

UNITED STATES PATENT OFFICE

2,454,543

POLYMERIC DETERGENTS

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Serial No. 553,478

10 Claims. (Cl. 260—49)

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This invention relates to surface-active or capillary-active agents. It relates to the preparation of materials which have high detergent action under a wide variety of conditions. More specifically, it relates to the preparation and use of polymeric, water-soluble detergents which have high molecular weights and contain within each molecule a multiplicity of hydrophobic and hydrophilic groups or portions so arranged and balanced as to become oriented at an interface.

It is generally recognized that surface-active agents, as, for example, alkali-metal soaps or quaternary ammonium compounds, exist in water in the form of micelles. While the exact nature of such micelles is not established, there is evidence that they are electrically charged aggregates of molecules. For example, when a sodium soap of a fatty acid is dispersed in water, it dissociates into positively charged sodium ions and into negative ions. Some of the latter apparently form aggregates with soap molecules and, as a result, negatively charged micelles are produced. Because the micelles carry a negative charge, this type of soap is known as an anion-active detergent. In contrast, detergents of the type of quaternary ammonium compounds yield positively charged micelles in aqueous solution and, hence, are known as cation-active soaps or agents. This conception of the formation of micelles is based on measurements of freezing points, vapor pressures, and electrical conductivities of aqueous dispersions of surface-active agents. It is further recognized that surface activity is related to the formation of such micelles and to the orientation of the micelles at an interface.

The individual molecules in colloidal micelles are held together only by physical forces or by weak secondary valences; and, as a result, the extent of micelle formation depends upon the prevailing conditions, and it is affected by such factors as the concentration of the surface-active agent, the presence of electrolytes, solvents, and other surface-active agents, and also upon the temperature. Thus, dilution of the solution, elevation of the temperature, or a change in the amount of any salts which may also be present in solution favor the reversion of micelles into simple molecules and/or ions with the formation of true solutions. As an example, synthetic detergents known heretofore have no value at very low concentrations or in very hot water because under these conditions the micellar structure reverts, the molecules then exist in true solution, and, as a result, detergency is lost. The neces-

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sity of using relatively high concentrations plus the higher cost of synthetic detergents combines to make the use of such detergents uneconomical and often impractical. Furthermore, the materials are ineffective in many laundering operations wherein extremely hot water is used in order to accelerate the removal of soil.

The products of this invention differ from—and have advantages over—detergents known heretofore in that their effectiveness is not dependent upon the formation of loosely bound micelles. By the process of this invention, water-soluble macromolecules are synthesized in which all of the bonds between atoms are primary valence links and, hence, are strong and are not affected by such factors as concentration and temperature. Furthermore, the synthesized macromolecules contain balanced hydrophilic and hydrophobic groups so positioned in the macromolecule that orientation can and does occur readily at an interface.

The products of this invention may be made by condensing hydrocarbon-substituted phenols with formaldehyde to produce polymeric materials which are in fact macromolecules and then introducing into said macromolecules hydrophilic groups. The hydrophilic groups, which impart water solubility, may be ether-alcohol groups or esterified ether-alcohol groups and are introduced, for example, by the reaction of ethylene oxide or a propylene oxide or a butylene oxide with the macromolecule. If desired, the terminal hydroxyl of said ether-alcohol group may be converted into a salt-forming ester group of a polybasic acid.

The resultant products may be considered to have three functional portions. Thus, they contain (a) as the hydrophobic portion, the hydrocarbon groups attached to the phenol nucleus; (b) as the hydrophilic portion, the modified or unmodified ether-alcohol groups, and (c) as the polymeric portion, the phenol nuclei joined by methylene bridges. The hydrocarbon groups attached to the phenol and the modified or unmodified ether-alcohol groups also attached to the phenol are so balanced as to assure water solubility and orientation at an interface. At the same time, the polymeric nature of the product assures such a high molecular weight that the product is in fact a macromolecule which imparts capillary- or surface-activity to a solution, as do micelles of ordinary soaps, but which is stable and is not dissociated as are the micelles of customary detergents under adverse conditions.

