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PREPARATION OF DETERGENT ALKYLATES

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This invention concerns the preparation of detergent alkylates whose monosulfonate derivatives are biologically soft, water-soluble surfactants. More particularly, the present invention relates to an improved process for alkylating benzene with a partially chlorinated detergent range n-paraffin or mixtures thereof to effect a higher yield of monophenyl alkylate product while concomitantly suppressing the formation of undesirable diphenylalkanes.

For approximately the past two decades, alkylbenzene sulfonates have been extensively used in synthetic detergent compositions. At present, the bulk of the commercial detergent compositions are based on this type of surfactant. The alkylbenzene sulfonate most generally employed in such compositions is dodecylbenzene sulfonate, obtained by alkylating benzene with a tetramer of propylene followed by sulfonating the alkylate and thereupon neutralizing the resultant sulfonic acid derivative. As a water-soluble surfacant for general household cleansing applications, dodecylbenzene sulfonate manifests excellent all-round properties; however it nonetheless possesses a notoriously deficient property, namely, that of being extremely resistant to biodegradation. Considerable investigation, consequently, has been directed of late to the development of surfactants of the alkylbenzene sulfonate variety which can be readily biodegraded.

A recently proposed method for preparing biologically soft alkylbenezene sulfonates involves initially converting a straight-chain paraffin of the so-called detergent range or mixtures thereof into an alkylatable derivative; thereupon benzene is alkylated with said derivative to yield an alkylate whose monosulfonate salt exhibits detersive properties similar to the bioresistant propylene tetramer derived substances. A suitable and perhaps best manner from an economical standpoint for converting the straight-chain paraffin into an alkylatable derivative is to form the monochloride thereof. This can be achieved to a reasonable degree by partially chlorinating the paraffin or mixture of paraffins. In such a procedure, it would be desirable, as indicated to form only monochloroalkanes; however it is not known how to limit the introduction of only one atom into one molecule of the alkane in a chlorination procedure of this type and yet convert a substantial portion of the alkanes present. For example, upon the reaction of only two tenths of an atom of chlorine per mole of alkane present, the resultant chlorination product, that is the alkanes reacted, will be composed of about 90 percent monochloroalkanes and the balance essentially dichloro derivatives. Moreover, as the extent of chlorination is increased, the selectively with respect to formation of monochloroalkanes will decrease. Since the mono-, dichloro-, and unreacted alkanes cannot be readily separated from one another, the total chlorination product must be used in the alkylation step; thus severe processing problems are encountered in the alkylation step if the initial chlorination is limited to the extent whereby essentially only monochloroalkanes are formed.

Originally it was thought that the presence of dichloroalkanes would disadvantageously result in the formation of diphenylalkanes which have no value as surfactant precursors. As a matter of fact, there is at present no known important use for diphenylalkanes; however it was found that a major amount of the dichloride content of a chlorination product when reacted with benzene resulted in the formation of alkyl Tetralins and indanes. Furthermore, it was ascertained that these particular polycyclic alkylates yield sulfonate salts having reasonably good detersive qualities and biodegradability properties.

Another by-product obtained in preparing biologically soft alkylbenzenes in accordance with the general procedure discussed is dialkylbenzenes. Perhaps it is significant to mention here that this by-product is also formed in the process of preparing the alkylbenzenes via the use of propylene tetramers. The dialkylbenzenes obtained in the practice of the instantly considered method for preparing n-alkylbenzenes, however, are very valuable by-products as they can be readily converted into desirable oil-soluble sulfonates, whereas the particular type of dialkylbenzenes resulting from the use of propylene tetramer as the alkylating agent is decidedly refractory in this regard.

In light of the foregoing discussion, it is evident that it would be desirable to ameliorate the effect of inherent features of the described process for the production of biologically soft detergents. These desiderata include the suppression of diphenylalkane formation and maximizing the yield of monophenyl alkylate product when employing an alkylatable component containing a given content of dichloroalkanes. Improvements in these regards, among others, constitute the objectives of this invention.

In accordance with this invention, the aforesaid improvements can be realized by carrying out the alkylation reaction step in the presence of an added amount of a diphenyl derivative of a higher alkane. The added diphenylalkanes for this purpose can most conveniently be supplied by recycling to the alkylation reaction mixture diphenylalkane bottoms obtained in a previous alkylation run. It is appreciated that it has hitherto been known that recycling of a reaction product inherently produced in any given reaction system will tend to suppress the formation of this component under otherwise renewed conditions. The surprising aspect of our finding, however, is that the presence of comparatively small amounts of the recycled component, specifically diphenylalkanes, will substantially completely obviate the formation of additional quantities of this component within the reaction system concerned. Another unexpected attribute of our discovery resides in the fact the presence of added diphenylalkane beneficially increases the yield of monophenyl alkylate product. Before discussing more specifically how our improvement can be carried out and the precise nature of the advantages realized in the practice thereof, it would be desirable first to particularize the process to which our invention is applicable.

