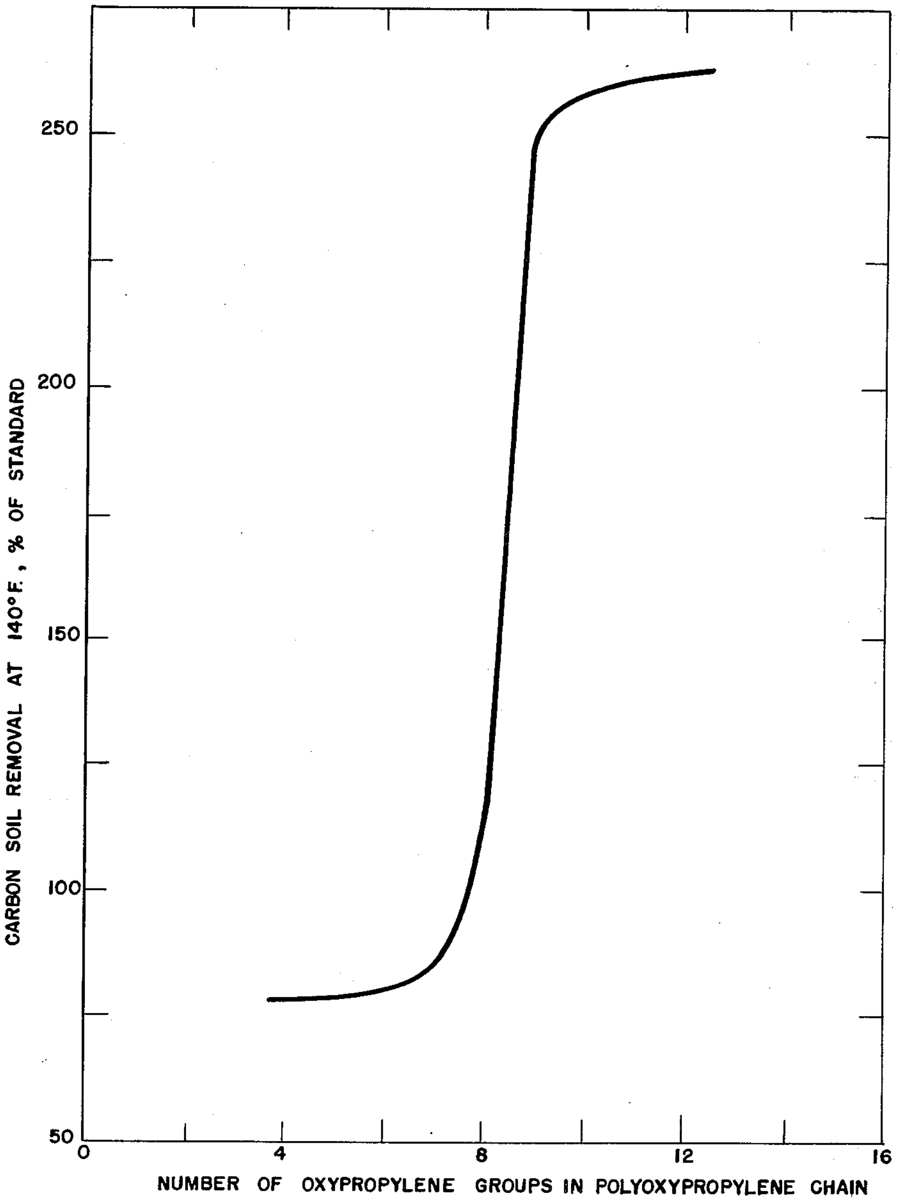
May 4, 1954 **D. R. JACKSON ET AL** **2,677,700**

POLYOXYALKYLENE SURFACE ACTIVE AGENTS

Filed May 31, 1951 3 Sheets-Sheet 1

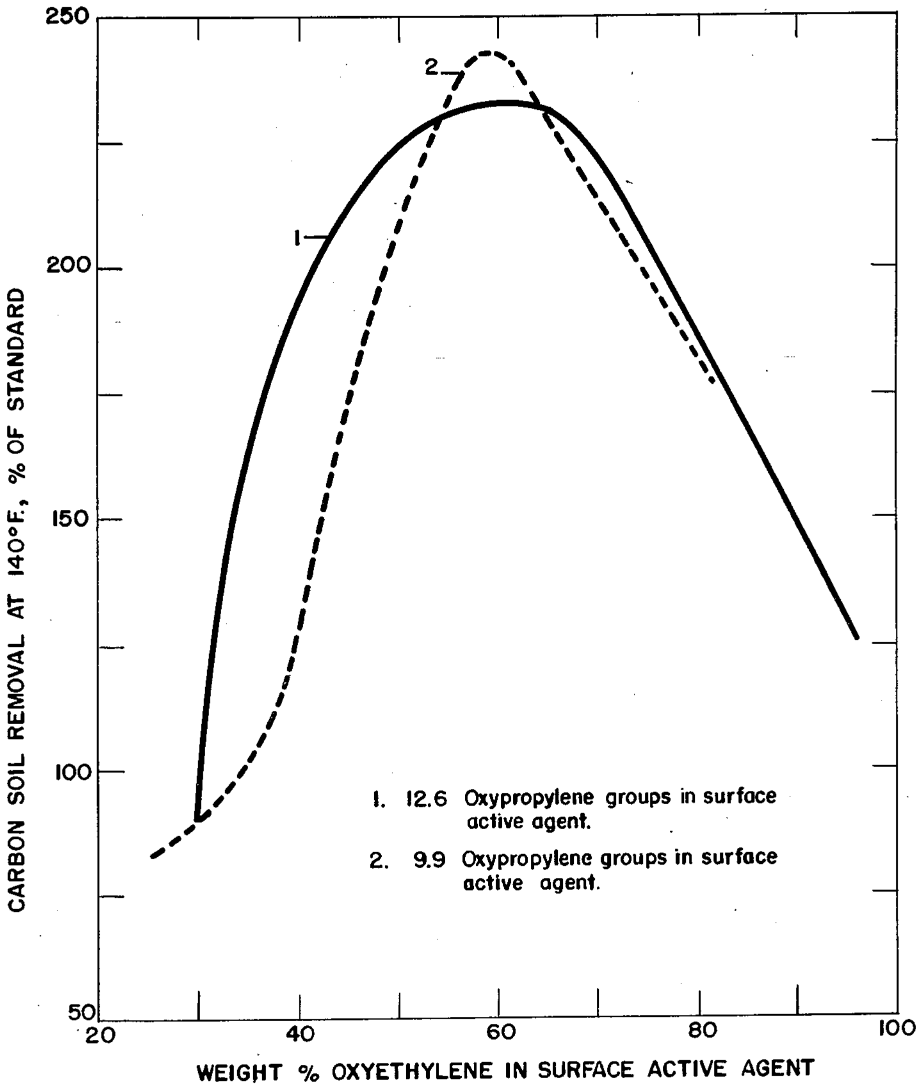
FIGURE I



Donald R. Jackson & Lester G. Lundsted
INVENTORS

BY Morton B. Lilly
Attorney

Figure II



Donald R. Jackson & Lester G. Lundsted
INVENTORS

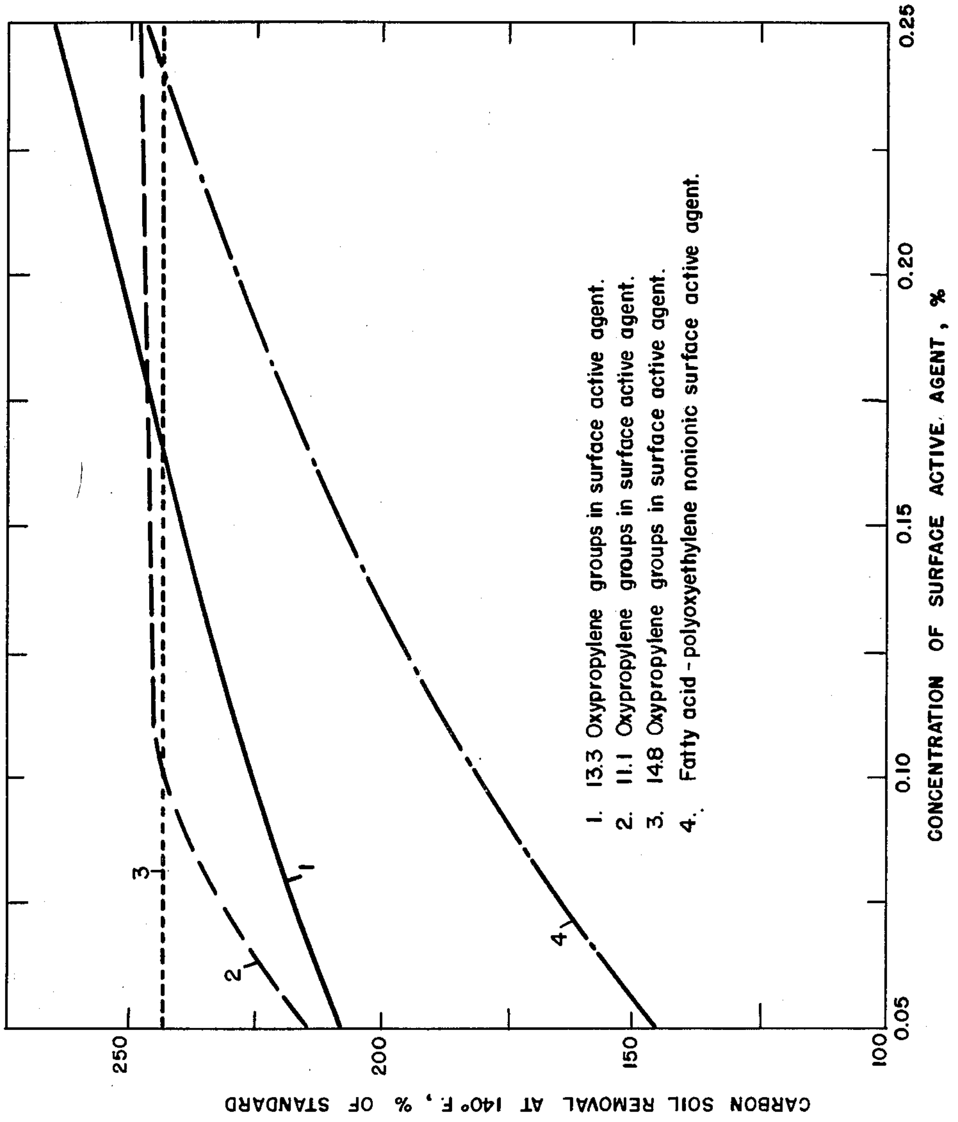
BY Merton B. Lilly
Attorney

May 4, 1954 D. R. JACKSON ET AL 2,677,700

POLYOXYALKYLENE SURFACE ACTIVE AGENTS

Filed May 31, 1951 3 Sheets-Sheet 3

FIGURE III



Donald R. Jackson & Lester G. Lundsted
INVENTORS

BY Merton B. Lilly
Attorney

UNITED STATES PATENT OFFICE

2,677,700

POLYOXYALKYLENE SURFACE ACTIVE AGENTS

Donald R. Jackson, Wyandotte, and Lester G. Lundsted, Grosse Ile, Mich., assignors to Wyandotte Chemicals Corporation, Wyandotte, Mich., a corporation of Michigan

