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SURFACE ACTIVE COMPOSITIONS

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This invention relates to surface active compositions, and more particularly, to surface active compositions useful in the processing and finishing of textile materials.

Compounds displaying a high degree of surface activity have attained a considerable degree of importance in the processing and finishing of textile materials. Especially is this true of a class of such compounds known as non-ionic surface active agents, particularly those compounds belonging to this group which are water-soluble. Such compounds are characterized by a high degree of wetting and penetrating action, particularly for aqueous solutions containing electrolytes and metallic salts. In this respect, the non-ionic surface active agents display a far greater stability toward hard water, alkali earth, or heavy metal salt solutions than do cationic or anionic surface active agents of a comparable degree of water solubility, and enables these compounds to perform their functions of wetting, cleansing, penetrating or emulsifying under a wide variety of operating conditions. Furthermore, the non-ionic surface active agents are usually little or not at all affected by limited contact with mild acid or alkalis and may be utilized under such conditions without appreciably altering their effectiveness.

Typical of such non-ionic surface active agents are the water soluble higher fatty acid esters of the polyethylene glycols (mol. weight approximately 400–750), and particularly the partial or mono-esters of predominantly saturated higher fatty acid materials with such polyethylene glycols. These particular compounds exhibit very good wetting properties, are effective detergents and emulsifiers, and as such have found wide use in scouring, desizing, dyeing and washing operations. Since these surface active agents are generally stable and effective in hard water and in aqueous solutions containing metallic salts, they have been found to be effective emulsifiers when used with soaps, preventing the formation of insoluble lime soaps which are ordinarily formed by soap in hard water and which have a tendency to cause specks upon the fabric being treated. Moreover, such lime soaps are ordinarily difficult to remove in the rinsing operation and when deposited upon the fabric act as a waterproofing agent which prevent uniform and even dyeing. The polyethylene glycol fatty acid monoesters are also good penetrants and, as such, act as effective dye assistants and leveling agents in the dyeing of various types of textile materials.

However, the surface active properties of the

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polyethylene glycol fatty acid esters and the effectiveness of these compounds for such purposes as are mentioned above are governed in large measure by the degree of esterification of the reaction product. Since the polyethylene glycols possess two hydroxyl groups available for esterification, upon such reaction with an ester forming material, there may be formed either the mono-ester, the di-ester, or a mixture of the mono-ester and the di-ester of the particular polyethylene glycol so treated, depending upon the proportions of the reacting materials to each other and the conditions of reaction. While it is evident that the properties and characteristics of these esters will be widely dissimilar from each other and among themselves when various kinds of ester forming materials are employed, it will also be found that the mono-ester and the di-ester of a polyethylene glycol will show widely divergent characteristics as regards their surface active properties, water solubility, etc., even when the ester forming material employed in preparing these products is the same in each case. For example, the saturated higher fatty acid mono-esters of polyethylene glycols having a molecular weight of approximately 400 and higher are completely soluble in water, decreasingly soluble in oil, and possess surface active characteristics peculiar to the non-ionic surface active agents mentioned above. The saturated higher fatty acid di-esters of polyethylene glycols having a molecular weight of 1000 and lower are water insoluble, oil soluble, and possess relatively few of the surface active properties useful in such textile applications as are set forth above, especially for such applications where complete water solubility is a necessity. Therefore, the presence of any substantial amount of the di-ester in admixture with the mono-ester would have a tendency to appreciably decrease the surface activity characteristic of the saturated higher fatty acid mono-esters of the polyethylene glycols and thereby seriously limit the usefulness of these compounds.

In preparing these esters in the conventional manner, by direct esterification of the fatty acid and the glycol, the degree of esterification is normally controlled by the amount of the reactants employed, that is, in molecular relation to each other, and by the conditions governing the reaction. Thus, for example, if equimolecular amounts of the fatty acid and polyethylene glycol are reacted together under conditions favorable for esterification, theoretically the mono-ester should essentially be formed in preference to the

di-ester. Similarly, if two moles of the fatty acid are reacted with one mole of polyethylene glycol and a substantially complete reaction is obtained, only the di-ester is formed. However, it has been found that in preparing the mono-ester of the polyethylene glycols, substantial amounts of the di-ester are formed, even when the molecular proportions of fatty acid to glycol are such as to favor the theoretical formation of only the mono-ester. Therefore, in order to obtain the pure mono-ester, a series of operations involving separation of the di-ester and the unreacted constituents must be employed, rendering the process more involved and more costly than is desirable.

