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SURFACE-ACTIVE LINEAR POLYESTERS

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5 Claims. (Cl. 260—75)

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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 necessity 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.

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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 are water-soluble, polymeric, surface-active linear polyesters containing in their chemical configuration a balanced arrangement of both hydrophilic and hydrophobic groups. The hydrophobic groups are alkylene groups containing six or more carbon atoms. The hydrophilic groups are sulfonate groups. The preferred method of making such polymeric detergents comprises first preparing a linear polyester of a relatively long-chained alkane-diol, that is, an unsubstituted glycol, and maleic acid or its equivalents and thereafter reacting therewith a water-soluble bisulfite salt. The bisulfite adds across the double bond of the maleic acid residue in the polyester to form a sulfonate. When the double bonds of all of the maleic acid residues become saturated by the addition of the bisulfite, the product is a linear polyester of sulfosuccinic acid. When some of the double bonds remain intact due to limited reaction of the bisulfite, the product is a mixed polyester of maleic and sulfosuccinic acids.

Generically, the products may be represented by the formula:

$$(\text{—G—M—})_x(\text{W})_{x(1-y)}$$

In this formula, G represents the residue of an unsubstituted glycol which is esterified by maleic acid or its equivalents. M represents the residue of esterified maleic acid. The parenthetical portion $(\text{—G—M—})_x$, therefore, represents a linear polyester containing x ester units of —G—M—, x being an integer greater than two and preferably from three to twelve. The letter W represents

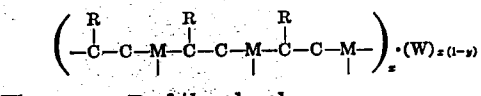
the hydrophilic sulfonate group which is joined across and thereby saturates the double bond of M, while y is a number from 0 to 0.5. Thus, the number of sulfonate groups (W) may vary from one to one-half times the number of maleic residues.

The product may be considered to have three functional portions. Thus, it contains (*a*) as a hydrophobic portion the alkylene residue of the glycol, (*b*) as the distinctly hydrophilic portion the sulfonate group (W), and (*c*) the remainder of the molecule which in reality is made up of a multiplicity of ester units taken x times, x being an integer greater than two. In the preferred cases, x is sufficiently large to assure resinification and is three to about twelve. In the molecule the size of the alkylene group must be sufficiently large to impart hydrophobic properties and to balance the hydrophilic properties of the sulfonate groups. At the same time, the polymeric nature of the material assures such a high molecular weight that the product is in fact a macromolecule having detergent properties like the micelles of ordinary soaps. The macromolecule, however, is stable and does not dissociate like the micelles of ordinary detergents under adverse conditions.

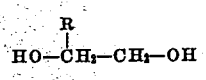
The above discussion is for purposes of theoretical explanation only, and it is to be understood that the so-called three portions of the macromolecule are not independent of one another but are, in fact, all combined in one large molecule which functions as a concerted whole.

The glycols which are operable are those containing six or more carbon atoms. Those containing less than six carbon atoms, for example ethylene glycol, are excluded because their products are inherently too hydrophilic. Although their products may have wetting properties, they do not have satisfactory detergent properties. The glycols containing over eighteen carbon are so hydrophobic as to be undesirable. Accordingly, glycols containing six to eighteen carbon atoms, inclusive, are required for the purposes of this invention. In the glycols the two hydroxyl groups may be on adjacent carbon atoms or on carbon atoms which are non-adjacent and which are in some cases widely separated.

Where the hydroxyls are on adjacent carbons, as, for example, in 1,2-dodecanediol, the polymeric products may be represented as follows, where M, W, x, and y have the same significance as above and R represents an alkyl group.

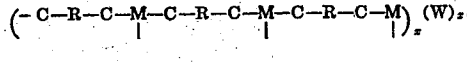


The groups R of the glycol



are said for convenience to be in a "parallel" arrangement. R may be a straight or branched chain.

In contrast to the parallel type, there is the so-called "series" type, resulting from the use of glycols in which the two hydroxyls are widely separated as, for example, in dodecanediol-1,12. This type is conveniently represented by the following formula in which the several characters have the significance noted above.



Both the "parallel" and "series" types are surface-active and both contain the hydrophobic groups, R, in the glycol and the hydrophilic groups, W, attached to and saturating the double bonds of the acid residue. A "parallel" type of product is much more effective as a detergent than the corresponding "series" type and is, therefore, much preferred. Glycols such as 1,4-octanediol or 1,12-octadecanediol give rise to products having arrangements of both the "parallel" and "series" type. Mixtures of glycols may also be used. Thus, it is possible to use two or more glycols, such as 1,2-hexanediol and 1,2-octanediol, both of which produce the "parallel" type of macromolecule, or a mixture of glycols such as 1,16-hexadecanediol and 1,18-octadecanediol, both of which produce the "series" type, or a mixture of, for example, 1,2-hexadecanediol and 1,18-octadecanediol, which produces a macromolecule in which the alkyl groups are in both a parallel and a series arrangement.

