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2,758,977

DETERGENT COMPOSITION AND METHOD OF PRODUCING SAME

Cecil M. Knowles, Plainfield, and Jackson J. Ayo, Jr., Elizabeth, N. J., assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

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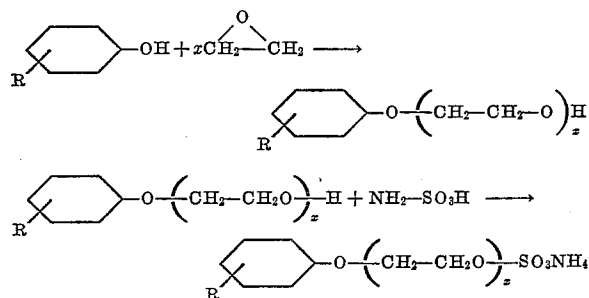
8 Claims. (Cl. 252-153)

This invention relates to a novel detergent composition, and process of producing it, comprising a concentrated solution of an alkylphenol polyglycol ether sulfate.

Many alkylphenol polyglycol ether sulfates of the type described in Steindorff et al. United States Patent No. 2,203,883 are valuable surface active agents having good detergency. A number of these compounds are extremely viscous to paste-like materials which are not convenient to use as household detergents. In order to make their use as household detergents more convenient it has been suggested that they be packaged and marketed in the form of solutions. However, in the case of those materials of this class which have the most desirable detergent properties for household use, it has heretofore been necessary to use relatively dilute solutions which, due to increased packaging and shipping costs, substantially increase their sales price.

We have now found that by selection of particular alkylphenol polyglycol ether sulfates and by careful control of their preparation, that a concentrated solution of material having good detergency and which is attractive from a sales standpoint may be prepared.

The novel products of the present invention and a convenient method of preparing them are illustrated by the following general equation wherein R represents one or two alkyl groups of from 8 to 10 alkyl carbon atoms and x represents about 4:



The products obtained from alkylphenols produced by alkylating phenol with a nonylene fraction obtained by the polymerization of propylene are particularly preferred since they have been found to possess particularly good household detergency properties. However, the products produced from octylphenols, particularly those from diisobutylphenol, have substantially equivalent properties and those obtained from di-amyphenol are also substantially equivalent in properties. However, as the alkyl group on the alkylphenol, from which the products are produced, is lowered below 8 carbon atoms or increased above 10 carbon atoms, the properties of the products have been found to change so that they are no longer as desirable as household detergents.

It has also been found that the number of ethenoxy units in the polyglycol ether group should be carefully controlled so that there are about four ethenoxy units present therein. The polyglycol ether alkylphenols,

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which are sulfated to produce the products of the present invention, are advantageously produced by condensing an alkylphenol with ethylene oxide in the presence of a small amount of alkaline catalyst. It has been found that in order to obtain good water solubility and good detergency approximately four mols of ethylene oxide must be condensed with one mol of alkylphenol so that in the major proportion of the intermediate and final products, illustrated in the equation above, "x" is 4, although small amounts of products in which "x" is slightly lower or higher than 4 may be present. When the amount of ethylene oxide condensed with the alkylphenol is reduced to about 3.7 to 3.8 mols of ethylene oxide per mol of alkylphenol, (so that the average value of x is 3.7 to 3.8) it has been noted that the water solubility of the final product begins to decrease slightly and, if the amount of ethylene oxide condensed with the alkylphenol is reduced below 3.5 mols of ethylene oxide per mol of alkylphenol, the water solubility of the final product is insufficient for highly concentrated solutions thereof to be produced. On the other hand, if more than about five mols of ethylene oxide are condensed with one mole of the alkylphenol, the foam obtained from the final product for use as a household detergent is not nearly as stable as the foam from products containing four to five ethenoxy units in the polyglycol ether radical, so that they are less desirable as household detergents and, if the amount of ethylene oxide is further increased so that the polyglycol ether radical contains above six ethenoxy units, the amount of foam rapidly decreases and the detergency of the final product is not as high. It will also be understood that the alkylphenol polyglycol ether, used in producing the novel compounds of this invention, may, if desired, be made condensing an alkylphenol with a polyether glycol containing 4 ethenoxy groups or a mixture thereof having an average of 4 ethenoxy groups.

The details of the present invention will be readily apparent from and may be most conveniently described by a consideration of the following specific example in which the parts are by weight.

