

# **SURFACTANTS, DETERGENTS AND SEQUESTRANTS**

**Developments Since 1979**

Edited by J.I. DiStasio

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**Edited by J.I. DiStasio**

**NOYES DATA CORPORATION**

**Park Ridge, New Jersey, U.S.A.**

**1981**

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## Foreword

The detailed, descriptive information in this book is based on U.S. patents, issued since July 1979, that deal with surfactants, detergents and sequestrants. This title contains new developments since our previous title *Surfactants and Sequestrants* published in 1977.

This book is a data-based publication, providing information retrieved and made available from the U.S. patent literature. It thus serves a double purpose in that it supplies detailed technical information and can be used as a guide to the 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 commercially oriented review of recent developments in the field of surfactants.

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 of 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 these 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.

### 16 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. Most important technological advances are described in the patent literature.
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. Identifying potential new competitors.
15. It is a creative source of ideas for those with imagination.
16. Scrutiny of the patent literature has important profit-making potential.



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## Introduction

Surfactants (surface active agents) are organic chemical wetting, cleaning and disinfecting agents. They find wide utility in such diverse products as detergent and washing compounds, water softeners, textile softeners, antistatic agents, lubricants, in oil well operations, in plastics manufacture, in shampoos, cosmetics, and medicinal agents. Detergency builders and sequestrants are often used in conjunction with surfactants. One outstanding property of sequestrants is the formation of stable, soluble complex ions with metals. The sequestrants, or chelating agents, can improve the washing power of surfactant mixtures, stabilize emulsion systems, and can also be used alone in certain specialized cleaning products such as for the removal of scale and sludge from metal surfaces.

This book contains about 240 patents issued since 1979 dealing with surfactants and sequestrants and their incorporation into a wide variety of products. Also included are a number of additives that are commonly used in surfactant compositions, such as bleaching agents, detergent perfumes and coloring agents, enzymes, etc.

There has been an emphasis in the past few years on the development of detergents with improved washing power which are also biodegradable and non-polluting. In the detergent industry, distinctions are drawn between cleaning compositions on the basis of their functional utility, for example, those used for laundering purposes, machine dishwashing purposes, and those used for hand dishwashing purposes. Generally, cleaning compositions for laundering purposes employ high foaming organic surfactants as the main cleansing agents. Foaming, unless it is excessive to the extent that it causes overflow from the washing machine, is generally considered beneficial since it helps loosen the soil from the fabrics by its local mechanical action.

In contrast, machine dishwashing methods utilize the high mechanical impact of the wash liquid sprayed on the articles to be cleaned to dislodge the soil and food particles. The surface active agents useful for machine dishwashing compositions should not only be low foaming material in themselves, but should

also be foam depressants, so that foaming caused by protein and food residues in combination with alkaline cleansing solutions is kept to a minimum. Accordingly the surfactant content of machine dishwashing compositions is very low. This situation, however, is quite different from hand dishwashing compositions, which preferably are high foaming and have more the attributes of laundry compositions.

A laundry detergent must wash both natural and synthetic fibers. It must provide good soil removal, including grease and oil, and good whiteness retention. The detergent must not damage or roughen the fabrics, or unduly shorten their service lives. It must not remove any permanent-press resin treatment on the fabric. It must not be toxic to the user, have a displeasing odor or color, or foam too much, or cost too much. Finally, it should not contain components which are ecologically undesirable.

The processes contained in this book include those which go a long way toward solving many of the above problems, as well as a number of processes directed toward the utilization of surfactants in other nondetergent types of compositions.

Surfactants (surface active agents) are organic chemical wetting, cleaning and dispersing agents. They find wide utility in such diverse products as detergent and washing compounds, water softeners, textile softeners, emulsants, agents, lubricants, in oil well operations, in plastic manufacture, in shampoos, cosmetics, and medicinal agents. Detergency builders and sequestrants are often used in conjunction with surfactants. One outstanding property of sequestrants is the formation of stable, soluble complex ions with metals. The sequestrants, or chelating agents, can improve the washing power of surfactant mixtures, stabilize emulsion systems, and can also be used alone in certain specialized cleaning products such as for the removal of scale and sludge from metal surfaces. This book contains about 240 patents issued since 1979 dealing with surfactants and sequestrants and their incorporation into a wide variety of products. Also included are a number of additives that are commonly used in surfactant compositions, such as bleaching agents, detergent perfumes and coloring agents, enzymes, etc.