Application May 31, 1951, Serial No. 229,128

19 Claims. (Cl. 260—488)

This invention relates to polymeric, anionic and nonionic surface active agents in which the essential hydrophobic element is a polyoxyalkylene chain of a prescribed minimum chain length, and to methods of preparing same. This invention further relates to surface active agents in which both the hydrophobic and hydrophilic elements can be simultaneously varied, both as to molecular weight and type, to prepare "tailored" surface active agents, and to methods of preparing same.

The surface active agent art is old and it is a well recognized principle that all such agents are relatively large molecules that contain both hydrophobic and hydrophilic elements. The hydrophobic element in the prior art surface active agents heretofore has always been a hydrocarbon radical, such as found in the long chain fatty acids and alcohols, or the alkylaryl group found in the popular alkylarylsulfonate type detergent. The hydrophilic element has been either ionic in nature, such as found in the alkali metal salts of long chain fatty acids, the quaternary ammonium compounds, the alkylarylsulfonates and the long chain fatty acid sulfates or nonionic, such as found in long chain hydrophilic polyethers obtained by the condensation of alkyl phenols with ethylene oxide or derivatives thereof. It is recognized that to obtain optimum surface active properties it is desirable to have a proper balance between hydrophobic and hydrophilic elements.

Heretofore many anionic and nonionic surface active agents have been known in the art and have gained wide public acceptance. Among such anionic surface active agents are alkali metal salts of long chain fatty acids, long chain fatty alcohol sulfates, long chain alkyl sulfonates and long chain alkylarylsulfonates. Well known nonionic surface active agents include, for example, the condensation products of ethylene oxide and long chain fatty acids and alcohols or long chain alkyl phenols.

A serious limitation of the prior art surface active agents is that the structure of any particular surface active agent is relatively fixed and it is difficult to modify either as to molecular weight or type. To prepare fatty acid and/or fatty alcohol base surface active agents having varying hydrophobic element chain lengths, it is necessary to use several different base materials. Because of the difficulties inherent in using several base materials, which require different reaction conditions in preparing surface active agents, it is not feasible to prepare surface active agents which differ from one another in small, uniform increments of hydrophobic element chain length. Similar difficulties are encountered in preparing petroleum base surface active agents which differ from each other only in small, finite increments of hydrophobic element chain length.

The prior art surface active agents suffer severe economic shortcomings. The available supply of natural fatty acids and alcohols does not always coincide with the demands of the surface active agent industry and, as a consequence thereof, such products are subject to extremely large price fluctuations. The dual problem of availability and price is particularly severe during periods of national emergency or war.

The prior art nonionic surface active agents that are highly active compounds are all liquids or pastes and have not been available in a solid form. While the physical form of a surface active agent does not affect its surface active properties, convenience in packaging, distribution and use makes a solid form highly desirable.

Polyoxyalkylene units have been used heretofore in surface active agents, but perform functions differing diametrically from that performed by the hydrophobic polyoxyalkylene units in the present invention. U. S. Patents 2,213,477; 2,454,434 and 2,454,542–545 teach the addition of ethylene oxide, propylene oxide, butylene oxide, etc. to hydrophobic alcohols and acids to form the hydrophilic element of nonionic surface active agents. In marked contrast to these teachings, it has been discovered that alkylene oxides having prescribed minimum oxygen/carbon ratios can be polymerized to critical minimum chain lengths to provide the essential hydrophobic element of anionic and nonionic surface active agents.

U. S. 2,174,761 teaches the preparation of surface active agents by the sequential addition of propylene oxide and ethylene oxide to long chain hydrophobic alcohols. In the surface active agents thus produced, the long chain hydrophobic alcohol is the essential hydrophobic element and not the polyoxyalkylene chain. Consequently, the required use of long chain hydrophobic alcohols again creates the problem of supply and high cost of materials.

It is an object of this invention to provide highly active polymeric, anionic and nonionic surface active agents, as well as commercially attractive methods for preparing same.

Another object of this invention is to provide highly active polymeric, anionic and nonionic surface active agents from cheap and readily available raw materials.

A further object of this invention is to provide highly active polymeric, anionic and nonionic surface active agents in which the essential hydrophobic element is a polyoxyalkylene chain.

Still another object of this invention is to provide highly active polymeric, anionic and nonionic surface active agents in which the essential hydrophobic element is a polyoxypropylene chain.

A still further object of this invention is to provide highly active polymeric, anionic and nonionic surface active agents in which both the hydrophilic and hydrophobic elements can be simultaneously varied or modified, both as to molecular weight and type.

Yet another object of this invention is to provide highly active polymeric nonionic surface active agents in a solid form.

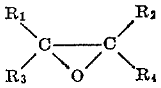
Other objects and advantages of this invention will become apparent from the following detailed description thereof when read in conjunction with the accompanying drawings, in which

Fig. 1 is a graph showing the effect of the hydrophobic polyoxyalkylene chain length upon carbon soil removal properties,

Fig. 2 is a graph showing the effect of variation of the hydrophilic group upon carbon soil removal properties, and

Fig. 3 is a graph showing the effect of concentration of the surface active agents of this invention upon carbon soil removal.

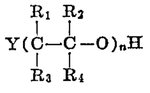
It has been discovered that an organic compound containing therein a single hydrogen atom capable of reacting with a 1,2 alkylene oxide can be condensed with a 1,2 alkylene oxide of the formula:



wherein:

R_1, R_2, R_3 and R_4 are selected from the group consisting of H, aliphatic radicals and aromatic radicals, at least one such substituent being a radical other than hydrogen.

to prepare polymeric compounds having the type formula:



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

wherein:

Y is the residue of an organic compound containing therein a single hydrogen atom capable of reacting with a 1,2 alkylene oxide,

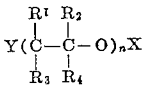
R_1, R_2, R_3 and R_4 have the same meaning as set forth above, and

n is greater than 6.4, as determined by hydroxyl number.

The terminal hydroxyl group of the above defined polymeric compounds may be used as a site of further reaction to introduce a water-solubilizing group into the molecule and prepare highly active surface active agents, which may be either anionic or nonionic depending upon the particular water-solubilizing group that is added to the hydroxyl group.

Structure of surface active agents

The surface active agents of this invention have the following type formula:



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nX$$

wherein:

Y is the residue of an organic compound containing therein a single hydrogen atom capable of reacting with a 1,2 alkylene oxide.

R_1, R_2, R_3 and R_4 are selected from the group consisting of H, aliphatic radicals and aromatic radicals, at least one such substituent being a radical other than hydrogen,

n is greater than 6.4 as determined by hydroxyl number, and

X is a water-solubilizing group.

Examples of Y include the residue from compounds such as the monofunctional alcohols, e. g. methanol, butanol, etc.; aliphatic acids such as formic acid, acetic acid, butanoic acid; secondary amines such as diethyl amine, ethyl butylamine, etc.; N-substituted amides such as methyl acetamide; aliphatic mercaptans such as methyl and butyl mercaptan; N-substituted sulfonamides such as N-propyl ethanesulfonamide and other compounds having a single active hydrogen, as above described. The Y group may be substituted with groups which do not contain an active hydrogen capable of reacting with a 1,2 alkylene oxide, e. g. Cl, Br, $-NO_2$, alkoxy, etc.

In defining R_1, R_2, R_3 and R_4 the terms "aliphatic radicals" and "aromatic radicals" are used in their broad generic sense. The term "aliphatic radical" includes both open chain and cyclic compounds that are free of benzenoid unsaturation but which may contain ethylenic and/or acetylenic unsaturation. This definition covers groups such as the cyclopentyl and cyclohexyl radicals. Included within such definition are structures in which two R groups on adjacent carbon atoms are members of a single alkylene ring, an example of such a structure being the oxycyclohexene group.

The term "aromatic radical" includes both mononuclear and polynuclear aromatics, such as the phenyl radical, the naphthyl radical, the biphenyl radical, etc.

As in the case of Y, above recited, both the aliphatic radicals and aromatic radicals can be substituted with radicals or groups that do not contain an active hydrogen capable of reacting with a 1,2 alkylene oxide.

Examples of such polyoxyalkylene chains which may be employed are polyoxybutylene, polyoxystyrene, polyoxycyclohexene, etc., and preferably polyoxypropylene.

The above-noted structural formula shows a homogeneous polyoxyalkylene chain. While a substantially homogeneous polyoxyalkylene chain is the preferred embodiment of this invention, it is to be understood that the polyoxyalkylene chain can be made up of mixtures of monomeric components so long as essentially each monomeric unit conforms to the definitions set forth above. Examples of such heteric structures are those obtained by condensing an active hydrogen compound with a mixture of 1, 2 alkylene oxides, e. g. propylene and butylene oxides, amylene and cyclohexene oxides, etc.

It will be recognized in the above-noted definition that at least one R group is a radical other than hydrogen, therefore the oxygen/carbon ratio of the hydrophobic polyoxyalkylene chain is equal to or less than 0.33.

The value of *n*, as determined by hydroxyl number, must be greater than 6.4. The method of determining the value of *n* is discussed under the section entitled "Preparation of surface active agents." Henceforth, whenever *n* is reported, it is to be understood that it was determined by hydroxyl number.

