low foamers (minimum foam when agitated). They are made by the addition of ethylene oxide to an alcohol.

Amphoterics are those surface active agents which can either be anionic or cationic, depending upon the pH of the system wherein they work. An important class chemically, they account for only a very small portion of the detergent market and little space will be given to them in this volume.

INDUSTRY STRUCTURE

The household detergent industry in the U.S. is dominated by three large companies. They are Procter & Gamble, Colgate-Palmolive and Lever Brothers. In the dry powder portion of the household market (⅞ of the total household market), Procter & Gamble has about 60% of the market, Colgate-Palmolive 15% and Lever Brothers about 11%, according to H.F. Whalen, Jr. The 14% balance of that portion of the household market (⅛ of that market) is shared by over 300 companies. Very few companies beyond the five largest produce and market products across the country. The smaller companies captured an appreciable portion of the market share of the big three with non-phosphate detergents before bad publicity put a damper on sales of some phosphate-free laundry detergents.

The three largest companies in the household market have plants in major metropolitan areas across the country. Not only are distribution costs impor-

tant, but also the large volume of products makes it possible for one company to build economical-sized plants in a number of locations. There are about thirty major plants for production of heavy-duty laundry detergents in the United States.

It is fairly common for the major companies to contract with other companies for toll processing. In these arrangements the soap and detergent company will buy synthetic detergent bases, send them to a second company for reaction, and have the product returned for further compounding. For example, detergent alcohols may be bought by a soap and detergent company and then toll ethoxylated by a petrochemical company and returned to the soap and detergent company for further processing. Another business arrangement is the production of packaged detergents by private label producers which are then sold by the major food chains under their own brand names.

The capital requirements for a spray-dried detergent bead plant limit the number of these units. To be competitive, these complexes produce volumes on the order of 13,620 kg per hour (30,000 lb/hr) and cost up to ten million dollars. Production of light-duty liquid detergents and dry blended products requires less capital and consequently many more producers are found. Freight is an important consideration in shipping liquids.

TYPES OF DETERGENT PRODUCTS

Laundry detergents are the largest category of products made by the soap and detergent industry. The number one selling brand has held about a 25% share of the U.S. market for over two decades. This brand is the industry standard for this category of product and the market leader fights hard to maintain his level of sales of household detergents. Other detergent companies constantly search for improved products containing better ingredients so they can get a bigger share of this market. The cost of the search for new and improved products has increased greatly because of the more sophisticated safety and environmental approaches now needed.

Liquid hand dishwashing detergents are next to laundry detergents in importance. Although the largest companies do dominate this market there are many private label products sold by supermarket chains and also quite a number of brands marketed by smaller companies.

Automatic dishwashing detergents are produced in sizable amounts by medium and small-sized firms as well as the large detergent companies. This category of product has grown very rapidly with the proliferation of the home automatic dishwasher. With only a third of the nation's households having automatic dishwashers great growth can be expected to continue.

Household specialty cleaners of all types are produced by hundreds of companies in successful competition with the big three. This is possible because

the specialties require less capital investment than spray-dried laundry detergents. Also, specialties are amenable to smaller and localized marketing and advertising programs.

DETERGENT RAW MATERIALS

The family tree of detergent raw materials, intermediates and finished active ingredients is shown in Figure 1. In the manuscript which follows, the production of each of these raw materials, intermediates and finished products will be discussed in some detail. Finally the formulation of finished detergent products will be described with attention to each of the ingredients going into such final products.

In general, the detergent industry has not integrated backwards toward their raw materials. Basic raw materials come from a host of supplier companies. Detergent alkylate, alcohols and nonionic surfactants usually come from large chemical and petrochemical companies. Some anionic surfactant is also produced by suppliers, but in general the detergent companies do most of their own sulfation and sulfonation. The inorganic builders and other additives come exclusively from supplier companies.

There are three routes open to the manufacturer of detergents:

(1) The end product may be produced from basic detergent raw materials such as alkylbenzenes by sulfonation and finishing processes. This requires high initial investment but gives the widest scope for developing a complete range of cleaning materials.
(2) A detergent material that has already been sulfonated may be used. This method still provides a fairly wide scope for development and avoids the necessity for erecting an expensive sulfonation plant which can only be operated by skilled labor and under expert chemical supervision.
(3) Already sulfonated and neutralized detergents in a highly concentrated form, either as a paste-slurry or in the form of spray-dried or drum-dried powder or flakes may be purchased. This material has then only to be diluted to obtain liquid products, etc.

The last-mentioned way of simply mixing detergent concentrates is the least expensive but also the least interesting from a profit standpoint. However, this method affords certain possibilities to a small-scale producer. By careful selection of those materials with which the detergent concentrates are compounded, quite interesting and valuable detergent products may be obtained.

Trends in detergent raw materials have been reviewed by D.H. von Hennig,