There has recently been developed for commercial use a series of mono-methylated polyethylene glycols, ranging in average molecular weight from approximately 350 to 750. These compounds have physical properties very similar to the polyethylene glycols of comparable molecular weight, and while the presence of the methoxy group increases their compatibilities with hydrocarbon-type materials, they are completely water soluble. These compounds, when esterified with the saturated higher fatty acids, especially those containing from about 12 to 16 carbon atoms, form non-ionic surface active agents not only similar in their properties and characteristics to the analogous polyethylene glycol mono-esters, but also of greatly enhanced surface activity and wetting power. Since the methoxy polyethylene glycols have only one hydroxyl group available for esterification, the possibility of di-ester formation such as normally occurs in the esterification of the polyethylene glycols is eliminated and essentially pure fatty acid mono-esters may be prepared. Therefore, such esters prepared by the direct esterification of the saturated higher fatty acids and the methoxy polyethylene glycols, represent a distinct improvement over the polyethylene glycol fatty acid esters in that they may be more easily prepared, that essentially the pure ester can be obtained, and in that such esters possess a higher degree of surface activity and wetting power than do the corresponding polyethylene glycol fatty acid esters.

However, in preparing these esters, we have discovered that the surface activity of such products prepared by the esterification of the methoxy polyethylene glycols and the saturated higher fatty acids may be further improved by limiting the extent of the reaction so that the resultant reaction product possesses an acid value within the range of approximately 26–43.

We have further found that optimum wetting power of such products is obtained only within the range of an acid value of 26–43.

By the term "acid value" as utilized in the present invention is meant the number of milligrams of potassium hydroxide required to neutralize a one gram sample of the material so tested.

By the term "wetting power" or "wetting efficiency," as utilized in the present invention, is meant the speed of wetting as determined by means of the Drave's test, which is the official method for the evaluation of wetting agents adopted by the American Association of Textile Chemists and Colorists, and outlined in the 1944 Year Book of the A. A. T. C. C., volume XXI, pages 199–206. This method of testing wetting agents consists essentially of finding the concentration of wetting agent that is required to cause the sinking of a 5 gram skein of unboiled, grey, 2 ply cotton yarn in a standard period of time when the skein, carrying a hook of standard weight, is held beneath the surface of the wetting solution by a heavier weight. The value of the concentration to cause sinking in the standard time is obtained by interpolation from a curve plotted from average values of sinking times determined with known concentration of wetting agents.

Inversely, this method also consists of determining the time required for 5 gram skeins of unboiled, grey 2 ply cotton yarn when weighted with a sinker of standard weight to sink when submerged in a solution of standard concentration of wetting agent. The time of sinking is an indication of the wetting qualities of the particular wetting agent utilized. This is the method utilized in the present invention to determine the comparative wetting power of the various compositions so tested. It will be noted that this test indicates the wetting quality of a solution of the wetting agent upon a textile surface and does not measure the surface tension directly.

In carrying out our invention, equimolecular amounts of a methoxy polyethylene glycol and a fatty acid material composed essentially of saturated higher fatty acids are charged to a suitable reaction apparatus, together with a small amount of a catalytic agent. The charge is then heated to a predetermined temperature, sufficient to promote reaction between the glycol and fatty acid material, the water of reaction being continuously removed as formed. At various time intervals, a small portion of the reacting materials is withdrawn from the reaction vessel and tested both for acid value and wetting power. In this manner, the wetting power of the reaction product is determined at various stages of esterification, and the trend of increased or decreased wetting power in relation to the acid value, which is an indication of the extent of the esterification reaction, may be followed, and the point or acid value range within which the wetting power is at its greatest may easily be determined.

To demonstrate the present invention, the following illustrative examples are set forth.

Example I

	Parts by weight
Methoxy polyethylene glycol (average mol. weight 550)	2125.0
Neofat 11 (approx. 90% lauric acid, 9% myristic acid, 1% unsaturated fatty acids) (mol. wt. 203; acid value—276)	430.0
Para-toluene sulfonic acid	8.15

The above materials are charged to a three-neck flask equipped with a tube arranged so as to extend beneath the surface of the charged material to provide entry for an inert gas, such as carbon dioxide, and with a condensor to collect and remove the water of reaction. Heating is begun and a stream of carbon dioxide is started bubbling through the admixture to provide moderate agitation of the reacting materials. The carbon dioxide also serves to provide an inert gaseous blanket to prevent discoloration of the reaction product from the air, and aids in the removal of the water of reaction. The reaction mixture is then brought to a temperature of 127°±3° C. which is maintained for the duration of the reaction. After reaching the reaction temperature, 100 grams samples of the reaction mixture are removed at regular time intervals and are tested for acid

value and wetting efficiency. It was found that the wetting efficiency of the samples so tested was at its maximum at an acid value of 33.5 and that it suddenly fell off at a point below an acid value of about 26.

The following table demonstrates the tests made.

Elapsed time after reaching reaction temperature before testing sample	Acid Value of sample	Draves Sinking Time 2 gm. per liter in distilled water at 25° C.
Hours		*Seconds*
1	40.5	11
2	33.5	10
3	30.0	10.4
4	26.0	11.1
5	19.4	19.8

Example II

The reaction described in Example I, employing the same materials in the same amounts, was repeated at a reaction temperature of 109°±1° C. The results obtained upon testing 100 grams samples, withdrawn at regular intervals, are as follows.