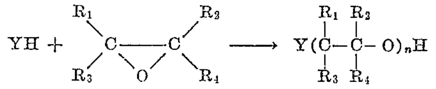
X is a water-solubilizing group and may be ionic in nature or may be a hydrophilic polyoxyalkylene chain wherein the oxygen/carbon ratio is equal to or greater than 0.5. Included among the ionic water-solubilizing groups are the sulfate group, the phosphate group and the borate group. The water-solubilizing polyoxyalkylene chains are those in which the oxygen/carbon ratio is equal to or greater than 0.5, a preferred example of such a chain being a polyoxyethylene chain.

When the water-solubilizing group is a hydrophilic polyoxyalkylene chain, this chain must be present in an amount sufficient to render the surface active agent water-soluble to at least the extent that such agents are used in ordinary applications, which is usually about 0.1% by weight. In order to meet the solubility requirement the hydrophilic polyoxyalkylene chain must constitute at least about 25%, by weight, of the surface active agent.

Preparation of surface active agents

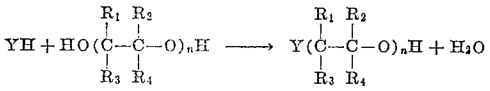
The preparation of the surface active agents of this invention involves two steps: first, the reaction of a compound containing a single active hydrogen atom with a 1,2 alkylene oxide, wherein the oxygen/carbon ratio is equal to or less than 0.33, or a polyoxyalkylene glycol corresponding thereto and, second, the reaction of the resulting intermediate compound with a second compound to introduce the water-solubilizing portion of the agent.

In the first step an organic compound containing therein a single hydrogen atom capable of reacting with a 1,2 alkylene oxide is condensed with a suitable 1,2 alkylene oxide, viz:



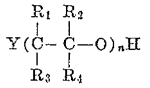
$$YH + \underset{R_3}{\overset{R_1}{}}\!\!>\!C\!\!-\!\!\!\underset{O}{}\!\!\!-\!C\!<\!\!\underset{R_4}{\overset{R_2}{}} \longrightarrow Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

(Hereinafter the organic compound containing therein a single hydrogen atom capable of reacting with a 1,2 alkylene oxide will be referred to simply as the "active hydrogen compound.") Alternatively, if desired, the 1,2 alkylene oxide noted above may be condensed with the glycol corresponding thereto to prepare a polyoxyalkylene glycol which may then be reacted with the active hydrogen compound to form the intermediate compound noted above, viz:



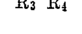
$$YH + HO(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH \longrightarrow Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH + H_2O$$

In the second step the



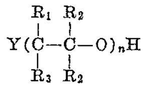
$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound is reacted with another compound to introduce a water-solubilizing group into the molecule. To prepare anionic surface active agents the terminal hydroxyl group of the



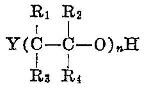
$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate product is esterified with a water-soluble, oxygen containing inorganic acid. Nonionic surface active agents are prepared by introducing a hydrophilic polyoxyalkylene chain, wherein the oxygen/carbon ratio is equal to or greater than 0.5, into the molecule by condensing the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_2}{\overset{R_2}{C}}-O)_nH$$

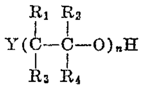
intermediate compound with a suitable 1,2 alkylene oxide or by etherifying the terminal hydroxy group of the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound with a polyoxyalkylene glycol, wherein the oxygen/carbon ratio is equal to or greater than 0.5.

In preparing the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound, the condensation of the active hydrogen compound with a suitable 1,2 alkylene oxide is normally carried out at elevated temperatures and pressures in the presence of an alkaline catalyst such as a sodium alkoxide, a quaternary ammonium base, or preferably sodium hydroxide.

Although the reaction may be carried out by simply heating a mixture of the reactants under pressure at a sufficiently high temperature, this procedure is not ordinarily used as the temperatures and pressures required are excessive and control of the reaction is difficult. For each mol of alkylene oxide reacting an estimated 25 kilogram-calories of heat is liberated which, in the presence of a large quantity of alkylene oxide, may increase the temperature and the reaction rate to such an extent that the reaction assumes an explosive nature.

The preferred method of carrying out the reaction is to add the alkylene oxide to a stirred, heated mixture of the desired active hydrogen compound and alkaline catalyst in a sealed reaction vessel. By adding the 1,2 alkylene oxide to the reaction vessel at such a rate that it reacts as rapidly as added, an excess of the 1,2 alkylene oxide is avoided and control of the reaction is simplified.

The temperature at which the reaction is run will depend upon the particular system in question and especially upon the catalyst concentration used. Generally, at higher catalyst concentrations the reaction can be run at lower temperatures and correspondingly lower pressures. The temperatures and pressures required for any given reaction will vary with the active hydrogen compound, the alkylene oxide and the type and concentration of catalyst used.

Examples 1 to 13 illustrate preferred methods for condensing 1,2 alkylene oxides with active hydrogen compounds.

EXAMPLE 1

Ninety-six grams (3 mols) of methanol and 12 grams of flaked NaOH catalyst were charged into a two gallon stainless steel autoclave equipped with a stirrer, thermocouple, pressure gage and reactant inlet tube whose outlet was directly under the stirrer. The autoclave was pressurized to 100 p. s. i. gage with dry nitrogen and vented three times to expel all oxygen from the system. The caustic catalyst and methanol were heated to 100° C. with stirring. A total of 4520 grams (78 mols) of 1,2 propylene oxide was then added to the reactor over a period of two hours while maintaining an average reaction temperature of 140° C. and an average operating pressure of 85 p. s. i. gage. Initially, the operating pressure exceeded 100 p. s. i. gage but as the methanol reacted with the propylene oxide the operating pressure fell to approximately 85 p. s. i. gage. The caustic catalyst was neutralized with 50% H_2SO_4 and 4565 grams of product was recovered. The molecular weight of the product, as determined by hydroxyl number, was 678, therefore, n, as used in the above type formula, was 11.1.

EXAMPLE 2

One hundred and eighty grams (3 mols) of redistilled n-propanol and 12 grams of flaked NaOH were charged into the stainless steel autoclave of Example 1. The autoclave was purged free of oxygen and the caustic catalyst and n-propanol were heated to 100° C. with stirring. A total of 4510 grams (78 mols) of 1,2 propylene oxide was added to the reactor at an average temperature of 140° C. and at an average pressure of 60 p. s. i. gage over a period of seven hours. The caustic catalyst was neutralized with 50% H_2SO_4 and 4528 grams of product was recovered. The molecular weight of the product, as determined by hydroxyl number, was 580, therefore, n was 9.0.

EXAMPLE 3

Example 2 was repeated except that 222 grams (3 mols) of n-butanol was substituted for n-propanol. The molecular weight of the product, as determined by hydroxyl number, was 808, therefore, n was 12.6.

EXAMPLE 4

Into a 1 liter 3-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer and propylene oxide feed inlet, were charged 51 grams (0.5 mol) of n-hexanol and 2 grams of flaked NaOH catalyst. The n-hexanol and NaOH catalyst were heated to 105° C. and 397 grams (6.85 mols) of 1,2 propylene oxide was added to the reaction mixture over a period of 7.5 hours. The catalyst was neutralized with 3 grams of 96% H_2SO_4 and the final product weighed 453 grams. The molecular weight of the product, as determined by hydroxyl number, was 600, therefore, n was 8.6.

EXAMPLE 5

The apparatus described in Example 4 was charged with 100 grams (0.538 mol) of technical lauryl alcohol and 0.6 gram of metallic sodium. The reaction mixture was heated to 150° C. and 561 grams (9.68 mols) of 1,2 propylene oxide was added to the reaction mixture over a period of 44 hours. The final product weighed 661 grams and had a molecular weight of 760, as determined by hydroxyl number, therefore, n was 9.9.

EXAMPLE 6

Into the apparatus of Example 4 were charged 132 grams (0.545 mol) of cetyl alcohol and 1.5 grams of metallic sodium. The reaction mixture was heated to 150° C. and 607 grams (10.47 mols) of 1,2 propylene oxide was added to the reaction mixture over a period of 53 hours. The final product weighed 729 grams and had a molecular weight of 734, as determined by hydroxyl number, therefore, n was 8.5.

EXAMPLE 7

Ninety-four grams (1 mol) of phenol and 5 grams of flaked NaOH catalyst were charged into the apparatus of Example 4. The reaction mixture was heated to 125° C. and 590 grams (10.2 mols) of 1,2 propylene oxide was added to the reaction mixture over a period of 53.7 hours. The product weighed 684.5 grams and had a molecular weight of 495, as determined by hydroxyl number, therefore, n was 6.92.

EXAMPLE 8

The apparatus of Example 4 was charged with 93 grams (0.5 mol) of N-ethyl benzenesulfonamide and 2 grams of flaked NaOH catalyst. The reaction mixture was heated to 120° C. and 291 grams (5.02 mols) of 1,2 propylene oxide was added to the reaction mixture over a period of 10.4 hours. The final product weighed 384 grams and had a molecular weight of 598, as determined by hydroxyl number, therefore, n was 7.1.

EXAMPLE 9

Into the two gallon stainless steel autoclave described in Example 1 were charged 304 grams (1.078 mols) of oleic acid and 4.3 grams of flaked NaOH catalyst. After purging the autoclave free of oxygen, as in Example 1, 1145 grams (19.73 mols) of 1,2 propylene oxide was added to the reaction mixture at an average temperature of 145° C. and at an average operating pressure of 50 p. s. i. gage over a period of 3.5 hours. The product had a molecular weight of 784, as determined by hydroxyl number, therefore, n was 8.65.

EXAMPLE 10

Sixty-one grams (0.277 mol) of nonyl phenol and 0.7 gram of metallic sodium were charged into the apparatus of Example 4. The reaction mixture was heated to 150° C. and 303 grams (5.23 mols) and 1,2 propylene oxide was added to the reaction mixture at an average temperature of 150° C. over a period of 32.7 hours. The product had a molecular weight of 875, as determined by hydroxyl number, therefore, n was 11.3.

EXAMPLE 11

Forty-eight grams (0.23 mol) of phenol and 2 grams of flaked NaOH were charged into the apparatus of Example 4 that was modified in that the propylene oxide feed inlet was replaced with a dropping funnel. The reaction mixture was heated to 120° C. and 52.6 grams (0.44 mol) of styrene oxide was added dropwise over a period of 5 hours. The reaction mixture was vacuum stripped to removed unreacted phenol and styrene oxide.