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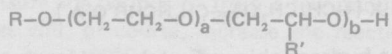
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# Syntheses of Various Surfactants

## NONIONIC SURFACTANTS

### Alkali-Stable Nonionic Surfactants

M. Scardera and F.R. Grosser; U.S. Patent 4,207,421; June 10, 1980; assigned to Olin Corporation describe a surfactant product which has the following formula:



wherein R is a linear alkyl hydrocarbon having an average of about 16 to 18 carbon atoms; R' is methyl or ethyl; a has an average value of 9 to 15; b has an average value of 3 to 5; the ratio of a:b being from 2.7:1-3.5:1.

The surfactant compositions may be prepared using any of the well-known methods of condensing an alkylene oxide with an alcohol. Such methods are described, for example, in U.S. Patents 2,677,700 and 3,340,309 and *Nonionic Surfactants*, Schick (1967), p. 102. In general, the compounds may be prepared by reacting a primary, linear, monohydric alcohol having from 16 to 18 carbon atoms with ethylene oxide in the desired amounts at an elevated temperature (in the range of about 140° to 200°C, preferably about 160° to 180°C) in the presence of about 0.005 to 1.0%, based on the alcohol weight, of alkaline catalysts, such as salts or hydroxides of the alkali metals or alkaline earth metals. The preferred catalyst is KOH.

Subsequent to the ethylene oxide addition, the ethoxylated product is condensed with propylene or butylene oxide, preferably propylene oxide, using the same type of catalyst and reaction conditions, to obtain the final surfactant product.

The surfactant products of the process are biodegradable, water-soluble, moderate to high sustained foaming, and stable on dry caustic. Such advan-



tageous properties make these surfactants useful in various applications, in particular alkaline compositions, such as detergent formulations, as wetting, washing, dispersing, etc., agents in the textile, leather, paper, paint, pharmaceutical and cosmetic industries, etc., as well as for household applications.

**Example:** Into a three-necked, 500 ml round bottom flask fitted with a dropping funnel, nitrogen inlet, thermometer, stirrer, dry ice condenser and vent, 79.8 g (0.3 mol) of Alfol 1618 (a blend of straight chain aliphatic alcohols having an average carbon chain length of  $C_{16-18}$ , primarily consisting of 16 carbon and 18 carbon alcohols) and 0.4 g potassium hydroxide (0.007 mol, 0.5% based on the alcohol weight) were added.

Under a nitrogen atmosphere, 138.6 g of ethylene oxide was introduced dropwise to the alcohol at a temperature of  $160^{\circ}$  to  $170^{\circ}\text{C}$ . Upon completion of the ethylene oxide addition, 63.2 g of propylene oxide (1.09 mols) is then placed in the dropping funnel and added to the reaction mixture (an alcohol-ethylene oxide adduct) dropwise at  $150^{\circ}$  to  $170^{\circ}\text{C}$ . After propylene oxide addition, the reaction product was stirred an additional half hour at reaction temperature. It was then allowed to cool and the potassium hydroxide was neutralized with acetic acid. The product weighed 281.8 g. The molecular weight of the final product was determined to be about 939 with an alcohol-ethylene oxide-propylene oxide ratio of 1.0:10.5:3.6.

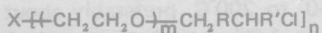
#### Onium Surfactants from Nonionic Surfactants

*R.F. Harris and E.H. Wagener; U.S. Patent 4,240,982; December 23, 1980; assigned to The Dow Chemical Company* describe onium surfactants which are represented by the formula:



wherein X is an n-valent hydrophobic radical derived by the removal of n-atoms of active hydrogen from an organic compound, m is an integer of at least 1 and is normally from 1 to about 200 and is most frequently from 4 to about 50; n is an integer of from 1 to 5; R is a divalent aromatic hydrocarbon radical of from 6 to about 14 carbon atoms (preferably 6 to 12 carbon atoms), the chain length of which can be interrupted by oxygen or sulfur atoms; R' is hydrogen or methyl and is methyl only when R is m- or p-phenylene; Q<sup>+</sup> is a quaternized atom of nitrogen or phosphorus or a tertiary atom of sulfur; and A<sup>-</sup> is a compatible anion.

The precursors are represented by the formula:



wherein X, R, R', m and n have the aforesaid meanings. The precursors are likewise surfactants.

**The Precursors:** The precursors are prepared by reacting nonionic surfactants with bischloromethylated aromatics in the presence of a strong base.