The above discussion is for purposes of theoretical explanation only, and it must be understood that the so-called three portions of the macromolecule are not independent of each other but are all combined in one large molecule which functions as a concerted whole.

The type of hydrocarbon group which is attached to the-phenol nucleus may vary as to kind but in every case must contain at least four carbon atoms. In reality, substituting groups of at least eight carbon atoms are much preferred. Generally, it is preferred that the substituent hydrocarbon group be a straight or branched chain acyclic group, such as n-butyl, iso-butyl, tertiary butyl, amyl, tertiary amyl, n-octyl, diisobutyl, decyl, dodecyl, hexadecyl, octadecyl, and the like. Alternatively, phenols substituted with alicyclic groups may be used. These are typified by cyclohexyl phenol, methyl-cyclohexyl phenol, butyl-cyclohexyl phenol, and dicyclohexyl phenol. While aryl-substituted phenols, such as p-phenyl phenol and p-naphthyl phenol, may be employed they are less satisfactory than those listed above unless they in turn contain an alkyl group. Thus, p-tolyl phenol is much preferred over p-phenyl phenol. Furthermore, a preference is given to the para-substituted phenols over those substituted in the ortho position. It is understood that although it is preferable to employ individual phenols, mixtures of phenols, for example, p-tert.-amyl- and p-diisobutyl-phenols, may be employed.

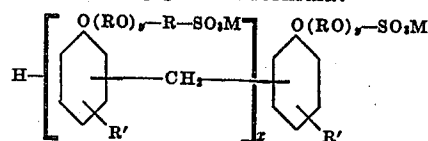
The ratio of formaldehyde should be between 0.5 and 1.0 mol per mol of phenol. The formaldehyde may be used in the form of a solution, such as the formalin of commerce, or in a polymeric form such as paraformaldehyde. Also, though not preferred, it may be in a form such as a formal or hexamethylene tetramine which will yield formaldehyde under the conditions of reaction.

Ordinarily, the substituted phenol and formaldehyde are reacted by condensing together in the presence of an acidic or alkaline condensation catalyst until the products have become relatively viscous. Solvents may be employed. Acidic condensation catalysts are preferred because of the ease with which the condensation may be controlled. Elevated temperatures naturally accelerate the rate of reaction. Condensation of formaldehyde and substituted phenols such as are here involved does not proceed to the infusible stage and, accordingly, no limit need be imposed upon the degree of condensation. In practice, it is convenient to follow the extent of condensation by means of viscosity measurements and the condensation may be halted at an early stage at which the molecular weight is low and the product on the average has no more than three or four phenolic units per molecule, or it may be continued until each macromolecule contains many more units. The condensation products may range in physical properties from oils to brittle solids, depending upon the degree of condensation and the nature of the substituent hydrocarbon group on the phenol.

Polymeric detergents in which the hydrophilic or water-solubilizing groups are alcohols or salt-forming partial esters thereof are the subjects of applications Serial Nos. 553,476, 553,477, and 553,479, filed of even date.

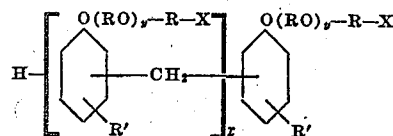
The polymeric detergents of this invention have salt-forming sulfonic acid radicals as their hydrophilic groups. The final products may be described as water-soluble sulfonates of polymeric

hydrocarbon-substituted phenoxy alcohols. They have the following general formula:



In this formula, R' is a hydrocarbon substituent of at least four, and preferably over seven, carbon atoms, R is an alkylene group, preferably of two, three, or four carbon atoms, γ is zero or an integer between one and twenty and preferably between one and seven, M is one equivalent of a metal, preferably of an alkali metal such as sodium, potassium, lithium, or a group II metal such as beryllium, magnesium, calcium, barium, or strontium, and x is an integer greater than one.