Forty-nine grams (0.3 mol) of the phenol-styrene oxide addition product described above and 1 gram of flaked NaOH were charged into the apparatus described immediately above. The reaction mixture was heated to 120° C. and 147.3 grams (1.2 mols) of styrene oxide was added dropwise over a period of 23 hours. The caustic catalyst was neutralized with H_2SO_4 and unreacted styrene ovide and other volatiles were stripped at a pot temperature of 110° C. and a pressure of 1 mm. over a period of 4 hours. From the increase in weight it was determined that 141.2 grams (1.18 mols) of styrene oxide reacted with the phenol. The final product had a molecular weight of 532, as determined by hydroxyl number, therefore, *n* was 3.66.

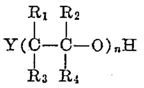
EXAMPLE 12

Into the apparatus of Example 11 were charged 21.9 grams (0.30 mol) of n-butanol and 1.3 grams of flaked NaOH. A total of 73 grams (0.75 mol) of cyclohexene oxide was added to the reaction mixture over a period of six hours at a temperature of 135–185° C. Unreacted alcohol, cyclohexene oxide and other volatile materials were removed by heating the mixture to 200° C. under a vacuum of 5 mm. The molecular weight of the resulting product, as determined by hydroxyl number, was 267, therefore, *n* was 1.97.

EXAMPLE 13

The apparatus of Example 4 was charged with 303.5 grams (1.3 mols) of N-phenyl benzenesulfonamide and 6.6 grams of flaked NaOH catalyst. The reaction mixture was heated to 145° C. and 1184.5 grams (20.4 mols) of 1,2 propylene oxide was added to the reaction mixture over a period of 34.3 hours. The product had a molecular weight of 676, as determined by hydroxyl number, therefore, *n* was 7.65.

To determine the value of *n*, the molecular weight of the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound is determined by hydroxyl number, using the method of Ogg et al. (see Ind. Eng. Chem., Anal. Ed. 17, 395 [1945]), the molecular weight of the active hydrogen compound is subtracted therefrom and the resulting molecular weight of the polyoxyalkylene chain is divided by the molecular weight of the monomeric oxyalkylene group to obtain the *n* value.

It will be noted in the above examples that while the 1,2 alkylene oxide reacts completely, yet *n*, as determined by hydroxyl number, is lower than the calculated value thereof. The magnitude of the difference between the calculated and observed value of *n* is influenced by a number of factors, the principal one being the total number of mols of 1,2 alkylene oxide added to the active hydrogen compound.

To illustrate this effect, varying quantities of 1,2 propylene oxide were added to n-propanol following the procedure of Example 2. Data showing the mols of propylene oxide added per mol of n-propanol, *n*, as determined by hydroxyl number, and *n* as a percent of the calculated value thereof are shown in Table I below:

TABLE I

Mols Propylene Oxide Added Per Mol n-Propanol	*n*, as determined by Hydroxyl Number	*n*, Percent of Calculated Value
3.98	3.95	99
5.0	4.5	90
10.2	7.17	70
24.9	10.3	42

It has been further observed that the magnitude of the difference between the calculated and observed value of *n* increases with the reaction temperature, the catalyst concentration and the water content of the reactants.

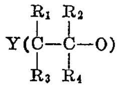
There are three possible explanations for the difference between the calculated and observed value of *n*:

1. The alkaline catalyst causes cleavage of the polyoxyalkylene chains thereby forming more chains, thus resulting in a lower average molecular weight.

2. Elevated temperatures cause thermal cleavage of the polyoxyalkylene chains thereby forming more chains, thus resulting in a lower average molecular weight.

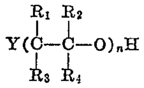
3. The water present as an impurity in the reactants condenses with the alkylene oxide thereby forming more chains, thus resulting in a lower average molecular weight.

It is probable that the value assigned *n*, as determined by hydroxyl number, is low, since the molecular weight of the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound is calculated on a basis of one hydroxyl group being present for each polyoxyalkylene chain. In all probability, glycols and polyglycols, each containing two hydroxyl groups per polyoxyalkylene chain, are present in minor amounts as impurities; therefore, the determined molecular weight of the



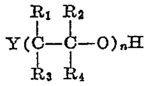
$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound is less than the true molecular weight and of course the value of *n* is correspondingly less than the true value thereof. While this method of determining *n* is subject to some absolute error, it forms a valid basis for comparing the effect of *n* upon surface active properties and is widely used in the art to determine molecular weights of polyoxyalkylene glycols and the monoethers thereof (see U. S. 2,448,664).

It is recognized in the art that the condensation of a molar excess of 1,2 alkylene oxide with an active hydrogen compound gives a heterogeneous mixture of high and low molecular weight products. Theoretically, it is possible that the empirical correlation of surface active properties with *n* is a simplification of a more complex system.

It was noted in Table I that the difference between the observed and the theoretical value of *n* increases as more 1,2 alkylene oxide is added to the active hydrogen compound. It is probable that, as more 1,2 alkylene oxide is added, the heterogeneity of the product increases and the final product is made up of many chains in which *n* is much larger than the average value thereof and a relatively large number of low molecular weight chains. There is reason to believe that the chains in which *n* is materially larger than 6.4 give rise to the surface active properties of the products of this invention. Nevertheless, *n*, as determined by hydroxyl number, is an empirically determined value that correlates well with observed surface active properties and is a valid, measurable parameter than can be relied upon to predict surface active properties when the teachings of this disclosure are followed.

Alternatively, if desired, the



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

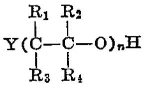
intermediate compound can be prepared by condensing the 1,2 alkylene oxide with the glycol corresponding thereto to produce a polyoxyalkylene glycol, and by reacting same with the active hydrogen compound. This procedure is illustrated in Example 14.

EXAMPLE 14

One hundred grams (0.313 mol) of a crude tall oil acid having an average molecular weight of 320, 238 grams (0.313 mol) of a polyoxypropylene glycol having an average molecular weight of 762 and 0.5 gram of H_2SO_4 were charged into a 1 liter 3-neck round bottom flask equipped with a thermometer, a fine capillary, such as used in vacuum distillations,, and an outlet attached to an oil-type vacuum pump. The reaction mixture was heated for one hour at 110° C. at a pressure of 8 mm. and for ten hours at 150° C. at 3 mm. pressure to esterify the reactants. In the final product, *n* was 13.1.

Generally this synthesis is not preferred in that it requires an additional step, thereby entailing additional expense, time, equipment, etc.

Having formed the



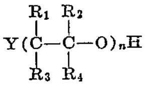
$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound, the surface active agents of this invention are prepared by treating said intermediate compound to introduce a water-solubilizing group. To prepare anionic surface active agents the intermediate product is treated with an oxygen-containing inorganic acid so as to esterify the terminal hydroxyl group of the intermediate compound. This reaction is effected in the usual manner by treating the intermediate product with chlorosulfonic acid, oleum, sulfur trioxide, sulfuric acid, phosphoric acid, boric acid, etc. If desired, said reaction may be carried out in the presence of solvents or diluents while cooling the reaction with external coolants. An illustration of such a water-solubilizing step is shown in Example 15.

EXAMPLE 15

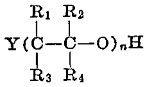
Four hundred and fifty-five grams (0.5 mol) of a product prepared by condensing sufficient 1,2 propylene oxide with n-propanol, in the manner set forth in Example 2, to produce an intermediate compound having an *n* value of 14.7 and 900 ml. of CCl_4 were charged into a 3 liter 3-neck flask fitted with a stirrer, dropping funnel, condenser and thermometer. Sixty grams (0.52 mol) of chlorosulfonic acid was added dropwise with stirring over a period of thirty minutes while maintaining the reaction temperature at 0° C. with external cooling; thereafter the reaction mixture was stirred for another five hours at room temperature to complete the reaction. The product was neutralized with NaOH and the solvent was stripped under reduced pressure to separate the sodium salt of the surface active agent. The surface active agent was soluble in water to the extent of about 50%, by weight, at room temperature.

The preferred surface active agents of this invention are nonionic in nature and are characterized by exceptionally high detergency, as measured by carbon soil removal. These compounds may be prepared by adding a hydrophilic polyoxyalkylene chain to the



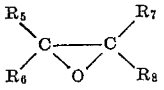
$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound. These preferred surface active agents may be prepared by condensing the



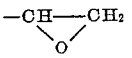
$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound with a 1,2 alkylene oxide of the formula:



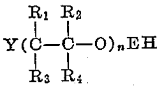
wherein:

R_5, R_6, R_7 and R_8 are selected from the group consisting of H, $-CH_2OH$ and



R_5, R_6, R_7 and R_8 being selected so that the oxygen/carbon ratio is equal to or greater than 0.5.

to prepare surface active agents having the type formula:



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nEH$$

wherein:

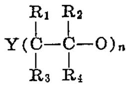
Y is the residue of an organic compound containing therein a single hydrogen atom capable of reacting with a 1,2 alkylene oxide,

R_1, R_2, R_3 and R_4 are selected from the group consisting of H, aliphatic radicals and aromatic radicals,

n is greater than 6.4, and

E is a polyoxyalkylene chain wherein the oxygen/carbon ratio is equal to or greater than 0.5, said polyoxyalkylene chain being present in an amount sufficient to render the surface active agent soluble to the extent of about 0.1% in distilled water.

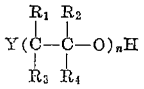
While E may be broadly any polyoxyalkylene chain wherein the oxygen/carbon ratio is equal to or greater than 0.5, a polyoxyethylene chain is the preferred embodiment of this invention in that the surface active properties are unusually good and ethylene oxide readily condenses with the



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

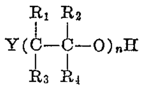
intermediate compound to prepare the surface active agents.

