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PURIFICATION OF DETERGENT ALKYLATES

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ABSTRACT OF THE DISCLOSURE

Suspended aluminum halide catalyst sludge is removed from crude detergent alkylate by introducing a sufficient amount of anhydrous ammonia to the detergent alkylate in order to coagulate the suspended sludge. The coagulated sludge can then be separated from the detergent alkylate.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to detergent alkylates. More particularly, the present invention relates to a method for removing suspended aluminum halide catalyst sludge from detergent alkylates thereby obviating the presence of color bodies and sulfonate color precursors from n-alkaryls prepared using alkyl chlorides or olefins as the alkylating agent prior to the conversion thereof to sulfonic acid salt derivatives by means of sulfonation with sulfonating agents such as sulfur trioxide, sulfuric acid, and oleum.

Description of the prior art

It is well known to prepare highly effective, water-soluble surfactants by sulfonating, either with oleum or sulfur trioxide, the detergent alkylates obtained by alkylating an excess of an aromatic compound, usually benzene, with an olefin having from about 8 to 18 carbon atoms. The art has become very advanced in the preparation of this type of surfactants, particularly with respect to techniques for obtaining relatively pure products approaching whiteness in color. While any moderate discoloration of alkyl benzene sulfonates has no discernible effect upon the surface active properties, nevertheless good color for these products has become a prime requirement on the part of the manufacturer or formulator of the detergent composition in which these surfactants are prevalently employed.

In the manufacture of detergent alkylates in accordance with the Friedel-Crafts reaction wherein an aluminum halide, such as aluminum chloride, is employed as the alkylation catalyst, a crude alkylate product is obtained containing an appreciable amount of suspended sludge. The sludge component consists mainly of complexes of the spent aluminum halide catalyst and aromatic hydrocarbon compounds. Most of the sludge will readily separate in a gravitational settling operation. However, a very small amount of the sludge, in the order of 0.7 percent or less, cannot be removed in this manner. The presence of even this small amount of sludge adversely affects alkylate product quality. In addition, any recycle stream of the alkylate product process should desirably be substantially free of sludge.

The purification procedures generally utilized for removing the sludge from the alkylate product in order to prepare light-colored sulfonate salts of the aforedescribed surfactants include time consuming mechanical separatory methods, such as filtration, prolonged settling, and the like, and expensive physical treatment methods, such as treating the crude alkylation reaction mixture with concentrated sulfuric acid prior to recovering a

suitable fraction of the alkylate for conversion to its sulfonic acid derivatives. Other methods include the addition of a small amount of water to the alkylate product to coagulate the suspended sludge so that the coagulated sludge may be separated. However, problems are encountered in the use of water to coagulate the suspended sludge because the water hydrolyzes the suspended sludge and thereby releases the organic portion of the catalyst complex, which is known as sprung oil, into the detergent alkylate and this results in quality deterioration of the detergent alkylate. Thus, new and improved methods for removing the remaining sludge from the alkylate product are constantly being sought.

SUMMARY OF THE INVENTION

The present invention resides in a purification method for obviating the presence of suspended sludge and thus certain sulfonate color precursors prone to be present in a detergent alkylate product prepared by an aluminum halide, such as aluminum chloride or aluminum bromide, catalyzed condensation of a partially chlorinated normal paraffin or olefin with an aryl compound, such as benzene. Specifically, this method basically involves introducing a sufficient amount of anhydrous ammonia to the crude detergent alkylate in order to coagulate the suspended sludge. The coagulated sludge is then separated from the detergent alkylate thus providing a purified detergent alkylate.

OBJECTS OF THE INVENTION

An object of this invention is to remove suspended aluminum halide catalyst sludge from crude detergent alkylate. Another object of this invention is to provide an economical, efficient and simplified method for removing suspended sludge from detergent alkylates thereby obviating the presence of color bodies and sulfonate color precursors from n-alkaryls prepared using alkyl chlorides or olefins as the alkylating agent prior to conversion thereof to sulfonic acid salt derivatives by means of a sulfonating agent.

DESCRIPTION OF PREFERRED EMBODIMENTS

The detergent alkylates purified by the present invention can be any detergent alkylates prepared wherein an aluminum halide, such as aluminum chloride or aluminum bromide, is employed as the alkylation catalyst in the preparation of detergent alkylates. In order to further illustrate the invention, the method for preparing detergent alkylates as set forth in U.S. Patent No. 3,316,294 (1967) is hereby incorporated in part.

In the preparation of detergent alkylates an n-paraffin having from about 8 to 18 carbon atoms is partially chlorinated so as to produce monochlorinated paraffns. Either conventional liquid or vapor phase chlorination of the paraffins can be employed, However, regardless of which of these chlorination techniques is employed, the degree of chlorination should be at least 10 mole percent and not over 35 mole percent.