In the preparation of biodegradable n-alkylbenzenes, the first step called for is the obtaining of a suitable alkane or mixture of alkanes which ultimately constitutes the alkyl moiety of the alkylate. Suitable among such alkanes are the straight-chain paraffins of C_{10}–C_{16} carbon atom lengths which are abundantly available as components in various virgin petroleum fractions such as, for example, kerosene. Mixtures composed of these alkanes can be readily segregated from kerosene by either the well-known molecular sieve or urea adduction methods. The art is replete on these techniques; consequently no further details concerning same will be given herein.

After suitably segregating a fraction of normal paraffins within the stated detergent range, it is desirable to further fractionate so as to obtain a mixture of normal paraffins wherein the difference in carbon atom length between the slowest and highest molecular weight member present does not exceed four carbon atoms. The reason for this is so that the resultant detergent alkylate can be recovered in a relatively pure state from the alkylation reaction mixture, inasmuch as adjacent higher alkanes boil within the range of the formed alkylates.

After the selected alkane or mixture thereof is obtained, it is then chlorinated. Either conventional liquid or vapor phase chlorination is applicable. The amount of chlorine reacted with the paraffin or mixture thereof can be within the range of from about 0.1 to 0.8 atom per molecule of paraffin present. More preferably, the degree of chlorination of the alkane is kept at less than about 40 mole percent, i.e., 0.4 or less atom of chlorine per molecule of paraffin.

Where liquid phase chlorination is observed, applicable temperatures range from about room temperature to 200° C. The preferred chlorination temperature for such a procedure is in the order of about 100–150° C. With photochemical or other catalysis, lower temperature can be used with the realization of good reaction rates. For vapor phase chlorination, temperatures of 230–370° C. are operable, although it is preferred to use a temperature within the range of 240–260° C.

As mentioned previously, it is not feasible to separate the chloroalkanes from the unreacted alkanes; consequently it is contemplated that the total chlorination product be employed as the alkylatable component in the subsequent alkylation step. In the latter step, a wide range of benzene to chloroparaffin molar ratios can be used, such as, for example, from about 5:1 to 15:1, respectively. More preferably, the molar ratio of benzene to chloroparaffins is from about 5:1 to 10:1, respectively.

While any of the Friedel-Crafts catalysts can be used to facilitate alkylation of benzene with chloroparaffins, aluminum chloride provides the best results when implementing our invention. Applicable amounts of aluminum chloride can range between about 1 and 10 percent, based on the amount of chloroparaffins present in the alkylation reaction mixture. The preferred manner of supplying the aluminum chloride catalyst to the reaction system consists of enriching a catalyst sludge obtained from a previous alkylation run with a sufficient quantity of finely divided metallic aluminum to effect in situ formation of aluminum chloride during the course of the alkylation reaction.

The alkylation reaction can be carried out at a temperature of from about room temperature to 80° C. A preferred temperature range is in the order of from about 60–70° C. Employing a temperature within the preferred range, effective contact time is in the order of about 15–60 minutes. The precise time needed for conducting the alkylation reaction is obviously dependent upon a host of factors, including amount of catalyst used, ratio of benzene to alkyl chloride employed, temperature, etc.

Following the alkylation reaction, the effluent is introduced into a separator where the spent catalyst and sludge products are removed. The resulting effluent is then desirably treated to remove acidic components. This can be readily accomplished by successively treating with sulfuric acid and caustic solution washings. After preliminarily treating the alkylation reaction effluent in the manner indicated, it is then fractionally distilled. Successive fractions of recycle benzene; recycle normal paraffins; alkylate products, including alkylbenzenes and other polycyclic alkylates falling within the alkylbenzene boiling range; and a bottoms fractions composed of diphenylalkanes and dialkylbenzenes are recovered in this manner.

The diphenylalkanes which are recycled to an alkylation reaction in accordance with the preferred embodiment of this invention can be obtained by further fractionating the bottoms fraction mentioned directly hereinabove. The diphenylalkanes present in the bottoms fraction can be easily recovered therefrom, since they boil at a substantially lower temperature than the dialkylbenzene constituent. The amount of diphenylalkanes that can be added to the alkylation reaction mixture in order to effectively suppress the formation of further diphenylalkanes during the alkylation reaction ranges between about 2 and 15 percent, based upon the weight of

chloroparaffins initially present in the alkylation reaction mixture. More preferably, the amount of added diphenylalkanes is between about 5 and 10 percent on the aforesaid basis, particularly where the alkylatable component is a chlorination product containing between about 0.1 and 0.4 atom of chlorine per molecule of normal paraffin.