Included within the class of suitable nonionic surfactants for use herein, the ethoxylated derivatives of linear primary alkanols or alkenols, linear alkanolic or alkenolic acids, and alkyl phenols having from about 12 to 24 carbon atoms

are preferred along with the polyoxyethylene-capped polymers of propylene oxide and/or butylene oxide initiated with a  $C_{1-4}$  alkanol, ethylene glycol, propylene glycol, butylene glycol or glycerol. The ethoxylated derivatives of alkyl phenols having from about 12 to 24 carbon atoms are the most preferred nonionic surfactants for use herein.

The bischloromethylated aromatic reactants are likewise a known class of compounds. They are represented by the formula  $ClCH_2RCHR'Cl$ , wherein R and R' are as defined above.

The preferred compounds are bischloromethylated derivatives of benzene, naphthalene, diphenyl oxide or diphenyl sulfide. The most preferred compounds are m- and p-bis(chloromethyl)benzene.

The stoichiometry of the reaction requires 1 mol of bischloromethylated reactant per hydroxy equivalent weight of nonionic surfactant (i.e., molecular weight of the surfactant divided by the number of terminal hydroxyethyleneoxy groups on the surfactant molecule). Best results are achieved by using an excess of the bischloromethylated aromatic reactant. This excess reduces the amount of undesirable by-product produced in the reaction (e.g., bisethers, etc.).

The reaction between the nonionic surfactants and the bischloromethylated aromatics is conducted in the presence of a strong base. Suitable bases include alkali metals (e.g., sodium, potassium), alkali metal alkoxides (e.g., sodium or potassium methoxide, ethoxide, tert-butoxide, etc.) and such. The base reacts with the HCl formed in the course of the reaction and tends to both catalyze the reaction and drive it to completion. The amount of base used can be varied but optimum results seem to be attained when the base is present in slight excess of 1 equivalent of base per hydroxy equivalent weight of nonionic surfactant.

The reaction is normally conducted with stirring at ambient conditions of temperature and pressure for periods of from a few minutes up to a few days. Elevated temperatures will, of course, increase the reaction rate and reaction temperatures of up to about  $80^\circ C$  have been used with success on combinations of reactants having a low rate of reactivity.

It was found convenient to conduct the reaction by adding the bischloromethylated aromatic reactant to a mixture of the nonionic surfactant and base. A liquid reaction medium may be used, if desired, to facilitate temperature control and contact between the reactants. Any inert solvent can be used and tert-butanol is particularly useful in this regard.

Precursors corresponding to the general formula given above in which R' is methyl can be prepared in an analogous but alternative procedure. Namely, m- or p-vinyl-benzyl chloride can be reacted with the nonionic surfactant to give a vinyl benzyl ether of the surfactant which in turn is reacted with HCl to give the desired product.

**The Onium Surfactants:** The onium surfactants are conveniently prepared by reacting the precursors with an appropriate nitrogen, phosphorus or sulfur-containing organic compound (e.g., a tertiary amine, a pyridine, a thiourea, a tertiary phosphine, a sulfide, etc.). Normally, this reaction is conducted in an inert liquid reaction medium (e.g., water or water/lower alkanol mixtures) and the onium product is recovered therefrom by conventional techniques. Ambient conditions of temperature and pressure are normally satisfactory but elevated temperatures (e.g., up to about  $80^\circ C$ ) can be used advantageously

in some instances. The course (extent) of the reaction can be easily followed by the production of ionic chloride.

**Example 1:**  $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{15}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$  was prepared as follows. An ethoxylated p-nonylphenol formula  $\text{p-C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{15}\text{H}$  (342 g, 0.4 mol) and tert-butanol (3 l) and metallic sodium (13.8 g, 0.6 mol) were charged under a nitrogen atmosphere to a 5 l, 3-necked flask equipped with a mechanical stirrer, thermometer and condenser. The mixture was warmed at gentle reflux with stirring until all of the sodium had reacted.

The temperature of the mixture was then brought to 40°C and 1,4-bis-(chloromethyl)benzene (350 g, 2.0 mols) was added in one shot with stirring. The temperature exothermed less than 2°C. Aliquots of the mixture were taken immediately after the addition of the 1,4-bis(chloromethyl)benzene and at periods of 2 and 4 hr thereafter (aliquots 1, 2 and 3, respectively). The amount of ionic chloride in milliequivalents in each aliquot was determined and is reported below.