Glycols which may be employed are exemplified by the following: 1,2-hexanediol, 1,6-hexanediol, 1,2-octanediol, 2-ethylhexanediol-1,3, 1,4-dihydroxy-2-t-butyl butane, 1,18-octadecanediol, 1,2-octadecanediol, 1,4-decanediol, and the like.

Maleic acid and its anhydride may be used interchangeably. Likewise, fumaric acid, isomer of maleic acid, may be employed. While the glycol and the maleic acid react in equimolecular proportions, that is, in the ratio of one mol of glycol to one mol of maleic acid or anhydride, it is preferred to have a small excess of glycol present during the esterification reaction by which the linear polyesters are made.

The linear polyesters may be made by well-known methods. Preferably, the glycol and maleic anhydride are mixed and heated with stirring at temperatures between about 150° and about 200° C. until condensation has progressed to the desired point. Temperatures higher than 200° C. are to be avoided, because above 200° C. there is a great tendency for the product to become insoluble and infusible, presumably due to cross-linking of the molecules at the double bond of the maleic acid. Ordinarily, it is preferred to conduct the esterification in a solvent such as toluene or solvent naphtha, which may be subsequently removed. The progress of the esterification can be followed by measurements of viscosity. It is desirable to remove the water produced during esterification, and this can be done by operating under reduced pressure or by removing it as an azeotropic mixture, with toluene, for example. As esterification progresses, the linear polyesters become syrupy and thereafter increase in viscosity to the point where they are highly resinous materials at room temperature in the undiluted form. In ordinary practice, the esterification reaction is advantageously stopped before the viscosity of a 50% solution of the product in toluene has reached five poises. While, in commercial practice, it is preferred to stop the esterification or condensation at the above viscosity, no upper limit need necessarily be imposed, however, because linear polyesters made, in the proper way under the right conditions, from dihydric alcohols and dicarboxylic acids do not become infusible as do the products made by esterifying acids and alcohols, either or both of which contain more than two functional groups. In any case, the linear polyesters are carried to a point beyond which more than two molecules each of the glycol and maleic acid are joined into

a single linear macromolecule and preferably to the stage where resinification has definitely occurred.

The linear polyesters are next reacted with a bisulfite salt of an alkali metal, such as sodium or potassium, or an alkaline earth metal such as calcium, barium, or magnesium. The bisulfites of the alkali metals are much preferred, especially those of sodium and potassium. Sodium metabisulfite is particularly suitable.

The reaction is conducted by heating a linear polyster and an aqueous solution or suspension of the bisulfite. While one-half to one mol of bisulfite is combined per mol of maleic acid, it is preferred to employ an excess over that which will combine in order to expedite the reaction. The reaction is most conveniently carried out under reflux at the boiling point of the aqueous solution. As the reaction progresses, sulfonate groups are added to the linear polyester and ultimately the product becomes water-soluble, at which point the reaction is sufficiently complete. The product is concentrated by removal of water, and the unreacted salt is removed by filtration. The water may be removed by any convenient means, for example, by distillation under vacuum or the addition of an organic solvent, such as toluene, which is then removed with the water as an azeotropic mixture. Any excess solvent may be stripped off at this point.

As stated above, the products of this invention are so prepared that a balance is maintained between the hydrophilic and hydrophobic properties. When the number of carbon atoms in the glycol approaches eighteen, the hydrophobic properties of the polyester are so high that they can be balanced only by the introduction of the maximum number of sulfonate groups possible. In such instances, the bisulfite salt is combined in the ratio of one mol per mol of maleic acid residue in the linear polyester. The product may then be considered as a linear polyester of a glycol and sulfosuccinic acid, and its salts of the alkali metals and alkaline earth metals are water-soluble. On the other hand, as the number of carbon atoms in the glycol decreases, the hydrophobic properties of the macromolecule become less pronounced and the proportion of hydrophilic groups required for purposes of solubility and balance of properties is less. The lower limit is reached when half of the maleic acid residues is sulfonated. Thus, the number of sulfonate groups which are added may be varied between 0.5 and 1 per residue of maleic acid in the linear polyesters and varies directly with the number of carbon atoms in the glycol. An excess of bisulfite may be employed in order to accelerate the rate of sulfonation, but the amount combined must be between 0.5 and 1.0 mol per mol of esterified maleic acid. In another sense, the products are linear polyesters of glycols, containing six to eighteen carbon atoms, inclusive, and maleic acid, at least half of the double bonds of the maleic acid residues being saturated by the addition of sulfonate groups. Or they may be accurately described as linear, salt-forming, water-soluble, polymeric, surface-active polyesters of glycols and both maleic and sulfosuccinic acids, the number of salt-forming sulfosuccinic acid residues in said ester being at least as great as the number of said maleic acid residues.

