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DETERGENT ALKYLATE AND THE SULFONATE DERIVATIVE

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This invention relates to improved detergent alkylates and to the sulfonate derivatives thereof amenable to complete biodegradation. More particularly, the invention pertains to detergent compositions comprising an alkali metal salt of a sulfonated alkaryl, and especially such salts of alkylated benzene products, wherein the alkyl substituents are derived from specified mixtures of substantially straight-chain paraffins having carbon atoms lengths ranging from 8 to 18. In narrower aspects, the present invention relates to alkylated benzene products obtained through the use of an alkylating agent consisting essentially of a mixture of monochloro isomers of petroleum derived n-paraffinic fractions whose alkane components range in carbon atoms length from n to $n+4$, where n is an integer of from 10 to 12, inclusive, and wherein each paraffin of the stated range is present to the extent of at least about 10 percent. The invention additionally concerns an improved method for preparing the detergent alkylates generally described above, which method features a novel modification of the step for chlorinating paraffinic mixtures and the subsequent use of the chlorinated mixtures in alkylating benzene.

Throughout about the past two decades, synthetic detergents have been increasingly displacing the traditional soaps in domestic cleaning applications in the United States. At the present time, it is estimated that about 75 percent of the combined sales of household cleansing surfactants are of the synthetic detergent type.

The household synthetic detergents presently used embrace a number of different products; however, the bulk of these detergents are of the alkyl benzene sulfonate type generally referred to as ABS. This type of detergent is made by alkylating benzene with a comparatively highly branched C_{12} and/or C_{15} olefin and then sulfonating the resultant alkylation product. While these materials are excellent cleansing agents, their use has posed a considerable problem. The specific problem involved is that the ABS detergents are not readily removed or decomposed in sewage treatment plants. These detergents will remain throughout the treatment step as such without being significantly decomposed by the bacteria present. This resistance to decomposition is not due to the lack of suitable strains of bacterial within the sewage effluent nor to the length of time that can be allotted for treatment, but is fundamentally due to the chemical structure of the surfactant which resolutely resists metabolic attack by any kind of bacteria. One of the adverse effects of the presence of ABS in sewage effluents is that voluminous foams are caused to be formed which result in difficult and hazardous working conditions at the disposal plants. Also, the persistent foam formed constitutes a health hazard since the bacteria contained in the foam is often as high as 20 times that contained within the liquid phase.

In addition to causing foam problems in the sewage plants, the presence of non-decomposable ABS in sewage effluents, including septic tank effluents, has already resulted in considerable contamination of the available drinking water supply in populous areas. While it is generally believed that the ABS-type surfactant is not

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toxic to man, a currently considered proposal for revising the Public Health Service Drinking Water Standards to include a limit on the amount of ABS in potable water most significantly foreshadows the necessity for detergent manufacturers to produce a soft type of detergent, that is, one which is completely and readily biodegraded.

It is accordingly the primary object of this invention to provide detergent alkylate compositions, which upon sulfonation give effective detergent agents which at the same time are substantially completely biodegradable.

It is also an object of this invention to provide an improved process for the preparation of biodegradable detergents wherein the organo portion consists of an n-alkyl benzene.

These and other objects of this invention will be better understood by those skilled in the art upon consideration of the detailed discussion and specific examples set forth hereinbelow.

Bacteriologists have noted that the branched configuration of the alkyl substituents of the conventional ABS surfactants is such preventing satisfactory bacteriological assimilation of these compounds, that is, degradation beyond the point where the compounds significantly lose their surface active properties. It has also been concurrently noted that straight-chain substituted aryls having such substituents in the detergent promoting range are subject to complete biodegradation.

The concept of the present invention is in full accord with this knowledge, although we additionally have observed that certain branched configuration of the alkyl substituent can be tolerated. As indicated in the summary hereinabove, the alkyl substituents of our detergent alkylates are derived from a mixture of straight-chain paraffins and therefore correspond in general structure to these mixtures. Our choice of such mixtures was primarily dictated in the attempted utilization of a plentiful and economical source of the higher molecular weight straight-chain paraffins, namely, normal paraffin-containing petroleum stocks. Accordingly, the process of the present invention provides an economical way for producing completely biodegradable detergent compositions. These soft detergent compositions additionally possess excellent physical properties from the standpoint of color and odor. Moreover, these compositions evidence improved detergent characteristics.