1188 parts of nonylphenol polyglycol ether obtained by condensation of 1 molar proportion of nonylphenol with 4 molar proportions of ethylene oxide were heated to 115-120° C. and there was slowly added thereto, at 115-125° C., 330 parts of sulfamic acid (about 10% excess of the amount required for complete sulfation of the alkylphenol polyglycol ether). The mixture was agitated at 120-125° C. for one hour, at which time the sulfation was complete and the mixture cooled to 65-70° C. 50 parts of monoethanolamine, i. e. an amount sufficient to substantially neutralize the excess sulfamic acid, was then added. The reaction mixture was thinned by the addition of 384 parts of ethanol and agitated for ¼ hour at 50-60° C. The pH of the mixture should then be within the range of 7.8 to 8.5 and further ethanolamine may be added if necessary to bring the pH within this range. There is then added 300 parts of fresh water and 6 parts of hydrogen peroxide. The mixture was then agitated for one hour at 50-60° C. and 6 additional parts of hydrogen peroxide were then added and agitation continued for another hour at 50-60° C. The mixture was then further diluted by the addition of 300 parts of fresh water containing 1.2 parts of sodium ethylenediamine tetra acetate and the mixture then made slightly acid, i. e. the pH adjusted to within the range of 6.5 to 6.9 by the addition of acetic acid. There was thus obtained a solution of ammonia salt of nonylphenol polyglycol ether sulfate containing about 58% alkylphenol polyglycol ether sulfate (ammonium salt), 25% water, 15% alcohol, and about 2% inorganic salts. This product was stable on storage and remained clear at temperatures of from 5° C. to 40° C. and had no odor of am-

monia. It was found to be a good household detergent having good detergency particularly in dish washing.

In producing the novel composition of the present invention it is desirable to employ a slight excess, about 10%, of sulfamic acid over that theoretically required in order to assure complete sulfation of the alkylphenol polyglycol ether. However, a greater excess of sulfamic acid should be avoided since it will result in too high a salt concentration in the final product so that there may be some sediment formed on standing. During the sulfation step it is desirable that the reaction be anhydrous, since the presence of water has been found to inhibit the sulfation and may also result in some decomposition (hydrolysis) of the desired sulfate. Temperatures above 125° C. are to be avoided during the sulfation step in order to prevent charring of the product. It is also necessary, on completion of the sulfation step, to neutralize the product before water or alcohol are added thereto in order to avoid decomposition of the product. It has been found that the product decomposes in the presence of water at a pH below about 3 and, therefore, care must be exercised that the sulfated product is not permitted to have access to water unless its pH is above 3. If the product is made in a single kettle, it is desirable to employ a suitable organic base such as methyl- or ethylamine or the ethanolamines. However, if the product is made in several kettles, it is possible to effect the sulfation in one kettle under anhydrous conditions and the sulfated product may then be transferred to a second kettle containing water or alcohol which contains a sufficient amount of base to bring the pH of the mixture above 3 and, in this case, aqueous alkalies may be used, preferably aqueous ammonium hydroxide. While it is only necessary to adjust the pH above 3 on completion of the sulfation in order to prevent decomposition of the product on addition of water or alcohol, it is desirable to employ a sufficient amount of base so that the sulfated product is slightly alkaline, i. e., has a pH of 7.8 to 8.5, if it is desired to decolorize the product by treatment with hydrogen peroxide since hydrogen peroxide does not bleach as effectively under neutral to acid conditions. The amount of hydrogen peroxide employed to bleach the product should be carefully controlled so that it is substantially all consumed during the processing of the material since, if excess hydrogen peroxide is present in the finished product, it may tend to oxidize the alcohol employed for thinning the product so that a wine-like odor develops and, if ethanolamines are employed as neutralizing agent, they too may be oxidized on standing with excess hydrogen peroxide so that the product is darker.

On completion of the decolorization, the product should again be made slightly acid by the addition of acetic acid so as to bring the pH within the range 6.5 to 6.9 as under alkaline conditions the product, being an ammonium salt, will develop an ammonia odor.

The ammonium salts of these alkylphenol polyglycol ether sulfates are preferred in the products of the present invention since the ammonium salt is directly produced in the sulfation using sulfamic acid and more concentrated solutions may be readily obtained than are produced from the sodium or potassium salts, 60 percent concentration of the active ingredient being readily obtainable. This is approximately the maximum concentration which can be readily prepared while still retaining a clear solution and one which is readily pourable.

It will be understood that the relative proportions of water and alcohol, which are employed as a solvent, may be varied somewhat. Larger amounts than 15 percent by weight of alcohol may be used but from an economic standpoint the minimum amount of alcohol necessary to obtain the desired fluidity will be employed.