Aliquot	meq Cl <sup>-</sup> /g	Conversion* (%)
1	0.127	58
2	0.199	91
3	0.210	96

\*Premised on amount of sodium consumed.

After a total of 4 hr at about 40°C, the mixture was filtered to remove the solids from the liquid product. The filter cake was washed with 2 l of benzene and the liquid wash combined with the original filtrate. The benzene and tert-butanol solvents were removed under reduced pressure at an elevated temperature (ca 80°C at 5 mm Hg) leaving the liquid product and unreacted 1,4-bis-(chloromethyl)benzene. The latter compound was removed by warming the mixture at 170° to 180°C at 1 mm Hg thereby leaving the desired product as a light yellow oil (382.4 g).

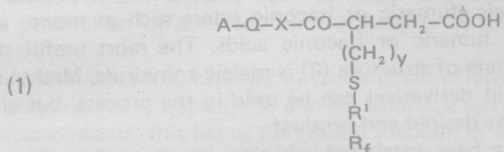
Hydroxyl titration and the nuclear magnetic resonance spectrum of this material indicated that it contained 5.7 wt % of unreacted ethoxylated nonylphenol, 6.6 wt % of the adduct of 2 mols of ethoxylated nonylphenol and 1 mol of 1,4-bis(chloromethyl)benzene and 87.7 wt % of the desired product, total weight basis in each instance. This represents a 78.8% product yield, based on ethoxylated nonylphenol added. A 0.1 wt % aqueous solution of the product had a surface tension of 32.8 dynes/cm at 25°C. The product is therefore a surfactant.

**Example 2:**  $\text{p-C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{15}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{S}^+(\text{CH}_3)_2\text{Cl}^-$  was prepared as follows. A portion of the product from Example 1 (90 g, 0.088 mol) was mixed with methanol (170 ml), water (30 ml) and dimethyl sulfide (37 ml, 0.5 mol) in a sealed vessel equipped with a mechanical stirring means. The reaction mixture was stirred at ambient temperature for several hours and the progress of the reaction measured by titration of ionic chloride in aliquots removed from the mixture. After 46 hr the conversion of the reactant to the corresponding sulfonium chloride seemed to level off at about 85% conversion. Water (300 ml) was added to the mixture and any unreacted dimethyl sulfide

was removed along with methanol and some water by subjecting the mixture to a reduced pressure at ambient temperature. The desired sulfonium chloride was thus obtained as a yellow aqueous solution containing 34 wt % sulfonium chloride solids. The surface tension of a 0.1 wt % aqueous solution of this sulfonium surfactant was 36.3 dynes/cm at 25°C.

### Fluorinated Nonionic Surfactants

K.F. Mueller; U.S. Patent 4,171,282; October 16, 1979; assigned to Ciba-Geigy Corporation describes perfluoroalkyl substituted half esters and amides having the formula:



wherein

$\text{R}_f$  is straight or branched chain perfluoroalkyl of 4 to 18 carbon atoms or the perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms;

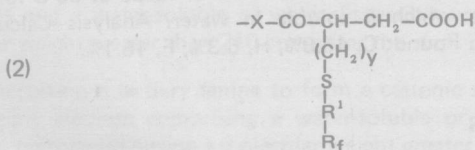
$\text{R}^1$  is branched or straight chain alkylene of 1 to 12 carbon atoms, alkyleneethioalkylene of 2 to 12 carbon atoms, alkyleneoxyalkylene of 2 to 12 carbon atoms or alkyleneiminoalkylene of 2 to 12 carbon atoms where the nitrogen atom contains as a third substituent, hydrogen or alkyl of 1 to 6 carbon atoms;

X is oxygen or NH;

y is 1 or zero;

Q is a polyether or polyester diradical moiety having a molecular weight of 300 to 5,000 or a polysiloxane having 5 to 80 repeating units; and

A is hydrogen, hydroxyl, amino, alkoxy of 1 to 21 carbons, phenoxy, alkylphenoxy of 7 to 20 carbons, dialkylamino where each alkyl has 1 to 18 carbons or the group:



Preferably  $\text{R}_f$  is a straight or branched chain perfluoroalkyl of 6 to 12 carbon atoms;  $\text{R}^1$  is alkylene of 1 to 6 carbons and most preferably ethylene; y is zero; Q is a polyalkylene oxide having from 10 to 50 repeating units, such as polyethylene oxide; and A is hydroxyl, amino, methoxy or alkylphenoxy of 7 to 15 carbon atoms.