These detergent products are preferably made by first reacting an alkali metal derivative of a hydrocarbon-substituted phenol-aldehyde polymer or macromolecule with a dihalogeno polyalkylene ether having the general formula, $\text{X}-\text{R}-\text{O}-(\text{RO})_\gamma-\text{R}-\text{X}$, in which X is a halogen, preferably chlorine, and R is an alkylene group, preferably of two to four carbon atoms, and γ is zero or an integer. The reaction is conducted in the presence of a strongly alkaline condensing agent, such as sodium or potassium hydroxides, and only one terminal halogen reacts with the sodium derivative of the macromolecule. In this way, substituted ether halides having the following general formula are produced:

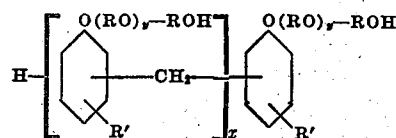


This product is then heated with a water-soluble salt of sulfurous acid in aqueous or aqueous-alcoholic solution, and the final product has the general formula shown above.

The dihalogeno polyalkylene ethers which may be used are typified by the following: β,β' -dichlorodiethyl ether, γ,γ' -dibromodipropyl ether, β,β' -dichlorodisopropyl ether, β -chloroethoxyethyl- β' -chloroethyl ether, and higher homologues.

The salts of sulfurous acid which are preferred are those of the alkali metals, especially of sodium, because these are water-soluble and most readily available.

As an alternative method, a polymeric condensate of a hydrocarbon-substituted phenol and formaldehyde may be condensed with an alkylene oxide, such as ethylene, a propylene oxide, or a butylene oxide, in the presence of an alkaline condensing agent. Preferably, more than one mol of oxide per mol of phenol in said condensate is used and, in such a case, the product is a phenoxyalkoxy alcohol having the general formula:

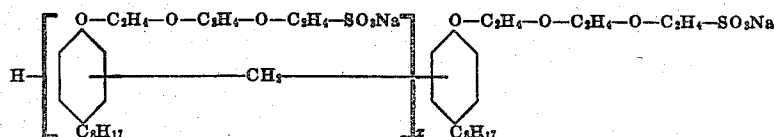


in which the various symbols have the above-noted significance. When only one mol of alkylene oxide is employed, the value of γ becomes zero and the product is a polymeric alcohol. The preparation of alcohols having the above general formula is discussed in application Serial No.

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553,476, filed of even date. It is possible to react more than one mol of alkylene oxide per mol of phenol in the macromolecule. In fact, as many as sixty have been reacted. However, a maximum of twenty is indicated as satisfactory and between one and eight is preferred. The terminal hydroxyl group of the compound is next converted to a halide, for example, by reaction with a halogenating agent such as phosphorous pentachloride, phosphorous oxychloride, or thionyl chloride. The halide is then reacted with an inorganic sulfite salt, such as sodium sulfite, to yield a sulfonate.

The products of this invention may be described as surface-active polymeric products of

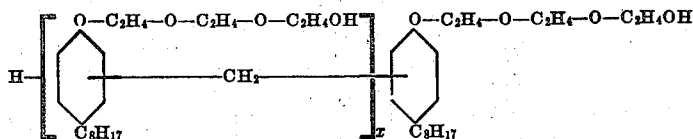


high molecular weight containing in their chemical structure a plurality of salt-forming hydrocarbon-substituted phenoxy-alkoxy sulfonate units joined through the nuclei of said phenoxy groups by means of methylene bridges.

Following is an example which indicates the preferred method of preparing the products of this invention.

Step 1.—Into a three-necked flask equipped with thermometer, mechanical agitator, and reflux condenser was charged the following: 412 grams of diisobutyl phenol, 162 grams of a 37% aqueous solution of formaldehyde, and 27.6 grams of water. The mixture was agitated and heated to a temperature of 90° C. At this point, 2.46 grams of oxalic acid and 0.92 gram of Twitchell's reagent dissolved in ten grams of water was added. While being agitated, the reaction mixture was refluxed for six hours. Two hundred grams of water and 384 grams of toluene were added, and refluxing was continued for an hour. Agitation was stopped and the contents of the flask were removed to a separatory funnel. The aqueous and resinous layers were separated and the solvent was removed from the resinous layer by vacuum distillation. After the removal of the solvent, heating at a reduced pressure of 1.5 to 2.5 mm. and at a temperature of 245° to 250° C. was continued for four and one-half hours. The condensate then had a viscosity of 4.0 poises when measured as a 60% solution in toluene and, on cooling, solidified to a brittle mass.