In every case, the important requirement is that the hydrophobic properties, which depend upon the number of carbon atoms in the glycol, and the hydrophilic properties, which depend upon the degree of sulfonation, be balanced. This requirement is ordinarily met when the glycol contains six to eighteen carbon atoms and the final product is soluble in water.

The following examples will serve to illustrate the preferred method of preparing the surface-active products of this invention.

Example 1

Into a three-necked flask equipped with a mechanical stirrer, a twenty-four-inch reflux condenser, and a thermometer, there was placed a mixture of two mols (196 grams) of maleic anhydride, 2.2 mols (444.4 grams) of 1,2-dodecanediol, and 200 grams of toluene. The mixture was heated at 180°–195° C. for 4.8 hours. The water which had formed as a result of the esterification reaction was removed by distillation. The toluene was then stripped off under vacuum. The resinous product which remained had a viscosity of 0.5 poise when measured as a 50% solution in toluene and an acid number of eleven.

One half of the above resin (equivalent to the amount produced from one mol of maleic anhydride) was placed in a flask and refluxed together with a solution of 1.5 mols (285 grams) of sodium metabisulfite in 450 grams of water. After two and one-half hours, the resin had completely dissolved. Toluene was then added, and the water was removed by distillation, after which the unreacted bisulfite was removed by filtration. The residual toluene was then stripped off under vacuum, and the product was isolated as a hard resinous mass.

This product, which is of the so-called "parallel" type, gave excellent results in deflocculation tests at 80° C. and in launderometer tests.

Example 2

In a process like that described in Example 1, a linear polyester was prepared by reacting two mols of maleic anhydride and 2.2 mols of 1,10-decanediol. The linear polyester was then heated with an aqueous solution of 2.5 mols of potassium bisulfite until the resinous polyester had dissolved in the aqueous solution. The product was then purified and concentrated as in Example 1.

This product, which is of the "series" type, proved to have good detergent properties when tested for removal of standard soil in a wash test.

Example 3

A detergent having both "parallel" and "series" types of configuration was made by first making, according to the process of Example 1, a linear polyester of maleic acid and 1,12-octadecanediol. The ester was concentrated by removal of water under vacuum and was then reacted with a solution of sodium metabisulfite containing the salt in the ratio of two mols of bisulfite per mol of maleic present in the polyester. Approximately 0.9 mol of bisulfite per mol of maleic acid actually combined with the polyester, and the product, which was water-soluble, had very good detergent properties.

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 may cause more rapid wetting of surfaces such as the surfaces of fibers as measured by the standard Draves sinking test. Their outstanding advantage, regardless of wetting properties which may be low, is their effec-

tiveness as detergents. In this capacity, as measured by deflocculation tests, wash tests, and laundering tests, they are outstanding, even though their wetting properties may be low, and they 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 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 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. The process of preparing linear, water-soluble, polymeric, surface-active polyesters which comprises preparing a resinous linear polyester by esterifying an alkane-diol containing six to eighteen carbon atoms and an equivalent amount of maleic acid at a temperature between about 150° and 200° C. and thereafter reacting by heating said linear polyester with a water-soluble bisulfite in the ratio of 0.5 to 1 mol of said sulfite per mol of esterified maleic acid at the double bond of the maleic acid.

2. A product having high detergent properties and having the formula

$$(\text{—G—M—})_x(\text{W})_{x(1-y)}$$

in which G represents an esterified alkane-diol containing six to eighteen carbon atoms, M represents maleic acid which is esterified by said alkane-diol, W represents a sulfonate group attached across the double bond of M, x is an integer having a value of three to twelve, and y is a number from 0 to 0.5.

3. A linear polyester having high detergent properties and having the formula:

$$(\text{—G—M—})_x(\text{W})_{x(1-y)}$$

in which G represents esterified 1,2-dodecanediol, M represents maleic acid which is esterified by said 1,2-dodecanediol, W represents a sulfonate group attached across the double bond of M, x is an integer having a value of three to twelve, and y is a number from 0 to 0.5.

4. A linear polyester having high detergent properties and having the formula:

$$(\text{—G—M—})_x(\text{W})_{x(1-y)}$$

in which G represents esterified 1,10-decanediol, M represents maleic acid which is esterified by said 1,10-decanediol, W represents a sulfonate group attached across the double bond of M, x is an integer having a value of three to twelve, and y is a number from 0 to 0.5.

5. A linear polyester having high detergent properties and having the formula:

$$(\text{—G—M—})_x(\text{W})_{x(1-y)}$$

in which G represents esterified 1,12-octadecanediol, M represents maleic acid which is esterfied by said 1,12-octadecanediol, W represents a sulfonate group attached across the double bond of M, x is an integer having a value of three to twelve, and y is a number from 0 to 0.5.

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