The ratio of chlorine to paraffin to be chlorinated thereby can be varied over the range from about 1:3 to 1:10, respectively, on the mole basis. However, it is preferred to operate at a ratio of about 1:5 moles of chlorine to paraffin, respectively, from an economical standpoint because use of very low amounts of chlorine necessitates excessive recycling of the paraffin. After suitably chlorinating the paraffin mixture, the halogenated product is then purged of by-product HCl and unreacted chlorine. Purging can be readily accomplished through the use of an inert gas, such as, for example, nitrogen.

For vapor phase thermal chlorination, temperatures of 230–350° C. are operable. However, more important than temperature is the space velocity and residence time.

In order to avoid uncontrolled combustion type reaction of chlorine and alkane, a linear velocity of at least about 88 feet per second is necessary. At this high velocity a residence time of about .5 to 1 second will give good conversion of reactants to products.

Liquid phase chlorination temperatures that can be used range from about room temperature to about 200° C. With photochemical or other catalysts, lower temperatures can be used and still obtain good reaction rates. It must be remembered that chlorination of an alkane is an exothermic reaction, consequently, when it is desired to conduct the reaction at any particular temperature, the reaction should be initiated at a temperature sufficiently below that ultimately desired in order to compensate for the increase in temperature which will result as a consequence of the heat of reaction. The time for chlorination varies extensively and depends on the ratio of chlorine to paraffin used, temperature, etc. The time necessary to effect the desired degree of chlorination under any particular set of conditions can be readily determined experimentally. The chlorination product is then employed as the alkylatable component in the subsequent alkylation step.

Similarly, the detergent alkylates purified by the present invention can be any detergent alkylates prepared by the alkylation of an aromatic hydrocarbon, such as benzene, homologs of benzene, including toluene, ethyl benzene, xylene, isopropylbenzene, butylbenzene, etc.; cymene and its homologs and naphthalene and its homologs, with olefins containing about 5 to 18 carbon atoms, such as ethylene isobutylene, hexylene, octylene, dodecene, and the like where an aluminum halide such as aluminum chloride or aluminum bromide is employed as the alkylation catalyst. Such a process is set forth in U.S. Patent No. 3,118,956 (1964), which is hereby incorporated in this application.

In the alkylation step an aryl hydrocarbon compound is contacted with the chlorination product or olefin, as the case may be, in the presence of an aluminum halide catalyst, such as aluminum chloride or aluminum bromide. The preferred catalyst is aluminum chloride. Benzene represents the preferred aryl compound for preparing detergent alkylates. However, other aromatic compounds, such as toluene, xylene, naphthalene, and the like, can be used.

The alkylation temperature will vary, depending upon whether the alkylation agent is an alkyl halide or an olefin. When alkyl halides are employed as the alkylation agent, the temperature can be varied over wide limits ranging from about room temperature to 80° C. A preferred temperature range is in the order of from about 40–50°. However, when an olefin is employed as the alkylation agent, the temperature ranges from about 5 to 35° C.

The ratio of aryl compound, specifically benzene, to the amount of alkyl halide or olefin alkylating agent can also be varied over wide limits. For example, such ratios can range from about 1 to 20 moles of the benzene to 1 mole of the alkyl chloride component of the alkylating stock. On the aforesaid basis, a preferred range of benzene to alkyl chloride ranges from about 5:1 to 10:1, respectively.

The amount of alkylating catalyst, specifically aluminum chloride, suitable for effecting alkylation can conveniently be based upon the weight of the alkyl chloride or olefin content of the alkylating stock.

The alkylation reaction can be carried out in a continuous or batchwise manner. In either manner, effective contact time between the catalyzed reactants is in the order of from about 5 to 50 minutes. The precise time needed for effecting alkylation is obviously dependent upon a host of factors, including the amount of catalyst used, ratio of benzene to alkyl chloride or olefin employed, temperature, etc.

The alkylation reaction effluent can be introduced into a separator where the majority of the aluminum halide catalyst sludge is removed. However, after the separation of the catalyst sludge from the crude detergent alkylate, a small amount of the catalyst sludge, generally in the order of about 0.1 to 0.7 weight percent and more often in the range of about 0.1 to 0.3 weight percent, remains suspended in the detergent alkylate. The presence of even this small amount of catalyst sludge, which consists mainly of complexes of the spent aluminum halide catalyst and aromatic hydrocarbon compounds, adversely affects the alkylate product quality in that the suspended sludge causes undesirable color in the sulfonation products of the detergent alkylate. Thus, it is to the removal of the suspended sludge in the detergent alkylate that the present invention is directed.

We have now found that when about 0.01 weight percent of anhydrous ammonia, based on the weight of crude detergent alkylate, was added to the detergent alkylate containing suspended sludge that the anhydrous ammonia coagulated and settled the suspended sludge thereby enabling the same to be readily removed from the detergent alkylate by any suitable means, such as settling, centrifuging, electrostatic precipitation and the like. Further, excessive amounts of anhydrous ammonia may be employed without deteriorating the detergent alkylate. However, we prefer to employ from about 0.01 to 0.2 weight percent anhydrous ammonia, based on the weight of the crude detergent alkylate, in practicing the present invention when the crude detergent alkylate contains about 0.7 weight percent, or less, suspended sludge.

