

UNITED STATES PATENT OFFICE

2,454,544

**POLYMERIC DETERGENTS COMPRISING
WATER-SOLUBLE SALTS OF THE HALF-
ESTERS OF DICARBOXYLIC ACIDS AND
THE FORMALDEHYDE CONDENSATES
OF HYDROCARBON-SUBSTITUTED PHE-
NOXY-POLYALKOXY ALKANOLS**

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Serial No. 553,479

5 Claims. (Cl. 260—53)

1

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 types 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 necessity of using relatively high concentrations plus

2

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.

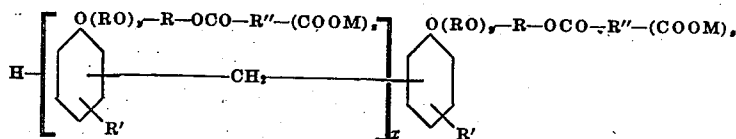
The products of this invention may be made by condensing hydrocarbon-substituted phenols with formaldehyde to produce polymeric materials which are in fact macromolecules and then introducing into said macromolecules hydrophilic groups. The hydrophilic groups, which impart water solubility, may be ether-alcohol 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 the

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 do 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.

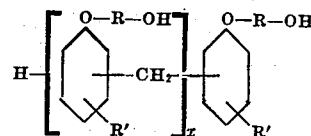
Polymeric detergents in which the hydrophilic or water-solubilizing groups are alcohols or salt-forming esters thereof are the subjects of applications Serial Nos. 553,476, 553,477, and 553,478, filed of even date.

The polymeric detergents of this invention have as their hydrophilic groups salt-forming carboxylic acid esters. The final products may be described as water-soluble, salt-forming carboxylic esters of polymeric hydrocarbon-substituted phenoxy alcohols. They have the following general formula:

5 The general formula:

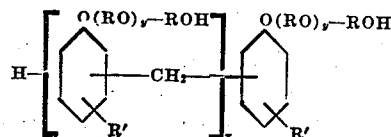
15 In this formula, R' is a hydrocarbon substituent of at least four, and preferably over seven, carbon atoms; R is an alkylene group, preferably of two, three, or four carbon atoms, inclusive; R'' is a hydrocarbon radical or group from the class consisting of alkyl and aryl radicals or groups containing preferably one to seven carbon atoms; y is an integer of a value of zero to twenty, inclusive, but preferably of a value between one and seven; M is one equivalent of a metal, preferably of an alkali metal such as sodium, potassium, or lithium or a group II metal such as beryllium, magnesium, calcium, barium, or strontium; z is an integer of a value equal to one or two, and x is an integer greater than one.

30 These detergent products are preferably made by partially esterifying with an organic polycarboxylic acid a polymeric hydrocarbon-substituted phenoxy alcohol. The polymeric alcohols from which the esters are prepared may be made in various ways, as shown in detail in application Serial No. 553,476, filed of even date. Alkylene oxides, such as ethylene oxide, a propylene oxide, or a butylene oxide, may be condensed with a substituted phenol-formaldehyde macromolecule. The condensation is preferably conducted in the presence of an alkaline catalyst, such as a hydroxide of the alkali metals, although in some instances no catalyst is required. While this reaction may be carried out at lower temperatures and at atmospheric pressure in the presence of solvents, it is preferred to conduct it at temperatures above 100° C. under superatmospheric pressure, also in the presence of solvents. One or more mols of the alkylene oxides may be reacted per mol of phenol condensed in the macromolecule. When one mol is reacted, a simple alkylol group, —ROH, becomes attached, through the oxygen atom of the phenol, to the phenol nucleus of the macromolecule. Such compounds have the general formula



in which R' is a hydrocarbon substituent of at least four carbon atoms, R is an alkylene group, and x is an integer greater than one.

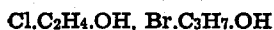
When, however, more than one mol of alkylene oxide is used, the group which becomes attached to the phenolic nucleus is an ether-alcohol group, and the product may be represented as follows:



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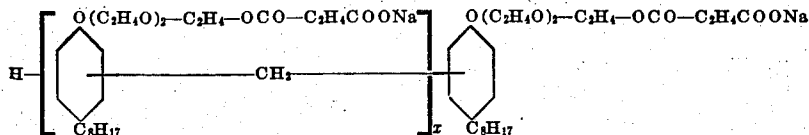
In addition to y , which is an integer, the symbols in this formula have the same significance as above. The values of y which are preferred are one to six, although compounds in which y is as high as ten are shown to be valuable detergents in the following examples and even those in which y is as high as twenty have merit.

Alcohols typified by the above general formulas may be made by another method. For example, halohydrins may be reacted with the sodium derivative of the phenol-formaldehyde condensate. Typical halohydrins include the following:

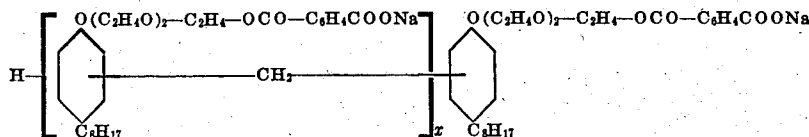


$\text{Br.C}_3\text{H}_7.\text{O.C}_3\text{H}_7.\text{OH}$, and the like. This reaction is also preferably conducted in the presence of an alkaline catalyst.

The alcohols described above may be esterified with polycarboxylic acids or their equivalents such as the anhydrides or acid halides. Suitable polycarboxylic acids include succinic, glutaric, adipic, phthalic, tricarballic, hexahydrophthalic, citric, tartaric, and maleic. When esterification takes place between the alcohols and the polycarboxylic acids, there remain unreacted or free acid groups which may then be neutralized to form salts. It is preferred to neutralize the partial esters of the acids with the hydroxides, oxides, carbonates or bicarbonates of the group I (alkali) metals or group II (especially alkaline earth) metals which produce water-soluble products. Obviously, salts of the heavy metals can be prepared in the same way.



