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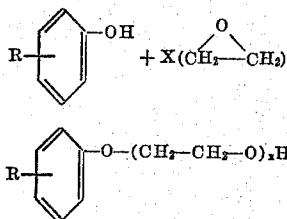
PROCESS FOR PREPARING AMMONIUM SALTS OF ALKYL PHENOL POLYGLYCOL ETHER SULFATES

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The present invention is concerned with a new process for making detergent compositions comprising ammonium salts of an alkyl phenol polyglycol ether sulfate.

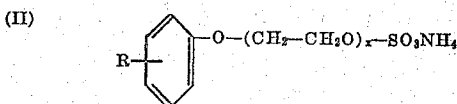
A special class of surface active agents characterized by excellent detergent properties are derived from alkyl phenol polyglycol ether sulfates. The polyglycol ether precursors of the sulfates are normally made by reaction of an alkyl phenol with an alkylene oxide, such as ethylene oxide, in accordance with the following equation:



wherein R preferably designates an alkyl group having between 8 to 12 carbon atoms and X is a number between 3 and 6, and preferably 4.

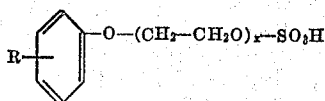
For detergent purposes the sulfates which may be obtained from compounds illustrated by Formula I are generally used in the form of their ammonium salts. The ammonium salts normally may be obtained by either one of two processes from the polyglycol ethers of Formula I.

In one process ethers, as illustrated by Formula I, may be reacted with sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) to form the following ammonium salt:



A process of the above type is disclosed in the patent to Knowles et al. 2,758,977, which disclosure is incorporated herein by reference. The resulting ammonium salt is frequently supplied as a concentrate in an alcohol-water solution. Such a process has the advantage of obtaining the desired ammonium sulfate salt of the polyglycol ether directly. Further, the sulfamic acid process substantially eliminates any undesired sulfonation of the aryl ring. However, this process is relatively expensive in view of the current cost of sulfamic acid.

The second process comprises initially reacting an alkyl phenol polyglycol ether of Formula I with SO_3 to obtain the following sulfated compound:



This sulfate is then neutralized with a sodium or ammonium base to form the corresponding salt, the ammonium salt being the same as that disclosed by Formula II above.

Such a process is less expensive than the first described process but has a disadvantage in that sulfonation of the benzene ring occurs, frequently to the extent that twenty percent of the benzene rings are sulfonated. Sulfonation of the benzene rings has an adverse effect on the detergent due to the fact that it tends to depress the formation of foam and also results in some separation of the

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polyglycol salt from the remaining components of the final detergent composition.

To overcome the problem caused by ring sulfonation and to avoid undue expense, it has been proposed to prepare ammonium salts of the polyglycol ethers by both processes and mix the two salts in about equal proportions. However, the resulting combined product has been found to still contain about half of the usual ring sulfonation, i.e. about ten percent, which for many applications is considered undesirable.

It has now been found that the advantage of the two types of processes can be obtained with the elimination of certain characteristic disadvantages by a new combination process. In the new process, as disclosed and claimed herein, a portion of the polyglycol ether is initially reacted with sulfur trioxide, the resulting half ester neutralized with, for example ammonia, and the remaining hydroxyl groups of the reaction product then reacted with sulfamic acid to form the ammonium sulfate salt. It has been discovered, for example, that when half of the polyglycol ether is initially reacted with the sulfur trioxide, followed by neutralization and the remainder of the ether reacted with sulfamic acid, a maximum of about five percent sulfonation of benzene rings occurs and, frequently, only about one percent sulfonation is present. This low degree of ring sulfonation compares to the aforementioned approximately ten percent ring sulfonation present in compositions composed of about fifty-fifty mixtures of salts obtained from the two prior art processes, as described above.

The specific reason for the markedly low degree of sulfonation obtainable by means of the new process has not been completely verified. It is believed the phenomenon is based upon the fact that, in the initial phase of the process, the sulfur trioxide is reacted with the polyglycol ether at a stage wherein a maximum amount of hydroxyl groups are present. It is generally understood that sulfur trioxide will react with hydroxyl groups present as well as the hydrogen on the benzene. However, it is also believed that the tendency or preference of the sulfur trioxide is toward a reaction with the hydroxyl groups rather than hydrogen of the benzene ring when both are available. As the hydroxyl group availability is reduced by reaction with sulfur trioxide, the preference of the sulfur trioxide for the remaining hydroxyl groups over the available hydrogen of the benzene ring is apparently reduced. This results in an increased tendency for sulfonation of the benzene by reaction with hydrogen of the ring. As indicated, the present process contemplates reaction of the sulfur trioxide with an alkyl phenol polyglycol ether when there is a large excess of hydroxyl groups present. Accordingly, since the complete sulfation of all hydroxyl groups by means of sulfur trioxide is not permitted, but only about half, there is always present in the reaction mass a relatively large supply of hydroxyl groups during the sulfur trioxide reaction. Hence, the chances of obtaining sulfonation of the benzene ring is appreciably reduced as borne out by the results.

The foregoing theory is further supported by the fact that if the two reactions were reversed, wherein half of the ether is initially reacted with sulfamic acid followed by reaction with sulfur trioxide, there is frequently a noticeable increase in the ring sulfonation derivative present.

In practicing the new process, sulfur trioxide is initially reacted with an alkyl phenol polyglycol ether in the molar ratio of about 0.4 to 0.6 mole of sulfur trioxide to one mole of the polyglycol ether, and preferably in a ratio of 1 to 2. This molar range comprises a balance between the economies which can be effected and the amount of ring sulfonation which is desired or can be tolerated for

commercial applications. Normally, to insure the presence of not more than about five percent ring sulfonation, a maximum of 0.6 mole of sulfur trioxide to one mole of polyglycol ether should be used. With a molar ratio of about 1 to 2, ring sulfonation can be maintained in approximately the one to three percent range.