It is not possible to accurately prescribe the length of the hydrophilic polyoxyalkylene chain that is required in the surface active agent for the development of surface active properties. While it is possible to determine the total quantity of the hydrophilic polyoxyalkylene compound that has been added to the



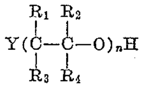
$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound, it is not possible to determine the chain length of the resulting hydrophilic polyoxyalkylene in the surface active agent since the intermediate compound is a heterogeneous mixture of both low and high molecular weight compounds and because some of the low molecular weight chains contain two hydroxyl groups per polyoxyalkylene chain. All of the hydrophilic alkylene oxide that is added to the



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound and not recovered is reported as having been added thereto. It is recognized that some of the unrecovered alkylene oxide may combine with impurities present in the

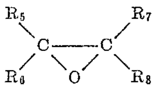


$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

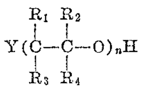
intermediate compound, e. g. water and glycols, nevertheless, this empirically reported value correlates well with observed surface active properties and is a valid, measurable parameter that can be relied upon to predict surface active properties when the teachings of this disclosure are followed.

Empirically it has been observed that the hydrophilic polyoxyalkylene must constitute at least about 25% of the resulting surface active agent for the development of surface active properties and that highly active products are obtained when the hydrophilic polyoxyalkylene constitutes 25—95% of the resulting surface active agent. Optimum surface active properties are obtained when the hydrophilic polyoxyalkylene chain constitutes 50—70% of the resulting surface active agent.

The addition of the 1,2 alkylene oxide of the formula:

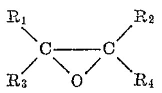


to the



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound is carried out in a manner analogous to the addition of the 1,2 alkylene oxide of the formula:



to the active hydrogen compound. The nature of effecting this addition is set forth in Examples 16 and 17.

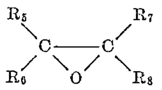
EXAMPLE 16

Two hundred grams (0.272 mol) of an intermediate compound prepared by condensing sufficient 1,2 propylene oxide with n-propanol, in the manner set forth in Example 2, so that *n* had a value of 11.7 and 1 gram of flaked NaOH were charged into the apparatus described in Example 4. The reaction vessel was flushed with nitrogen and 202 grams (4.6 mols) of ethylene oxide was added to the reaction mixture at an average reaction temperature of 125° C. over a period of 7.1 hours. The final product contained 50%, by weight, of the hydrophilic polyoxyethylene. The resulting surface active agent was readily soluble in water at room temperature.

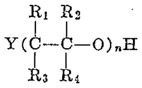
EXAMPLE 17

Example 16 was repeated except that the intermediate compound used was prepared by condensing sufficient 1,2 propylene oxide with n-butanol, as described in Example 3, so that *n* had a value of 9.8. The addition of the ethylene oxide to the intermediate compound required 5.3 hours and the final product contained 50%, by weight, of hydrophilic polyoxyethylene. The product was dissolved in water to form a good detergent solution.

If desired, the 1,2 alkylene oxide of the formula:



may be condensed with the glycol corresponding thereto to prepare a hydrophilic polyoxyalkylene glycol which can then be etherified with the



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound to prepare the surface active agents. This procedure is not ordinarily preferred in that it requires an additional step thereby entailing additional expense, etc.

Evaluation tests for surface active agents

The following test procedures were used to evaluate the surface active properties of the products of this invention:

Carbon soil removal test procedure.—A standard soiled cotton fabric is first prepared as follows:

Fourteen pieces of a standard muslin ("Indian Head" muslin 53 x 47, 5.15 oz. per sq. yd. manufactured by Nashua Mfg. Co.) are definished or pre-treated in order to remove the sizing or finish and to shrink the material, by a treatment with caustic soda solution, followed by a wash with sodium stearate, which is then followed by a number of rinses with soft water. The water used in this operation is softened to below one grain $CaCO_3$ equivalent to a gallon. Following such pre-treating operation, the muslin is extracted for 5 minutes and tumbled to dryness in a commercial gas-heated laundry dryer. The definished standard muslin, cut in pieces measuring 10½" x 36" are placed in a Monel metal wash wheel containing an emulsion of colloidal carbon black and water-soluble mineral oil. After thorough impregnation of the standard muslin in the carbon black and oil emulsion, it is removed piece by piece and passed once without folding through a power-driven household type wringer to squeeze out any residual aqueous dispersion, the wringer pressure being so adjusted as to leave in the cloth an amount of standard soil solution equal to 120%±5% of the dry weight of cloth. The standard soiled muslin or test cloth is then dried and cut into test pieces measuring 2½" x 3½". Before actual use of the so-prepared standard soiled cloth, it is given a final check by the following described carbon soil removal test in a standard detergent solution, and over a range of several solution concentrations.

To evaluate the soil removal characteristics of synthetic detergent compositions, 0.25% by weight solutions of the composition to be tested are prepared in distilled water and 100 ml. portions of such solution are added to each of 10 one-pint jars of a "Launder-Ometer" (type 12Q-EF-SPA, manufactured by Atlas Electric Devices Company) standard laundry test machine.

Fifteen ¼" diameter stainless steel balls are placed in each jar, after which two pieces of the previously prepared standard soiled cloth are added to each of nine jars. In the tenth jar are placed two pieces of unsoiled but pre-treated cloth and this latter jar serves as a blank for determining the turbidity of the detergent solution. The so-prepared jars, heated to a temperature of 140° ± 2° F. in a constant temperature bath are then placed in the "Launder-Ometer" and run for 10 minutes at a speed of 42 ± 1 R. P. M. The jars are then removed from the test machine and replaced in the constant temperature bath. The contents of each jar to which the standard soiled cloth has been added are poured through a coarse screen to separate the steel balls and the standard soiled cloth from the soil suspension which is collected in a large beaker. The composite suspension thus attained is mixed thoroughly and a sample placed in a 10 mm. light absorption cell. The light absorption of this composite solution, as well as the light absorption of the solution in the tenth or "blank" jar containing the unsoiled cloth test pieces is then measured (by a "Fisher Electrophotometer"). By means of a calibration curve for the "Fisher Electrophotometer," such curve being constructed by obtaining light absorption values of known quantities of carbon black dispersion added to distilled water, the carbon soil removal value sought (in mg. of carbon per liter of solution) is obtained by taking the difference between the converted values of the light absorption of the composite solution or suspension from the nine jars and of the light absorption of the suspension in the blank jar.

The carbon soil removal values are then reported as a percentage of that of a standard detergent solution used as a reference or control material; viz. by dividing the mg. of carbon removal value of the test material composition by the mg. of carbon removal value for the standard or control detergent solution which is determined concurrently in the same test run and on the same standard soiled test cloth, and multiplying by 100.

The standard detergent solution used throughout the tests reported herein was a 0.25% solution of sodium kerylbenzenesulfonate in distilled water. The sodium kerylbenzenesulfonate was prepared by effecting a Friedel-Crafts condensation of a chlorinated petroleum hydrocarbon distillate (derived from a hydrocarbon distillate having 9–16 carbon atoms and boiling in the range of 150–300° C.) with benzene and thereafter sulfonating the kerylbenzene compound to form the kerylbenzenesulfonic acid, which was subsequently neutralized with caustic soda to form the water-soluble sodium kerylbenzenesulfonate. After the neutralization of the sulfonic acid, sufficient sodium sulfate was added so that the final product contained 40% sodium kerylbenzenesulfonate and 60% sodium sulfate.

Whiteness retention test procedure.—Bleached, unfinished, clean Indian Head muslin, count 58 x 47, weight 4.7 oz./sq./yd. (Nashua Manufacturing Company) is cut into swatches measuring 2½" x 3½". The light reflectance of each side of every swatch is measured by means of a "Hunter Multipurpose Reflectometer" equipped with a green filter, using a standard white backing with a reflectance of 68.8% behind the cloth swatch. The average of such values of each side of each test piece is calculated and recorded. A standard soil suspension is prepared by diluting 28.55 grams of an aqueous carbon dispersion containing 35% carbon ("Aqua Blak B," Binney and Smith Co.) to 1 liter in a volumetric flask of distilled water.

A 0.25% distilled water solution of the detergent compound to be tested is then made up by adding 2.5 grams of the compound to a small amount of distilled water in a 1 liter volumetric flask. The previously prepared soil suspension is shaken vigorously and 50 ml. then pipetted into the flask containing the detergent. Sufficient distilled water is then added to this flask to make up to the one-liter mark.

The resultant mixture of detergent and carbon soil suspension is pipetted in 100 ml. portions into each of 5 "Launder-Ometer" jars, each jar containing fifteen ¼" stainless steel balls. The jars and contents are brought to a temperature of 140° ± 2° F. in a constant temperature water bath, then placed in the "Launder-Ometer" and rotated for 5 minutes at 42 ± 2 R. P. M. The "Launder-Ometer" is thereafter stopped and without removing the jars from the machine, the lids are opened and two standard cloth swatches, prepared as previously described, are placed in each jar after soaking for exactly 1 minute in distilled water without subsequent draining. The lids are replaced on the jars and the latter are rotated for an additional 30 minutes in the "Launder-Ometer." The swatches are then removed and immediately rinsed by flowing 3 liters of distilled water continuously through a rinsing flask while shaking, and for a period of 5 minutes. Immediately after rinsing, the swatches are removed from the rinsing flask and placed on flat clean paper towels. The swatches are pressed dry on a laundry press set at a temperature of 328.338° F. After pressing, the reflectance of both sides of each swatch is again measured by the "Hunter Reflectometer" and the average reflectance of all swatches calculated and recorded. The whiteness retention value is then calculated as follows:

$$\%\text{ Whiteness retention (W. R.)}=\frac{\text{Ave. reflectance after soiling}\times 100}{\text{Ave. reflectance before soiling}}$$

The whiteness retention values are reported herein as a percentage of that determined in the standard detergent solution described under the "Carbon Soil Removal Test Procedure"; viz. by dividing the percent whiteness retention determined in the test material by the percent whiteness retention determined in the standard control detergent solution which is determined concurrently in the same test run and on the same standard test cloth, and multiplying by 100.

Effect of hydrophobic polyoxyalkylene chain length on surface active properties

A fundamental feature of this invention resides in the discovery that polyoxyalkylene chains, wherein the oxygen/carbon ratio is equal to or less than 0.33, are sufficiently hydrophobic at a critical chain length to serve as the hydrophobic element of surface active agents. The effect and criticalness of the polyoxyalkylene chain length upon surface active properties is shown in Example 18.