The final products, which are preferably water-soluble, are in reality a combination of a salt and an ester and have the general formula given above. They may be described as surface-active polymeric products of high molecular weight containing in their chemical structure salt-forming partial esters of organic polycarboxylic acids and hydrocarbon-substituted phenoxy alcohol units in which the hydrocarbon substituent contains



at least four carbon atoms, said phenoxy alcohol units being joined by means of methylene bridges.

Following are examples of a preferred method of preparing the products of this invention.

Example 1

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 were 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.

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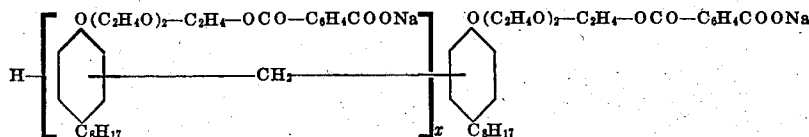
Agitation was stopped and the contents of the flask were removed to a separatory funnel. The aqueous and resinous layers were separated and the solvent was removed from the resinous layer by vacuum distillation. After the removal of the solvent, heating at a reduced pressure of 1.5 to 2.5 mm. and at 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 hundred eighteen parts of the product of step 1 was dissolved in 145.3 parts of toluene. (This corresponded to approximately one molar part of diisobutylphenol.) To this solution was added 2.0 parts of solid NaOH and 133 parts (3.0 mols) of ethylene oxide, and the mixture was heated with stirring for one hour at 120°–136° C. in an autoclave. At the end of one hour, the pressure in the autoclave had dropped to twelve pounds per square inch at 136° C., indicating substantially complete reaction of the ethylene oxide. The product was a viscous solution having a solids content of 76.1% and a hydroxyl number of 118.

Step 3.—To the above solution was added 100 parts of succinic acid anhydride. The mixture was refluxed for two hours, after which the product was dissolved in 400 milliliters of a 10% solution of NaOH. Toluene was removed by steam distillation. The product, which had very good detergent properties, had the formula:

Example 2

In a similar manner, the product of step 2 of Example 1 was esterified with one mol of phthalic anhydride and neutralized with one mol of sodium carbonate in aqueous solution. The product maintained its detergent properties both in very dilute solution and at high temperatures. It had the formula:



Although the above examples are 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. As the 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.

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 Sink-ing 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 hereto-fore.

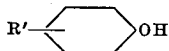
As detergents the products described herein may be used in hard water or in water of high salt content. Their advantage over synthetic detergents resides in the fact that they are not micellar but are in fact macromolecules which do not revert as do micelles. Thus, they are excel-lent detergents at very 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 gen-eral. They may be used for preparing dispersions of oil in water or dispersions of polymerizable 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 pig-ments, and as assistants in dyeing.

The products of this invention are particularly useful when used in conjunction with other capil-lary-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 de-grees of wetting and detergent properties.

We claim:

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

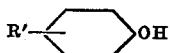


in which R' is a saturated hydrocarbon sub-stituent containing eight to eighteen carbon atoms and wherein the modification of said con-densation product consists of the group



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, R'' is a saturated hydrocar-bon radical, containing one to seven carbon atoms, from the class consisting of alkylene and arylene radicals, y has a value of 0 to 20, M is a metal from the class consisting of alkali and al-kaline earth metals, and z has a value of 1 to 2.

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

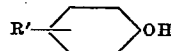


in which R' is a saturated hydrocarbon sub-stituent containing eight to eighteen carbon atoms and wherein the modification of said con-densation product consists of the group

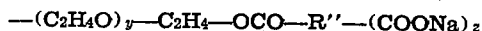


replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R in both occurrences is the same saturated alkylene group containing two to four carbon atoms, R'' is a saturated hy-drocarbon radical, containing one to seven car-bon atoms, from the class consisting of alkylene and arylene radicals, y has a value of 0 to 20, and M is a metal from the class consisting of alkali and alkaline earth metals.

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

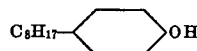


in which R' is a saturated hydrocarbon substit-ent containing eight to eighteen carbon atoms and wherein the modification of said condensa-tion product consists of the group

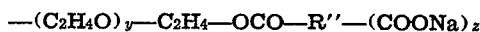


replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R'' is a saturated hydro-carbon radical, containing one to seven carbon atoms, from the class consisting of alkylene and arylene radicals, y has a value of 0 to 20, and z has a value of 1 to 2.

4. A modified phenol-formaldehyde condensa-tion product having detergent properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mole of formaldehyde and one mole of an octyl phenol having the formula



and wherein the modification of said condensa-tion product consists of the group

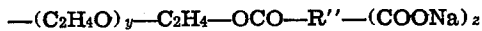


replacing the original phenolic hydrogen atoms and being attached to each phenol nucleus in said condensate through the phenolic oxygen atom thereof, wherein R'' is a saturated hydrocarbon radical, containing one to seven carbon atoms, from the class consisting of alkylene and arylene radicals, y has a value of 0 to 20, and z has a value of 1 to 2.

5. A modified phenol-formaldehyde condensa-tion product having detergent properties wherein the phenol-formaldehyde condensate is an oily to brittle resinous condensation product of from 0.5 to 1.0 mole of formaldehyde and one mole of an octadecyl phenol having the formula



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'' is a saturated hydrocarbon radical, containing one to seven carbon atoms, from the class consisting of alkylene and arylene radicals, y has a value of 0 to 20, and z has a value of 1 to 2.

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JAMES L. RAINEY.

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