A typical, and frequently preferred, alkyl phenol polyglycol ether for detergents is that obtained by alkylating phenol with a nonylene polymer of propylene. However, other alkylating compounds wherein R is an alkyl group having between 8 to 12 carbon atoms, as described above, may be readily employed.

The sulfur trioxide, usually as a 2-5 percent mixture with nitrogen, is normally reacted with the ether at room temperature by introducing the gaseous mixture beneath the surface of the liquid ether. In order to improve the reaction conditions the reaction mass is generally heated to reduce the viscosity of the ether and prevent swelling of the reaction mass under pressure of the gas reactant.

After the reaction has progressed to the desired stage, the introduction of sulfur trioxide is stopped and the sulfated reaction product neutralized, preferably with ammonia forming the ammonium salt of the half sulfate ester. Neutralization is generally conducted in a separate reaction vessel from that used in the initial sulfation reaction to avoid forming, as much as possible, undesirable salts.

Following neutralization, as described, the resulting product is then reacted with sulfamic acid under anhydrous conditions substantially in accordance with the process disclosed in the aforementioned patent to Knowles et al. Generally, a molar ratio of approximately 0.6 to 0.4 mole of sulfamic acid to ether is used, depending upon the extent of the previous sulfur trioxide reaction, although a slight excess of not more than about five percent sulfamic acid is frequently employed as a practical matter. The solid sulfamic acid is normally added to the half ester at a temperature of from 110 to about 125° C. with agitation. After the reaction is completed, the reaction mass is usually cooled to between 60-75° C. Generally, a small portion of a nitrogenous base such as ethanolamine, methylamine, ethylamine or ammonia is added to the resulting product to neutralize any remaining sulfamic acid. If the color of the product is considered poor, a bleaching agent, such as hydrogen peroxide, may be incorporated in sufficient amounts to improve the clarity. The pH of the product is preferably adjusted to substantially neutral or on the slightly acid side to avoid an ammonia odor (pH 6.5-6.9).

The ammonium salt is normally obtained as a relative viscous syrup and thinning is usually accomplished by adding a mixture of water and an alcohol such as ethanol, isopropanol or some similar alkanol. Preferably, a concentration of about 60 percent of the active component in the solution is desirable for commercial bulk purposes.

For a more specific description of an exemplary process the following example is presented:

A large 5 liter reaction vessel was charged with 1956 g. (5.0 moles) of Monsanto Sterox N.D. (ethoxylated nonyl phenol having an M.W. of 389). The SO₃ generator was charged with 200 g. (2.5 moles) of liquid SO₃ supplied by General Chemical under the name Sulfan B. The nitrogen carrier for the SO₃ was adjusted such that the SO₃ concentration in the gas stream was between 2-4 percent and this mixture was passed into the phenol over a period

of approximately three hours. The reaction temperature rose spontaneously but was held to 35-40° C. by means of a water bath. Pure nitrogen was then passed through the reaction vessel for about 15 minutes to purge SO₃. Ammonia gas was then introduced until the pH of the mixture was approximately 9. This pH level may be easily anticipated, as the ammonolysis is quite exothermic, and the exotherm ceases as an equivalent of ammonia is added. The ammonolysis temperature was maintained between 50-55° C. to insure proper viscosity for the ammonolysis. The resulting product is a white, extremely viscous material, having an appearance similar to that of beaten egg whites. The product weighed 2152 g. representing about a 99% yield. On standing, there is a slight separation into an upper foamy layer and a lower, yellow oil. However, the lower layer is less than about 5 percent by volume of the total. The product analyzed as 50.35 percent nonionic or unreacted component.

To a charge of 1575 g. of the above half ester ammonium salt were added 5.5 g. of urea to decrease the viscosity and moderate the sulfamic acid reaction, and the mixture was heated to 60° C. Under a N₂ flow, and while the temperature was slowly raised to 120°, 177 g. of sulfamic acid were added during a period of about ½ hour. The reaction mixture was stirred at 120° for 1.5 hours and 10 g. of ethanolamine were then added to bring the pH to 7.5. The odor of NH₃ was now quite noticeable. The resulting product had a light amber color and twenty-five ml. of 50 percent H₂O₂ was added to bleach the product. This final product contained substantially 98 percent active component. The product is normally dissolved in a solution comprising a water-alcohol mixture.

What is claimed is:

1. A method of producing an ammonium salt of an alkyl phenol polyglycol ether sulfate characterized by a relatively low degree of benzene ring sulfonation which comprises initially reacting a mole of the alkyl phenol polyglycol ether with between about 0.4 to 0.6 mole of sulfur trioxide, neutralizing the reaction product with ammonia to form the ammonium salt of the half ester and subsequently completing the formation of the ammonium salt of the polyglycol ether sulfate by reacting the half ester salt with sulfamic acid.

2. A method as described in claim 1 wherein the alkyl phenol polyglycol ether is an alkyl phenol having 8-12 alkyl carbon atoms and in which the polyglycol ether radicals have an average of between 3-6 ethenoxy groups.

3. A method as described in claim 2 wherein the alkyl phenol polyglycol ether is nonylphenol polyglycol ether having an average of about 4 ethenoxy groups.

4. A method as described in claim 1 wherein the sulfur trioxide is reacted with the alkyl phenol polyglycol ether in the molar ratio of about 1 to 2.

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