Another advantage of utilizing anhydrous ammonia to coagulate and thus settle the coagulated sludge is that one is not faced with the necessity of removing the coagulated sludge within a relatively short period of time to prevent hydrolysis of the sludge. The anhydrous ammonia does not hydrolyze the sludge, and thus one is not faced with the problem of releasing the organic portion of the catalyst complex into the detergent alkylate.

The anhydrous ammonia employed in the present invention can be in the gaseous or liquid state. However, due to normal processing conditions, gaseous anhydrous ammonia is preferred. This is further borne out by the fact that the crude detergent alkylate is normally maintained at a temperature in the range of about 20 to 90° C., preferably from about 25 to 60° C., during the addition of the gaseous anhydrous ammonia. However, if for any reason it is desirable to maintain the crude detergent alkylate at a sufficiently lower temperature, then one can employ the anhydrous ammonia in a liquid state.

The anhydrous ammonia employed to coagulate and precipitate the suspended sludge present in the detergent alkylate can also be introduced into the detergent alkylate as dissolved anhydrous ammonia in a hydrocarbon carrier. Any suitable hydrocarbon carrier can be employed. However, preferably the hydrocarbon carrier is the same aryl compound, such as benzene, toluene, xylene, naphthalene, and the like, in the alkylation step in the production of the detergent alkylates.

In order to illustrate the invention further, the following example is set forth. However, the example is given primarily for purposes of illustration; and any enumeration of details contained therein shall not be construed as limitations upon the invention except as such are expressed in the appended claims.

EXAMPLE

A sample of crude detergent alkylate reaction product mixture obtained by the aluminum chloride catalyzed alkylation of benzene with partially chlorinated C_{12}–C_{14} n-paraffins and containing about 0.15 weight percent of suspended aluminum chloride catalyst sludge was treated with 0.01 weight percent gaseous anhydrous ammonia, based on the weight of detergent alkylate reaction mixture at about 25° C. Upon the addition of the anhydrous ammonia the suspended sludge coagulated and settled out rapidly leaving a clear, near-white crude detergent al-

kylate. Samples of the crude detergent alkylate were drawn after 1 and 30 hours standing over the settled sludge. U.V. absorbances on a control untreated sample and the treated samples after neutralization and drying were as follows:

	U.V. absorbance at 368μ M	Settling time, hours
Control run	[1] 0.75	
Sample treated with 0.01% anhydrous ammonia	[1] 0.24	1
Do	[1] 0.22	30

[1] Measurements made after neutralizing the detergent alkylate with a 5% sodium hydroxide solution and drying the purified crude detergent alkylate.

The above data readily illustrates that anhydrous ammonia is an excellent means of removing sludge. Further, the data illustrates that the detergent alkylate so treated does not deteriorate with time and thus one is not faced with the problem of quickly separating the coagulated sludge to prevent the sludge from undergoing slow hydrolysis and thus releases sprung oil into the detergent alkylate which would then be difficult and expensive to separate.

The U.V. absorbance of the resulting neutralized detergent alkylates in the above Example is illustrative of the relative measure of the amount of suspended catalyst sludge in each of the samples of the purified detergent alkylate.

Having thus described the invention, we claim:

1. A method for removing suspended aluminum halide-aromatic hydrocarbon sludge from crude detergent alkylate prepared by alkylating aryl hydrocarbons with chloroparaffins, or olefins, in the presence of an aluminum halide catalyst comprising:

(a) introducing a sufficient amount of anhydrous ammonia into said crude detergent alkylate to coagulate and precipitate said sludge; and

(b) separating said detergent alkylate from the coagulated and precipitated sludge and recovering a purified detergent alkylate.

2. The method of claim 1 wherein said suspended sludge is present in an amount in the range of about 0.1 to 0.7 weight percent based on the total weight of the detergent alkylate.

3. The method of claim 1 wherein step (a) is carried out at a temperature within the range of about 20° C. to 95° C.

4. The method of claim 3 wherein said temperature is within the range of about 25° C. to 60° C.

5. The method of claim 1 wherein said aluminum halide catalyst is selected from the group consisting of aluminum chloride and aluminum bromide.

6. The method of claim 4 wherein said anhydrous ammonia is in a gaseous state and is present in the amount within the range of about 0.01 to 0.2 weight percent.

7. The method of claim 6 wherein said anhydrous ammonia is dispersed in an aryl hydrocarbon carrier similar to said aryl hydrocarbon employed in the alkylation step for preparing detergent alkylates.

8. The method of claim 7 wherein said aryl hydrocarbon carrier is benzene.

References Cited

UNITED STATES PATENTS

2,648,594 8/1953 Olson ..... 208—13

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