Step 2.—Two parts of solid NaOH, 133 parts of ethylene oxide, and 218 parts of the product of step 1 were mixed with 145 parts of toluene and heated at 120°–135° C. under pressure for two hours. This ratio corresponds to three mols of ethylene oxide per mol of phenol present in the product of step 1. The product, a viscous solution, was further diluted to 50% solids content with toluene. Its structure may be represented as follows:



Step 3.—To 934 grams of a solution prepared as in step 2 was added 213 grams of benzyldimethylamine and 185 grams of thionyl chloride. The reaction mixture was heated for two hours

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on a steam bath, diluted with 250 milliliters of benzene, and then washed with two portions of 400 milliliters each of water. The product was dried with anhydrous K_2CO_3 , and the benzene and toluene were stripped off. A yield of 457 grams was obtained of a product having a chlorine content of 7.68% and a hydroxyl number of 11.

Step 4.—A mixture of 396 grams of the product of step 3, 140 grams of sodium sulfite, and 800 grams of water was heated and stirred in an autoclave for four hours at 160°–174° C. The product, a turbid paste, was soluble in water and was surface-active in dilute aqueous solution. It had the following general formula:

Although the above example is directed to the use of ethylene oxide, it is understood that a propylene oxide or a butylene oxide may be employed in a similar manner. In order to impart a given degree of water-solubility, it is advisable to use a greater amount of the higher oxides than the amount of ethylene oxide required. Furthermore, as the entire length of the hydrophilic group is increased, the product ordinarily becomes more water-soluble. It is, therefore, advisable to increase the hydrophobic group proportionately. This can be done by increasing the size of the hydrocarbon substituent of the phenol, as represented by R' in the above general formula. In this way, a balance is maintained between the hydrophilic and hydrophobic portions of the macromolecule so that the product is water-soluble and at the same time capillary-active, in that it becomes oriented at an interface.

All of the products of this invention function as capillary-active or surface-active agents. As such, they become oriented at an interface, lower the surface tension of water, and cause more rapid wetting of surfaces such as the surfaces of fibers as measured by the standard Draves Sinking Test. Their outstanding property is their effectiveness as detergents. In this capacity, as measured by wash tests and laundering tests, they are outstanding and are far superior to soaps and synthetic detergents known heretofore.

As detergents the products described herein may be used in hard water or in water of high salt content. They may be employed under acidic or alkaline conditions. Their advantage over synthetic detergents resides in the fact that they are not micellar but are in fact macromolecules which do not revert as do micelles. Thus, they are excellent detergents at very low concentrations or at very high temperatures where former synthetic detergents failed.

They are uncommonly advantageous in the

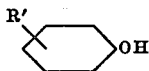
laundering of cotton fabrics and in the scouring of wool, sized, dyed, and printed fabrics in general. They may be used for preparing dispersions of oil in water or dispersions of polymer-

izable materials prior to the polymerization thereof. Also, they serve to break water-in-oil emulsions such as are encountered in oil-fields. And they have been found to be very satisfactory in the treatment of leather, in the dispersion of pigments, and as assistants in dyeing.

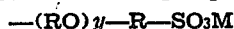
The products of this invention are particularly useful when used in conjunction with other capillary-active agents, including fatty acid soaps and synthetic detergents such as those shown in United States Patents 2,115,192 and 2,143,759. Such combinations have extraordinarily high degrees of wetting and detergent properties.

We claim:

1. A modified phenol-formaldehyde condensation product having detergent properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula



in which R' is a saturated hydrocarbon substituent containing four to eighteen carbon atoms, and wherein the modification of said condensation product consists of the group



replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R in both occurrences is the same saturated alkylene group containing two to four carbon atoms, y has a value of 0 to 19 inclusive, and M is a metal from the class consisting of alkali and alkaline earth metals.