EXAMPLE 18

Seven intermediate compounds were prepared by condensing 1,2 propylene oxide with n-propanol following the procedure of Example 2. The *n* values of the intermediate compounds were 3.9, 6.4, 7.2, 8.0, 9.0, 9.8 and 11.7, respectively. Each of the above intermediates was reacted with sufficient ethylene oxide, following the procedure of Example 17, to prepare surface active agents which contained from 38–61%, by weight, of polyoxyethylene. The surface active agents were evaluated for carbon soil removal and whiteness retention by the test procedures heretofore set forth and these data are recorded in the following Table II:

TABLE II

n, by Hydroxyl Number	Wt. percent C_2H_4O in product[1]	Carbon Soil Removal Value, 0.25% at 140° F.	Whiteness Retention Value, 0.25% at 140° F.
3.9	50	78	----------
6.4	38	82	----------
7.2	44	94	----------
8.0	52	106	----------
9.0	45	248	340
9.8	47	258	342
11.7	61	261	337

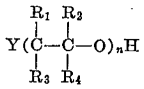
[1] In several cases varying quantities of polyoxyethylene were added to the intermediate compound and in these cases the compound giving the maximum carbon soil removal value is reported.

The data of Table II are plotted in Fig. 1. Referring to Fig. 1, it will be noted that at *n* values below 6.4 the curve is quite flat, i. e. the change of carbon soil removal with chain length (CSR/*n*) is small, viz. 1.6% CSR/unit of *n* between $n=3.9$ and $n=6.4$. At an *n* value of 6.4 there is a point of inflection and the CSR/*n* is tenfold larger than below 6.4, viz. 15% CSR/unit of *n* between $n=6.4$ and $n=8.0$. When an *n* value of 8.0 is reached, there is a very marked change in the contour of the curve and it rises almost perpendicularly at a rate almost a hundred fold greater than below 6.4, viz. 142% CSR/unit of *n* between $n=8.0$ and $n=9.0$. Between $n=9.0$ and 9.8 there is a "shoulder" in the curve and above $n=9.8$ the curve flattens and the CSR/*n* is again small, viz. 1.6% CSR/unit of *n* between $n=9.8$ and $n=11.7$.

It can be seen from Fig. 1 that the chain length of the hydrophobic polyoxyalkylene is extremely critical. The surface active agents of this invention have *n* values greater than 6.4 and preferably greater than 8.0, i. e. above the critical point of inflection in Fig. 1.

It is recognized that the precise critical chain length of the hydrophobic polyoxyalkylene will be somewhat dependent upon the molecular weight of the monomeric oxyalkylene employed, and in particular, when a relatively high molecular weight oxyalkylene is employed, e. g. oxycyclohexene or oxystyrene, a somewhat shorter hydrophobic polyoxyalkylene chain may be used without seriously lowering the surface active properties. While higher molecular weight alkylene oxides and somewhat shorter hydrophobic polyoxyalkylene chain lengths may be used, it is highly desirable to use the lower molecular weight polyoxyalkylenes derived from, e. g. propylene and butylene oxides, and having *n* values greater than 6.4 and preferably greater than 8.0 for the following reasons:

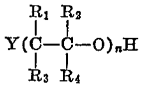
1. The lower molecular weight alkylene oxides are readily available in large supply and at low cost from the petroleum industry.
2. The lower molecular weight alkylene oxides react much more readily with active hydrogen compounds to prepare the



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

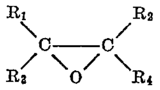
intermediate compound and require less strenuous reaction conditions.
3. The lower molecular weight alkylene oxides will react with "sluggish" active hydrogen compounds which would react with the higher molecular weight alkylene oxides, if at all, only with great difficulty.
4. The molecular weight of the hydrophobic polyoxyalkylene chain can be varied in small increments of molecular weight. This is an important factor in preparing "tailored" surface active agents.

The value of *n* required to make the



$$Y(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_nH$$

intermediate compound sufficiently hydrophobic to serve as the hydrophobic element of surface active agents is dependent upon the chain length of active hydrogen compound condensed with the 1,2 alkylene oxide of the formula:

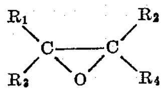


when the chain length of the active hydrogen compound is greater than 6, *n* may be slightly less than 6.4 and the intermediate compound can still serve as the hydrophobic element of surface active agents. As the chain length of the active hydrogen compound is increased the limiting critical value of *n* decreases until at an active hydrogen compound chain length of about 12, the active hydrogen compound, itself, is sufficiently hydrophobic to serve as the hydrophobic element of surface active agents, and no additional hydrophobic polyoxyalkylene is required.

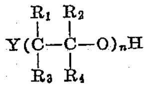
Surface active agents wherein *n* has a value less than 6.4 are not included within the scope of this invention and are not equivalents therefor, since the polyoxyalkylene chain cannot provide the essential hydrophobic element thereof. When *n* is less than 6.4, higher molecular weight active hydrogen compounds must be used to provide the hydrophobic element of the surface active agent and the resulting products constitute an entirely different group of compounds.

Effect of Y on surface active properties

The active hydrogen compound furnishes an active hydrogen atom to initiate the polymerization of the 1,2 alkylene oxide of the formula:



to form the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound. So long as the organic compound contains a single active hydrogen atom to initiate the above-noted polymerization, any such organic compound can be used to prepare the surface active agents of this invention.

The active hydrogen compounds of this invention are restricted to those which contain a single hydrogen atom capable of reacting with a 1,2 alkylene oxide. Surface active agents derived from active hydrogen compounds containing a plurality of hydrogen atoms capable of reacting with 1,2 alkylene oxides are more fully disclosed and claimed in the copending application of Lester G. Lundsted, Serial No. 386,945 filed October 19, 1953, now U. S. Patent 2,674,619.

The preferred active hydrogen compounds of this invention contain therein only aliphatic groups containing 1 to 5 carbon atoms, as for example:

Aliphatic alcohols such as methanol, ethanol, propanol, isopropanol, butanol, secondary butanol, tertiary butanol, n-amyl alcohol, the monomethyl ether of ethylene glycol, the monomethyl ether of diethylene glycol, 2-chloroethanol, etc.

Aliphatic carboxylic acids such as formic acid, acetic acid, mono-, di- and tri-chloroacetic acid, propanoic acid, butenoic acid, pentanoic acid, etc.

Secondary aliphatic amines such as dimethylamine, diethylamine, dipropylamine, dibutylamine, N-methylethylamine, N-ethylpropylamine, etc.

N-substituted aliphatic carboxylic acid amides such as N-methyl formamide, N-methyl acetamide, N-ethyl butanoic acid amide, N-butyl propanoic acid amide, N-methyl pentanoic acid amide, etc.

N-substituted aliphatic sulfonamides such as N-methyl ethane sulfonamide, N-ethyl propane sulfonamide, N-methyl butane sulfonamide, N-propyl pentane sulfonamide, etc.

Aliphatic mercaptans such as methyl mercaptan, ethyl mercaptan, propyl mercaptan, tertiary butyl mercaptan, isobutyl mercaptan, amyl mercaptan, etc.

While the preferred active hydrogen compounds contain therein only aliphatic groups containing 1 to 5 carbon atoms, it is possible to use higher molecular weight aliphatic and aromatic compounds, such as:

Aliphatic and aromatic hydroxyl compounds such as hexanol, lauryl alcohol, phenol, ortho-, meta-, and para-creosol, chlorophenol, alpha-, and beta-naphthol, nonyl phenol, etc.

Aliphatic and aromatic carboxylic acids such as hexanoic acid, oleic acid, stearic acid, benzoic acid, ortho-, meta- and para-toluic acid, alpha- and beta-naphthoic acid, etc.

Secondary amines such as dihexylamine, N-methyl stearylamine, N-methyl aniline, phenyl-beta-naphthylamine, etc.

N-substituted carboxylic acid amides such as N-methyl lauric acid amide, N-ethyl-benzoic acid amide, etc.

N-substituted sulfonamides such as N-ethyl benzenesulfonamide, N-phenyl toluenesulfonamide, etc.

Aliphatic and aromatic mercaptans such as dodecyl mercaptan, thiophenol, thiocreosol, alpha- and beta-thionaphthol, etc.

Any of the active hydrogen compounds set forth above may include substituents which do not contain hydrogen atoms capable of reacting with 1,2 alkylene oxides, e. g. Cl. Br, I, $-NO_3$ alkoxy radicals, etc.

Surface active agents prepared from various active hydrogen compounds are shown in Example 19.

EXAMPLE 19

1,2 propylene oxide was condensed separately, with methanol, n-propanol, n-butanol, n-hexanol, technical lauryl alcohol, phenol, N-ethyl benzenesulfonamide, oleic acid, N-phenyl benzenesulfonamide, nonyl phenol and a crude tall oil acid (m. w.=320) following the procedures outlined in Examples 1 to 13 so as to prepare intermediate products in which *n* had a value greater than 6.4. These intermediate products were then condensed with sufficient ethylene oxide, following the procedures of Examples 16 and 17, so that the polyoxyethylene constituted 41–80%, by weight, of the surface active agents. These products were evaluated for carbon soil removal following the procedure heretofore set forth. The Y compound used, the value of *n*, the weight percent of polyoxyethylene present in the product and carbon soil removal values are shown in the following table:

TABLE III

Y Compound	*n*	Wt. Percent C_2H_4O in product	Carbon Soil Removal Value, 0.25% at 140° F.
CH_3OH	11.1	51	242
C_3H_7OH	11.7	50	220
C_4H_9OH	12.6	53	210
$C_6H_{11}OH$	8.6	45	224
$C_{12}H_{25}OH$	9.9	71	175
C_6H_5OH	6.9	70	240
$C_6H_5\text{-}SO_2\overset{\overset{C_2H_5}{\vert}}{N}H$	7.1	41	250
Tall Oil Acid (m. w.=320)	13.1	49	202
$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	8.65	80	164
$C_9H_{19}C_6H_4OH$	11.3	80	164
$C_6H_5SO_2\text{-}\overset{\overset{C_6H_5}{\vert}}{N}H$	7.65	51	328

The above examples illustrate that so long as *n* is greater than 6.4 any active hydrogen compound can be used in preparing the surface active agents of this invention.