The detergent compositions prepared in accordance with this invention are relatively complex in nature. From the standpoint of acquiring an optimum balance of physical properties, the mixture is to include alkylate entities consisting essentially of those having alkyl substituents ranging in carbon atom length from 10 to 16. However, in order to obtain the maximum advantages of this invention, there should be a difference of only 4 in the carbon atom content between the lowest alkyl substituent and the highest alkyl substituent present in the detergent alkylate composition. Also, in order to realize the maximum advantages of the detergent alkylates of this type, the alkylate mixture containing the range of alkyl substituents as specified above should include each member in the amount of at least about 10 percent. In other words, the detergent alkylate compositions particularly contemplated herein include those mixtures of alkylate entities wherein the alkyl radicals associated with the aryl molecule range in carbon length from C_n to C_{n+4} where n represents an integer from 10 to 12, inclusive, and where each alkyl radical in the range stated is present to the extent of at least about 10 percent on a weight basis.

Additionally contemplated herein are those compositions which represent blends of the mixtures described directly hereinabove. For example, a blend can be made

of C_8 - C_{12} and C_{14} - C_{18} products which have been separately prepared by the process taught herein.

The alkyl substituents present in our detergent alkylate compositions are, for the most part, attached to the aryl nucleus through a secondary carbon atom of the alkyl group. It has proved to be largely impractical to characterize the isomeric constitution of the detergent alkylate mixtures prepared in the practice of this invention. This will be fully understood upon consideration of a specific example given hereinbelow which reveals the complexity of the isomeric composition when, for example, a given normal paraffin is used in accordance with our process.

The art has heretofore taught the production of alkyl benzene sulfonates wherein the alkyl substituents consist of a major amount of straight-chain radicals. This teaching is exemplified in a number of patents which deal with the preparation of an alkylating stock from kerosene, usually a chlorinated product of such distillate, for alkylating benzene. It was originally thought that the kerosene distillate fractions used contained substantially all straight-chain paraffins. However, this was subsequently learned not to be the case. The sulfonate detergents prepared using these kerosene derivatives have never been especially successful in a commercial sense. While such detergents inherently possessed biodegradable properties, somewhat better than ABS from propylene tetramer, the reasons they could not compete with the ABS types turned on different considerations. The prior products derived from kerosene in the manner indicated were generally obtained in relatively low yield, possessed dark colors and invariably had an objectionable odor. While our detergent compositions are similar in a number of respects to the above prior art compositions, they nevertheless represent vast improvement thereover.

More recently, it has been taught that an acceptable type of biodegradable detergent alkylate can be made by growing tribenzylaluminum in the presence of ethylene. However, there are several objections to a process of this type insofar as the starting materials used in the process are difficult to obtain and consequently expensive; and the reaction itself is tedious to carry out and certainly cannot compete economically with a reaction such as the alkylation reaction practiced in the preparation of detergent alkylates of our invention.

Another development in this art is that of cracking petroleum waxes to produce mixtures rich in straight-chain olefins and the use of such cracked products to alkylate benzene. However, the prominent disadvantage of detergents prepared in this manner is that they are not completely biodegraded.

As indicated above, the detergent compositions of this invention can be readily obtained through well-known procedures, although the practice of this invention contemplates several modifications of these generally known procedures. This aspect will be more fully explained hereinbelow in connection with a detailed discussion of the overall process by which our compositions can be obtained. Generally stated, the improved process for the preparation of the compositions of this invention consists firstly of segregating or obtaining a fraction of normal paraffins from a suitable petroleum source. This fraction, however, is to correspond in alkane content according to that described hereinabove. Particularly suitable sources of normal paraffins are the kerosene cuts obtained in the conventional crude topping units.

We prefer two alternative methods for effecting the necessary segregation of the paraffinic mixtures from the source thereof selected: one being the urea adduction method and the other selective fractionation through the use of molecular sieves. After obtaining the desired fraction of paraffins, the second step of the process of this invention involves halogenating, and more specifically chlorinating, the said fraction to a limited but definite extent. After suitably chlorinating the paraffinic mixture,

same is then used to alkylate a selected type of aryl compound in the presence of an alkylating catalyst. After proper alkylation, the detergent alkylate is recovered and then converted into an active detergent by means of sulfonation and then formation of the desired salt thereof. The latter steps involving purification of the alkylate, sulfonation and salt formation are well known in the art and consequently form no part of the present invention. Before setting forth specific examples illustrating the practice of this invention, a detailed discussion of each of the aforementioned process steps will be set forth.

SEGREGATION OF ALKYLATE PRECURSORS

In order to secure the desired fraction of paraffins for the preparation of the instant compositions, as indicated, any suitable petroleum fraction relatively high in paraffin content can be used. A naphtha fraction corresponding to a kerosene cut represents an excellent source of straight-chain paraffins having the necessary molecular weight distribution for use in preparing our detergent compositions.