Elapsed time after reaching reaction temperature before testing sample	Acid Value of sample	Draves Sinking Time 1 gm. per liter in distilled water at 25° C.
Hours		*Seconds*
0	53.5	30.2
½	43.0	26.5
1	36.0	26.4
1½	33.8	28.2
2¼	28.2	28.4
3¼	22.7	40.2
4¼	18.5	42.1

The percentage of ester formed in the above reaction at an acid value of 43 is approximately 43% by weight of the components present in the reaction mixture.

From the above table it can be seen that the optimum wetting efficiency of the reaction product at various stages of esterification lies within the range of acid value of approximately 28 to 43. At a point slightly below acid value 28, the wetting efficiency begins to decrease and becomes worse as the reaction nears completion. Therefore, the above trend indicates that not only will the wetting efficiency of the pure ester obtained by carrying the reaction to completion be lower than the wetting power of a reaction mixture exhibiting in the instant case, an acid value within the range of approximately 28 to 43, but also that the optimum wetting efficiency of the products secured by such reaction lies within a certain specific range of acid value. These facts are further borne out in the following example.

Example III

	Parts by weight
Methoxy polyethylene glycol (average mol. weight, 550)	820
Distilled coconut fatty acids (mol. weight, 224) (acid value—250)	335
Para-toluene sulfonic acid	5.97

The reaction was carried out according to the procedure outlined in Example I and the following results were obtained.

Elapsed time after reaching reaction temperature before testing sample	Acid Value of sample	Draves Sinking Time 4 gms. per liter in distilled water at 25° C.
Hours		*Seconds*
¾	43	15.1
1½	31	13.6
2¼	27	12.4
3	21.5	16.7
4	17.4	17.1
5	14.4	24.7
6	11.9	34.9

The percentage of ester formed at an acid value of 43, utilizing the above reactants in the proportions set forth, is approximately 40.0% by weight of the components present in the reaction mixture.

Here again, optimum wetting efficiency was obtained within a specific acid value range, with a sudden deterioration of the wetting efficiency occurring at an acid value slightly less than approximately 27 and continually becoming worse as the reaction approached completion.

Therefore, by limiting the extent of the reaction involving the methoxy polyethylene glycols and the saturated higher fatty acids to a point within an acid value range of approximately 26 to 43, compositions may be obtained which not only exhibit pronounced surface active properties, but which also possess wetting powers substantially superior to those of the analogous pure esters.

The compositions of the present invention are readily water soluble, and when agitated produce a voluminous amount of foam. These compositions possess excellent cleansing and emulsifying properties and may be utilized in conjunction with soap to prevent the formation of insoluble lime soaps or to disperse any lime soaps already formed. They are stable in hard water and under mildly acid and alkaline conditions and show no appreciable decrease in the effectiveness of their wetting properties under such conditions. The compositions of the present invention are also excellent dispersants and as such may be utilized to promote more level dyeing of fabrics.

While the products of the present invention and the processes of making the same, as outlined above, constitute preferred embodiments of the present invention, changes may be made therein without departing from the scope of the present invention as defined in the appended claims.

What is claimed is:

1. A surface active composition comprising, in admixture, at least 40 per cent by weight of an ester of a mono-methylated polyethylene glycol having a molecular weight within the range of approximately 350–750 and a fatty acid material, said fatty acid material being composed essentially of saturated higher fatty acids, a monomethylated polyethylene glycol, having a molecular weight within the range of approximately 350–750, and a fatty acid material composed essentially of saturated higher fatty acids, the said glycol and the said fatty acid material being present in approximately equivalent molar proportions, said composition having an acid value within the range of 26–43.

2. A surface active composition comprising in admixture, at least 40 per cent of an ester of a

mono-methylated polyethylene glycol having a molecular weight within the range of approximately 350–750 and coconut fatty acids, a monomethylated polyethylene glycol having a molecular weight within the range of approximately 350–750, and coconut fatty acids, the said glycol and the said fatty acids being present in approximately equivalent molar proportions, said composition having an acid value within the range of 26–43.

3. A surface active composition comprising, in admixture, at least 40 per cent by weight of an ester of a mono-methylated polyethylene glycol having a molecular weight within the range of approximately 350–750 and lauric acid, a monomethylated polyethylene glycol having a molecular weight within the range of approximately 350–750, and lauric acid, the said glycol and the said fatty acid being present in approximately equivalent molar proportions, said composition having an acid value within the range of 26–43.

4. A surface active composition comprising, in admixture, at least 40 per cent by weight of an ester of a mono-methylated polyethylene glycol having a molecular weight within the range of approximately 350–750 and myristic acid, a monomethylated polyethylene glycol having a molecular weight within the range of approximately 350–750, and myristic acid, the said glycol and the said fatty acid being present in approximately equivalent molar proportions, said composition having an acid value within the range of 26–43.

5. A method of preparing a surface active composition comprising the process of effecting esterification of approximately equivalent molar proportions of a fatty acid material with a monomethylated polyethylene glycol having a molecular weight within the range of approximately 350–750, said fatty acid material being composed essentially of saturated higher fatty acids, wherein said esterification is carried to at least 40 per cent completion of esterification and wherein the esterification is halted within an acid value range of 26–43.

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