While any active hydrogen compound, as above defined, may be used in preparing the surface active agents of this invention, significantly superior results are obtained by using active hydrogen compounds which contain therein only aliphatic groups containing 1 to 5 carbon atoms. These lower molecular weight aliphatic active hydrogen compounds are advantageous in that:

1. They are readily available in large quantities at low cost.
2. They react more readily with 1,2 alkylene

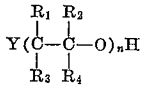
oxides, thereby shortening the reaction time and giving rise to concomitant economies.

3. They will react with "sluggish" 1,2 alkylene oxides which would react only with the greatest difficulty with higher molecular weight active hydrogen compounds.

4. They permit greater variation in the polyoxyalkylene compound and thus more effective "tailoring" of the surface active agent.

Effect of X on surface active properties

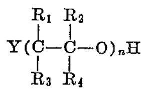
The addition of any water-solubilizing group to the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound will give an active surface active agent, although the properties thereof will be affected somewhat by the choice of the solubilizing group X.

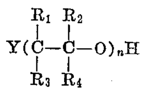
Anionic surface active agents are prepared by esterifying the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

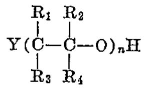
intermediate compound with phosphoric, sulfuric or boric acid, as set forth in the section entitled "Preparation of surface active agents" and as specifically illustrated in Example 15. The properties of the anionic surface active agents of this invention are exemplified by the sulfated propanolpropylene oxide condensation product of Example 15. The surface active agent was evaluated by the methods heretofore set forth and had a carbon soil removal value of 159% and a whiteness retention value of 274%. A unique property of this anionic surface active agent was that it produced very little foam in contrast to other types of anionic detergents which normally produce considerable quantities of foam.

In preparing the nonionic surface active agents of this invention the quantity of the hydrophilic polyoxyalkylene compound added to the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound has a pronounced effect on the surface active properties. As noted in the section entitled "Preparation of surface active agents" the precise, critical length of the hydrophilic polyoxyalkylene chain has not been determined, but empirically it has been observed that the hydrophilic polyoxyalkylene should constitute at least about 25%, by weight, of the resulting surface active agent to develop surface active properties, although even smaller quantities may be used, if desired. It has been further observed that after the minimum quantity of hydrophilic polyoxyalkylene compound has been added, the surface active properties are improved by the further addition of the hydrophilic polyoxyalkylene compound until the hydrophilic polyoxyalkylene constitutes about 60%, by weight, of the surface active agent and thereafter the further addition of hydrophilic polyoxyalkylene oxide causes a slight decrease in detergency, as measured by carbon soil removal values, although excellent products are obtained where the hydrophilic polyoxyalkylene constitutes as much as 95%, by weight. The quantitive effect of the addition of hydrophilic polyoxyalkylene compound to the



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nH$$

intermediate compound is shown in Example 20.

EXAMPLE 20

Two intermediate compounds were prepared by adding sufficient 1,2 propylene oxide to *n*-butanol, following the procedure of Example 3, to prepare compounds in which *n* had a value of 9.9 and 12.6, respectively. Each intermediate product was divided into aliquot portions and varying quantities of ethylene oxide were added thereto, following the procedure of Example 17, to prepare surface active agents in which the weight percent hydrophilic polyoxyalkylene therein varied from 26% to 90%. The surface active agents were evaluated for carbon soil removal value by the method heretofore set forth and the results are shown in Table IV and plotted in Fig. 2.

TABLE IV

Y Compound	*n*	Wt. Percent C_2H_4O in product	Carbon Soil Removal Value, 0.25% at 140° F.
C_4H_9OH	9.9	26	84
C_4H_9OH	9.9	40	128
C_4H_9OH	9.9	50	211
C_4H_9OH	9.9	59	243
C_4H_9OH	9.9	67	221
C_4H_9OH	9.9	79	185
C_4H_9OH	12.6	30	89
C_4H_9OH	12.6	38	181
C_4H_9OH	12.6	46	214
C_4H_9OH	12.6	68	228
C_4H_9OH	12.6	80	189
C_4H_9OH	12.6	90	151

Referring to Fig. 2, it will be noted that between 25–95% polyoxyethylene content "bell shaped" curves are obtained which define the area of good detergency. The limits of 40–75% polyoxyethylene content encompass the "hump" of the curve, which represents the preferred compounds of this invention, while the limits of 50–70% polyoxyethylene content pin point the area of maximum detergency. Above about 75% polyoxyethylene content the detergency falls off, but is compensated for by the fact that the surface active agents are solids and can be flaked for ease of packaging and use.

Applications of surface active agents

The surface active agents of this invention are suitable as wetting agents, dispersing agents, etc. in the textile, leather, paper, lacquer, rubber and like industries. An outstanding property of these surface active agents is their exceptional detergency, as measured by carbon soil removal and whiteness retention values. The nonionic surface active agents of this invention are exceptionally good textile lubricants.

The anionic surface active agents of this invention have excellent detergency properties and, unlike the prior art anionic surface active agents, have little tendency to produce foam. Their freedom from foaming makes such surface active agents particularly efficacious in formulations intended for use in mechanical dishwashing machines and automatic clothes washing machines.

The nonionic surface active agents of this invention are very stable in alkaline and acidic media and retain their excellent surface active properties in concentrated ionic solutions. The combination of chemical stability and high detergency makes them particularly suitable in formulations for use in hard water, oxidizing and reducing media, etc.

The nonionic surface active agents of this invention that contain at least 70% of a hydrophilic polyoxyalkylene compound are hard, solid products and can be used, for example, to prepare solid bars for washing applications.

A very desirable property of the surface active agents of this invention is that they have excellent detergency properties in extremely dilute aqueous solutions. The data of Example 21 show the change of carbon soil removal value with concentration.

EXAMPLE 21

Three nonionic surface active agents were prepared by condensing methanol, n-propanol and n-butanol, respectively, with 1,2 propylene oxide following the procedures of Examples 1, 2 and 3, and the resulting intermediate compounds were subsequently condensed with ethylene oxide following the procedures of Examples 16 and 17. The carbon soil removal values of the three surface active agents were determined in distilled water at 140° F. at concentrations of 0.25%, 0.10% and 0.05%. Carbon soil removal values were determined for a commercially available nonionic surface active agent that is prepared by condensing ethylene oxide with a commercial mixture of long chain fatty acids, such as derived from tallow. The Y compound used, the value of *n*, the weight percent polyoxyethylene present in the product and carbon soil removal values at the three concentrations are shown in Table V below. Included for comparison are the carbon soil removal values for the previously described commercially available nonionic surface active agent at the same concentrations. The data of Table V are plotted in Fig. 3.

TABLE V

Y Compound	*n*	Wt. Percent C_2H_4O in product	Carbon Soil Removal Value at 140° F.		
			0.25%	0.10%	0.05%
CH_3OH	11.1	55	264	255	208
C_3H_7OH	14.8	52	240	246	246
C_4H_9OH	13.3	66	245	249	215
Commercial Nonionic[1]	------	----------	248	181	145

[1] A nonionic surface active agent prepared by condensing ethylene oxide with a commercial mixture of long chain fatty acids.

Fig. 3 shows that, whereas the prior art nonionic surface active agent exhibits a conventional detergency concentration relationship, the products of this invention, most unexpectedly, show a negligible decrease in detergency over a wide range of active agent concentration and have outstanding surface active properties in extremely dilute aqueous solutions. In many industrial applications, such as the continuous bleaching of cotton fabrics with hypochlorites, it is desirable to use a nonionic surface active agent in concentrated salt solutions. Because of the "salting out" effect, it is difficult to maintain a sufficient concentration of surface active agent in the solution to obtain the desired wetting action. The outstanding efficiency of the surface active agents of this invention at low concentrations makes them eminently suitable for such applications.

A desirable characteristic of the surface active agents of this invention is that both the hydrophobic and hydrophilic elements thereof can be varied, both as to molecular weight and type, to prepare "tailored" surface active agents. By merely changing the quantity of hydrophobic alkylene oxide added to the active hydrogen compound it is possible to prepare a wide range of hydrophobic elements that differ from one another in small, finite increments of hydrophobic polyoxyalkylene chain length. Similarly, varying quantities of hydrophilic alkylene oxide can be added to any of the above-described hydrophobic elements to prepare surface active agents, which differ from each other only in small, finite increments of hydrophilic polyoxyalkylene content. By proper selection of reaction conditions, it is possible to vary over a wide range: (1) the hydrophobic polyoxyalkylene chain length, (2) the hydrophilic polyoxyalkylene content and (3) the hydrophobic polyoxyalkylene chain length/hydrophilic polyoxyalkylene content ratio. The facility with which the structure of surface active agent can be varied is highly advantageous in that surface active agents can be "tailor made" to perform specific functions.

The solid nonionic surface active agents of this invention may be formulated with quarternary ammonium compounds to prepare excellent detergent sanitizer compositions. The cationic nature of quaternary ammonium compounds requires the use of a nonionic detergent and the prior art compounds heretofore available have been unsuitable in that they could not be formulated to prepare free flowing powders.

The surface active agents of this invention are eminently suitable for use in pharmaceutical preparations such as toothpastes, etc. in that they are colorless, odorless, tasteless and nontoxic. A most unusual and unexpected feature of the nonionic products of this invention is that they do not hemolyze red blood cells and have no effect upon the lipoproteins present in whole blood. This property suggests that these products be used in cleaning equipment used in blood banks, etc. and such products may possibly be used as stabilizers to increase the storage life of whole blood.

The polyethers structure of the nonionic products of this invention makes them highly satisfactory for use as plasticizers in dextrine-base adhesives, vinyl resins, phenolic resins and synthetic rubbers. The liquid nonionic products of this invention have extremely low vapor pressures, good lubricating properties and exceptionally good thermal stability, therefore, can be used as lubricants, hydraulic fluids, heat transfer media and in other applications in the industrial arts where such a combination of properties is desirable.