It has been found that by the use of a solvent composed of about 3 parts by weight of alcohol to 5 parts by weight of water, a solution having good fluidity is obtained. However, if a more viscous solution is desired

the amount of alcohol may be decreased so that the solvent is composed of as little as 1 part of alcohol to 3 parts of water before the solutions show a noticeable tendency toward gelation at ordinary temperatures. It has also been found that the relative amount of alcohol in the solvent may be slightly decreased if the concentration of active ingredient (ammonium salt of alkylphenol polyglycol ether sulfate) is slightly lowered. Thus solutions containing as low as 50% active ingredient are included within the scope of this invention since they are more concentrated than the prior art solutions, and with such solutions, solvents containing an amount of alcohol approximating the lower limit therefore specified above may be used.

It will be understood that in place of ethanol, other aliphatic alcohols, such as isopropanol, butanol or amyl alcohol, may be employed and are substantially equally effective as thinning agents. Ordinarily, however, ethanol is preferred since its use presents somewhat less of a problem from an odor standpoint in formulating an attractive product.

The presence of the sodium salt of ethylene diamine tetraacetic acid is not essential in the products of the present invention but is preferred in order to obtain a clear solution when ordinary tap water is employed, since it is generally more economical to incorporate a small amount of this material and thus permit the use of tap water rather than using distilled water in formulating the solutions.

We claim:

1. The method of producing a clear fluid concentrated solution of the ammonium salt of an alkyl phenol polyglycol ether sulfate which comprises heating under anhydrous conditions at a temperature below 125° C. an alkyl phenol polyglycol ether of an alkyl phenol having from 8-10 alkyl carbon atoms and in which the polyglycol ether radicals have an average of 3.5-6 ethenoxy groups with about 10% excess sulfamic acid to thereby form a reaction product consisting of said ammonium salt of said polyglycol ether sulfate and free sulfamic acid; adding to and mixing with the thus obtained reaction product a predetermined amount of a base, selected from the group consisting of methylamine, ethylamine, ethanolamine and aqueous ammonia, to adjust the pH of said reaction product within the range of 3 to 8.5 and mixing the thus obtained product with from 1 to 0.8 part by weight thereof of a solvent consisting essentially of a lower alkanol and water in relative proportions of 1:1 to 1:3 parts by weight, said mixing being effected in the presence of the base specified, and adjusting the pH of the thus formed solution to from 6.5 to 6.9.

2. The process as defined in claim 1, wherein the polyglycol ether specified is the polyglycol ether of a nonyl phenol.

3. The method of producing a clear fluid concentrated solution of the ammonium salt of an alkyl phenol polyglycol ether sulfate which comprises heating under anhydrous conditions at a temperature below 125° C. an alkyl phenol polyglycol ether of an alkyl phenol having from 8-10 alkyl carbon atoms and in which the polyglycol ether radicals have an average of 3.5-6 ethenoxy groups with about 10% excess sulfamic acid to thereby form a reaction product consisting of said ammonium salt of said polyglycol ether sulfate and free sulfamic acid; adding to and mixing with the thus obtained reaction product a predetermined amount of a base, selected from the group consisting of methylamine, ethylamine, ethanolamine and aqueous ammonia, to adjust the pH of said reaction product within the range of 3 to 8.5, and mixing said reaction product in the presence of said base with from 1 to 0.8 parts by weight thereof of a solvent consisting essentially of a lower alkanol and water in relative proportions of 1:1 to 1:3 parts by weight, adjusting the pH of the thus formed solution to 7.5 to 8.5, adding a predetermined amount of hydrogen peroxide to

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said solution to decolorize the same and thereafter adding acetic acid to said solution to adjust the pH thereof to from 6.5 to 6.9.

4. The process as defined in claim 3 wherein the polyglycol ether specified is the polyglycol ether of a nonyl phenol.

5. A clear fluid solution of the ammonium salt of an alkyl phenol polyglycol ether sulfate consisting essentially of 50 to 60 per cent by weight of said ammonium salt of an alkyl phenol polyglycol ether sulfate of an alkyl phenol having from 8-10 alkyl carbon atoms and in which the polyglycol ether radical has an average of 3.5 to 6 ethenoxy groups, containing not over 10 molar per cent of a salt of sulfamic acid selected from the group consisting of methylamine, ethylamine, ethanolamine and ammonium salts of sulfamic acid and 50 to 40 per cent by weight of a solvent consisting of a mixture of a lower alkanol and water in relative proportions by weight of from 1:1 to 1:3.

6. A composition as defined in claim 5 containing a

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minor amount of an ion sequestering agent consisting of an alkali metal salt of ethylene-diamine tetracetic acid.

7. A composition as defined in claim 5 wherein the ammonium salt of an alkyl phenol polyglycol ether sulfate specified is the ammonium salt of nonyl phenol polyglycol ether sulfate having an average of 3.5 to 6 ethenoxy units in the polyglycol ether radical.

8. A composition as defined in claim 7 containing a minor amount of an ion sequestering agent consisting of an alkali metal salt of ethylene-diamine tetracetic acid.

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