2. A modified phenol-formaldehyde condensation product having detergent properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula



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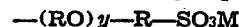


replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R in both occurrences is the same saturated alkylene group containing two to four carbon atoms, y has a value of zero to seven inclusive, and M is a metal from the class consisting of alkali and alkaline earth metals.

3. A modified phenol-formaldehyde condensation product having detergent properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula



in which R' is a saturated hydrocarbon substituent containing eight to eighteen carbon atoms, and wherein the modification of said condensation product consists of the group

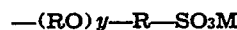


replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R in both occurrences is the same saturated alkylene group containing two to four carbon atoms, y has a value of 0 to 19 inclusive, and M is a metal from the class consisting of alkali and alkaline earth metals.

4. A modified phenol-formaldehyde condensation product having detergent properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula

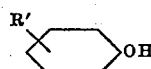


in which R' is a saturated hydrocarbon substituent containing eight to eighteen carbon atoms, and wherein the modification of said condensation product consists of the group

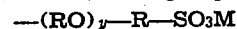


replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R in both occurrences is the same saturated alkylene group containing two to four carbon atoms, y has a value of zero to seven inclusive, and M is a metal from the class consisting of alkali and alkaline earth metals.

5. A modified phenol-formaldehyde condensation product having detergent properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula



in which R' is a saturated hydrocarbon substituent containing eight to eighteen carbon atoms, and wherein the modification of said condensation product consists of the group



replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R in both occurrences is the same saturated alkylene group containing two to four carbon atoms, y has a value of zero to seven inclusive, and M is an alkali metal.

6. A modified phenol-formaldehyde condensation product having surface-active properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula



in which R' is a saturated hydrocarbon substituent containing 4 to 18 carbon atoms, and wherein

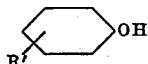
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the modification of said condensation product consists of the group

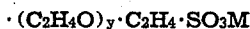


replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein y has a value of 0 to 19 inclusive, and M is a metal from the group consisting of alkali and alkaline earth metals.

7. A modified phenol-formaldehyde condensation product having surface-active properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula

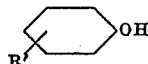


in which R' is a saturated hydrocarbon substituent containing 4 to 18 carbon atoms, and wherein the modification of said condensation product consists of the group



replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein y has a value of 0 to 7 inclusive, and M is a metal from the group consisting of alkali and alkaline earth metals.

8. A modified phenol-formaldehyde condensation product having surface-active properties wherein the phenol-formaldehyde condensate is an oily brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula



in which R' is a saturated hydrocarbon substituent containing 4 to 18 carbon atoms, and wherein the modification of said condensation product consists of the group



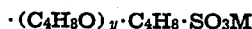
replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein y has a value of 0 to 19 inclusive, and M is a metal from the group consisting of alkali and alkaline earth metals.

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9. A modified phenol-formaldehyde condensation product having surface-active properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol from the class consisting of ortho-substituted and para-substituted phenols, said phenol having the formula

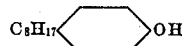


in which R' is a saturated hydrocarbon substituent containing 4 to 18 carbon atoms, and wherein the modification of said condensation product consists of the group



replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein y has a value of 0 to 19 inclusive, and M is a metal from the group consisting of alkali and alkaline earth metals.

10. A modified phenol-formaldehyde condensation product having surface-active properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mol of formaldehyde and one mol of a phenol having the formula



and wherein the modification consists of the group



replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein y has a value of 0 to 19 inclusive.

LOUIS H. BOCK.
JAMES L. RAINEY.

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The following references are of record in the file of this patent:

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2,213,477	Steindorff et al.	Sept. 3, 1940

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Number	Country	Date
576,177	Germany	May 8, 1933

Certificate of Correction

Patent No. 2,454,543.

November 23, 1948.

LOUIS H. BOCK ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 4, in the formula following line 2, right-hand portion thereof, for "O(RO)₂—SO₂M" read O(RO)₂—R—SO₂M;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of April, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.