Illustrative examples of surface active agents of this invention

In order to more fully disclose the present invention to those skilled in the art, the following table of anionic surface active agents is set forth:

TABLE VI

Y	$(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_n$ Chain	n	X
CH_3O-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
C_2H_5O-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$H\overset{CH_3}{\underset{CH_3}{C}}O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
C_4H_9O-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$H\overset{C_2H_5}{\underset{CH_3}{C}}O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$(CH_3)_3CO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$(CH_3)_2CH-CH_2O$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_5H_{11}O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_6H_{13}O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_4H_9-\underset{C_2H_5}{CH}-CH_2O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_{12}H_{25}O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$CH_3(CH_2)_7CH=CH(CH_2)_7CH_2O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$HCOO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
CH_3COO-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$ClCH_2COO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_6H_{13}COO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_{12}H_{25}COO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_{17}H_{35}COO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$(CH_3)_2N-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$(C_2H_5)_2N-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$(C_5H_{11})_2N-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_{18}H_{37}-\underset{CH_3}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$CH_3-CO\underset{CH_3}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_6H_{13}CO\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
CH_3S-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$

TABLE VI—Continued

Y	$(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_n$ Chain	n	X
C_4H_9S-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_{12}H_{25}S-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_2H_5SO_2\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
C_6H_5O-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$CH_3-C_6H_4O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
C_6H_5COO-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$CH_3C_6H_4COO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_6H_5\underset{CH_3}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_6H_5\underset{C_{10}H_7}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$CH_3C_6H_4\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_6H_5CO\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
C_6H_5S-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$C_6H_5SO_2\underset{CH_3}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$
$CH_3C_6H_4-SO_2\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$-SO_3M$

Equally satisfactory surface active agents may be obtained when the sulfate group in Table VI is replaced with a phosphate group, a borate group or other oxygen-containing inorganic acid ester group. Similarly, comparable surface active agents may be obtained when the polyoxypropylene chain is replaced with a polyoxybutylene chain, a polyoxyamylene chain, a polyoxycyclohexene chain, a polyoxystyrene chain, or other polyoxyalkylene chain in which the oxygen/carbon ratio is equal to or less than 0.33.

The following table of nonionic surface active agents is set forth to more fully disclose the scope of the present invention:

TABLE VII

Y	$(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_n$	n	E	Wt. percent E in product
CH_3O-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
C_2H_5O-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$H\overset{CH_3}{\underset{CH_3}{C}}O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
C_4H_9O-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$H\overset{C_2H_5}{\underset{CH_3}{C}}O-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95

TABLE VII—Continued

Y	$(\overset{R_1}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_4}{C}}-O)_n$	n	E	Wt. percent E in product
$(CH_3)_3CO-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$(CH_3)_2CH-CH_2O-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_5H_{11}O-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_6H_{13}O-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_4H_9-\underset{\underset{C_2H_5}{\vert}}{C}H-CH_2O-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_{12}H_{25}O-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$CH_3(CH_2)_7CH=CH(CH_2)_7CH_2O-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$HCOO-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
CH_3COO-	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$ClCH_2COO-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_6H_{13}COO-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_{12}H_{25}COO-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_{17}H_{35}COO-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$(CH_3)_2N-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$(C_2H_5)_2N-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.5-25.0	$(CH_2-CH_2-O)_m$	25-95
$(C_5H_{11})_2N-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_{18}H_{37}-\underset{\underset{CH_3}{\vert}}{N}-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$CH_3-CO\underset{\underset{CH_3}{\vert}}{N}-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_6H_{13}CO\underset{\underset{C_2H_5}{\vert}}{N}-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
CH_3S-	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
C_4H_9S-	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_{12}H_{25}S-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_2H_5SO_2\underset{\underset{C_2H_5}{\vert}}{N}-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
C_6H_5O-	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$CH_3-C_6H_4O-$	$(CH_2-\overset{CH_3}{\overset{\vert}{C}}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95

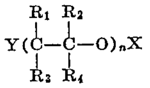
TABLE VII—Continued

Y	$(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_n$	n	E	Wt. percent E in product
C_6H_5COO-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$CH_3C_6H_4COO-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_6H_5\underset{CH_3}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_6H_5-\underset{C_{10}H_7}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$CH_3C_6H_4\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_6H_5CO\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
C_6H_5S-	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$C_6H_5SO_2\underset{CH_3}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95
$CH_3C_6H_4-SO_2\underset{C_2H_5}{N}-$	$(CH_2-\overset{CH_3}{C}H-O)_n$	6.4-25.0	$(CH_2-CH_2-O)_m$	25-95

The polyoxypropylene chain in the products of Table VII can be replaced with a polyoxybutylene chain, a polyoxyamylene chain, a polyoxycyclohexene chain, a polyoxystyrene chain or other polyoxyalkylene chain in which the oxygen/carbon ratio is equal to or less than 0.33 to obtain comparable surface active agents. The hydrophilic polyoxyethylene chain in the products of Table VII (or the corresponding products in which other hydrophobic polyoxyalkylene chains, as above described, are used) may be replaced with other hydrophilic polyoxyalkylene chains in which the oxygen/carbon ratio is equal to or greater than 0.5, such as a polybutadiene dioxide chain, a polyglycidol chain, etc. to obtain excellent surface active agents.

Summary

The surface active agents of this invention have the following type formula:



$$Y(\underset{R_3}{\overset{R_1}{C}}-\underset{R_4}{\overset{R_2}{C}}-O)_nX$$

wherein:

Y is the residue of an organic compound containing therein a single hydrogen atom capable of reacting with a 1,2 alkylene oxide,

R_1, R_2, R_3 and R_4 are selected from the group consisting of H, aliphatic radicals and aromatic radicals, at least one such substituent being a radical other than hydrogen,

n is greater than 6.4, as determined by hydroxyl number, and

X is a water-solubilizing group.

A fundamental characteristic of this invention is that a polyoxyalkylene chain, having a maximum oxygen/carbon ratio of 0.33 and an average chain length greater than 6.4, as determined by hydroxyl number, is the essential hydrophobic element of the surface active agents.

The novel surface active agents of this invention are characterized by excellent detergency, as measured by carbon soil removal values, excellent detergency in dilute aqueous solution and chemical structures in which both the hydrophobic and hydrophilic elements can be simultaneously varied, both as to molecular weight and type, to prepare "tailored" surface active agents.

In the appended claims, the term "cogeneric mixture" is used. This is a term that has been coined to designate a series of closely related, touching homologues that are obtained by condensing a plurality of alkylene oxide units with a reactive hydrogen compound (see United States Patent 2,549,438, particularly the section beginning column 12, line 40).

What is claimed is:

1. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n\text{EH}$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, n is an integer, and E is a polyoxyalkylene chain wherein the oxygen/carbon atom ratio is equal to or greater than 0.50; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and E constituting 25–95%, by weight, of the mixture.

2. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n\text{EH}$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, n is an integer, and E is a polyoxyalkylene chain wherein the oxygen/carbon atom ratio is equal to or greater than 0.50; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and E constituting 40–75%, by weight, of the mixture.

3. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n\text{EH}$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, n is an integer, and E is a polyoxyalkylene chain wherein the oxygen/carbon atom ratio is equal to or greater than 0.50; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and E constituting 25–95%, by weight, of the mixture.

4. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, and n and m are integers; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

5. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, and n and m are integers; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 40–75%, by weight, of the mixture.

6. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, and n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

7. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, and n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 40–75%, by weight, of the mixture.

8. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound containing therein only aliphatic groups containing from 1 to 5 carbon atoms, and one hydrogen atom capable of reacting with 1,2 propylene oxide, n and m are integers; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

9. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound

containing therein only aliphatic groups containing from 1 to 5 carbon atoms, and one hydrogen atom capable of reacting with 1,2 propylene oxide, n and m are integers; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 40–75%, by weight, of the mixture.

10. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound containing therein only aliphatic groups containing from 1 to 5 carbon atoms, and one hydrogen atom capable of reacting with 1,2 propylene oxide, n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

11. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an organic compound containing therein only aliphatic groups containing from 1 to 5 carbon atom, and one hydrogen atom capable of reacting with 1,2 propylene oxide, n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 40–75%, by weight, of the mixture.

12. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of a 1 to 5 carbon atom aliphatic alcohol containing one active hydrogen atom, and n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

13. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of a 1 to 5 carbon atom aliphatic carboxylic acid containing one active hydrogen atom, and n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

14. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of a secondary amine containing one active hydrogen atom, and n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

15. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m H$$

where: Y is the residue of an N-substituted arylsulfonamide containing one active hydrogen atom, and n and m are integers; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

16. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m\text{H}$$

where: Y is the residue of a phenol containing one active hydrogen atom, and n and m are integers; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

17. A cogeneric mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n(\text{oxyethylene})_m\text{H}$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, said organic compound being selected from the group consisting of alcohols, carboxylic acids, secondary amines, N-substituted carboxylic acid amides, N-substituted sulfonamides, phenols and mercaptans, and n and m are integers; the average value of n in the mixture being at least 8.0, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

18. A cogeneric mixture of compounds having the formula:

$$\text{Propyl-O-}(\text{oxypropylene})_n(\text{oxyethylene})_m\text{H}$$

where: n and m are integers; the average value of n in the mixture being at least 6.4, as determined by hydroxyl number, and the average value of m in the mixture being such that the oxyethylene groups constitute 25–95%, by weight, of the mixture.

19. The method of preparing the compounds of claim 4, which comprises condensing an organic compound containing one active hydrogen atom with sufficient 1,2 propylene oxide to prepare a mixture of compounds having the formula:

$$Y(\text{oxypropylene})_n\text{H}$$

where: Y is the residue of an organic compound containing one active hydrogen atom capable of reacting with 1,2 propylene oxide, and n is an integer; where the average value of n in the mixture is at least 6.4, as determined by hydroxyl number, and subsequently condensing therewith sufficient ethylene oxide to prepare a product containing 25–95%, by weight, oxyethylene content.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,164,431	Schoeller	July 4, 1939
2,174,761	Schuette et al.	Oct. 3, 1939
2,425,755	Roberts et al.	Aug. 19, 1947
2,481,278	Ballard et al.	Sept. 6, 1949
2,496,582	Enyeart	Feb. 7, 1950
2,508,035	Kosmin	May 16, 1950
2,508,036	Kosmin	May 16, 1950
2,549,435	De Groote et al.	Apr. 17, 1951

OTHER REFERENCES

Mark et al., "Physical Chemistry of High Polymeric Systems", pages 372, 381, 401 and 417, Publ. by Interscience Publishers, Inc., New York (1950).