In order to illustrate further this invention, the following specific example is set forth in which all parts are parts by weight unless otherwise specified. As indicated, this example is given primarily for the purpose of illustration; and accordingly, any enumeration of details contained herein is not to be interpreted as a limitation on the invention except as indicated in the appended claims.

EXAMPLE

In this example, an alkylatable stock was prepared by chlorinating n-dodecane in liquid phase at a temperature between 70–110° C. for a period of twenty minutes. The chlorine was slowly introduced at a temperature of 70° C. whereupon the heat of reaction caused the chlorinated mass to rise to about 110° C. upon complete addition of the chlorine. The amount of chlorine reacted in this manner was 4.5 percent, based upon the weight of dodecane. This represented a degree of chlorination of 22 mole percent. Following chlorination, the product was purged with an inert gas in order to remove traces of unreacted chlorine and HCl formed during the course of reaction.

Three alkylation runs were then conducted, employing as the alkylatable stock the chlorination product described above. In each of these runs a mole ratio of benzene to chlorododecane of 10:1 was employed. The respective runs were catalyzed with aluminum chloride in the amount of 4 weight percent, based on chlorododecane content of the chlorination product. The alkylation conditions observed in each instance consisted of stirring the reaction mixture for a period of 90 minutes while maintaining a temperature of 65° C. throughout the reaction. Following alkylation, the crude alkylate of each run was settled to remove sludge and thereupon washed with 6 percent of concentrated sulfuric acid, followed by a 20 volume percent washing with 5 percent sodium hydroxide. Following the aforedescribed preliminary purification procedure, the effluent was then fractionated. The unreaction benzene was first distilled at atmospheric pressure. Next the unreacted dodecane fraction was recovered, following which a detergent alkylate fraction boiling within the range of between 165 and 205° C. at 20 mm. Hg was recovered, thus leaving a bottoms fraction essentially composed of diphenylalkanes and dialkylbenzenes.

The yields of the various reaction products obtained in the three runs of this example in terms of mole percent based on chloro-n-dodecane consumed are set forth in the following Table I. It is to be noted that run No. 1 was a standard run, whereas runs No. 2 and No. 3 were conducted in the presence of the various indicated quantities of recycled diphenylalkane, based on the weight of chlorododecane present in the alkylation reaction mixture.

Table I

Run No.	1	2	3
Percent Added (Recycle) Diphenylalkane	0	4	8
Product Yield:[1]			
Monophenyl detergent alkylate [2]	83.0	84.4	85.9
Diphenylalkanes (net)	2.4	0.8	0.03
Dialkylbenzenes	2.5	3.1	2.5

[1] Mole percent based on n-paraffins consumed.
[2] A mixture of a major amount of n-dodecylbenzene and a minor amount of polycyclic alkylate consisting mainly of alkyl substituted 1,2,3,4-tetrahydronaphthalenes of about 240 M.W.

What is claimed is:

1. An improved process for preparing detergent alkylates which comprises reacting a chlorination product of from 0.1–0.8 atom of chlorine per mole of an alkane selected from the group consisting of C_{10}–C_{16} normal

paraffins and mixtures thereof with a substantial stoichiometric excess of benzene in the presence of $AlCl_3$ catalyst and an added amount of a diphenyl substituted higher alkane.

2. A process in accordance with claim 1 wherein said diphenyl substituted higher alkane is recycled diphenylalkane.

3. A process in accordance with claim 2 wherein the mole ratio of benzene to chloroparaffin content of said chlorination product is between about 5 and 15.

4. A process in accordance with claim 3 wherein the amount of recycled diphenylalkane is from about 2–15 percent based on the weight of the chloroparaffin content of said chlorination product.

5. An improved process for preparing detergent alkylates which comprises reacting at a temperature between about 45° and 75° C. a chlorination product of from 0.1–0.4 atom of chlorine per mol of an alkane selected from the group consisting of C_{10}–C_{16} normal paraffins and mixtures thereof with a substantial stoichiometric excess of benzene in the presence of $AlCl_3$ catalyst and an added amount of a diphenyl substituted higher alkane.

6. A process in accordance with claim 5 wherein said diphenyl substituted higher alkane is recycled diphenylalkane.

7. A process in accordance with claim 6 wherein the mole ratio of benzene to chloroparaffin content of said chlorination product is between about 5 and 10.

8. A process in accordance with claim 7 wherein the amount of recycled diphenylalkane is from about 2–10 percent based on the weight of the chloroparaffin content of said chlorination product.

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