The kerosene or any other distillate relatively rich in n-paraffin content and at same time substantially devoid of olefins, can be suitably fractionated either through the use of molecular sieves or by the urea adduction method. The economics of the two fractionation processes are substantially the same; consequently the selection of either is primarily one of choice. However, it can be stated though that the molecular sieve method tends to give a normal paraffin fraction in which the concentration of the lower alkanes making up the fraction is more prominent. Conversely, in the use of the urea adduction method, there is obtained a fraction wherein the concentration of the higher alkanes is greater than that of the lower members present therein.

In the use of the molecular sieve method for the separation of normal paraffins from a hydrocarbon mixture containing the same, a suitable zeolitic sieve is contacted with the hydrocarbon feedstock at a temperature within the range from about 200° F. to about 500° F. and at a pressure within the range of about 200 to 1000 p.s.i. The zeolitic sieve is continuously contacted with the hydrocarbon feed until the effluent leaving the absorption unit begins to evidence an increased amount of normal paraffin content. It might be mentioned that the time of contact between the hydrocarbon feed and the absorption medium is that time sufficient to permit absorption of a substantial amount of normal paraffins present in the charge and is dependent on the nature of the feedstock, temperature employed, etc. This, however, can be readily and conveniently checked by gas liquid partition chromatography (GLPC) analysis. After the medium, specifically the zeolitic sieve, is saturated with sorbed hydrocarbons, said hydrocarbons are then removed and recovered therefrom. A number of methods can be used for desorption. A common, although not preferred, procedure for removal is to heat the saturated sieve under vacuum. More preferably, a desorbing or eluting agent is used. The desorbing agent can be either a gas or a liquid. When employing a gaseous desorption agent, it is generally desirable to operate the elution process under a vacuum. A particularly suitable method of desorbing resides in the use of a normal liquid paraffin having a molecular weight substantially lower than that of the lowest constituent of the sorbed fraction. Applicable eluting agents of this type include the normal C_3 - C_7 alkanes. In recovering the preferred fractions contemplated for use in the practice of this invention, heptane represents a particularly efficient and economical desorbing agent. When using heptane as a desorbing agent, we prefer to carry out the molecular sieve operation at a temperature of about 500° F., and then desorb with liquid heptane at approximately the same temperature. In an isothermal operation of this type, the desorbing agent, specifically heptane, exists near its critical temperature; and accordingly, the desorbing agent can be readily removed from the segre-

gated fraction with consequent savings in utilities. Also, other closely related normal paraffin desorbing agents can be similarly utilized in an isothermal sorption-desorption process.

Any number of suitable solid sorbent materials may be used for sieving purposes. Among the solid sorbents which can be used there are the aluminosilicates, such as calcium aluminosilicate, magnesium aluminosilicate, barium aluminosilicate, sodium aluminosilicate, potassium aluminosilicate, etc. The preferred sieving materials are the crystalline calcium aluminosilicates. Many of the above enumerated types, particularly the calcium aluminosilicates, are commercially available. The zeolitic sieve should desirably have pore diameters of about 5 angstrom units, which is slightly larger than the critical diameter of the straight-chain paraffin molecules but somewhat smaller than the diameter of isoparaffins, cycloparaffins and aromatics.

The well known urea adduction method provides an alternative method to that of the molecular sieve fractionation process discussed above for selectively separating normal paraffins from hydrocarbon mixtures rich in these paraffins. The principle of urea adduction is that when urea is crystallized in the presence of a mixture of hydrocarbons containing straight-chain components, the linear alkanes will be selectively absorbed by formation of a reasonably stable crystalline complex with urea which in turn is separable by filtration. In forming a complex, the urea molecules wrap around the straight-chain molecules in a hexagonal spiral and these spirals form channels sufficiently large enough to accommodate substantially straight-chain molecules but not highly branched chain or cyclic molecules.

The quantity of urea required for the formation of an adduct with a straight-chain hydrocarbon is about 3.5 parts of urea per part of the hydrocarbon desired to be adducted. Larger and even somewhat smaller amounts of the urea based on the hydrocarbon can be used but it is preferable to employ near the numerical ratio stated above. The use of an activator in conjunction with urea is necessary, at least to the extent of several percent based on the weight of urea present. Examples of some well known activators include methanol, methyl ethyl ketone, acetone and analogous solvents. The preferred activator is methanol. The amount of activator employed is preferably considerably larger than the above-mentioned quantity needed for "activation" purposes. Desirably, sufficient activator should be present so as to maintain any free or uncomplexed urea existing in the adduction mixture soluble at a temperature as low as about 25° C.

The procedure for effecting adduction by the urea method consists of adding the hydrocarbon feedstock to the solution of urea and activator while constantly stirring the mixture. The time in which the complexes are formed is relatively short, that is, usually one hour and generally not in excess of about two hours. After complexing has occurred, the mixture is filtered and then washed with a suitable hydrocarbon solvent, such as for example, butane, pentane, hexane, etc. The washed crystals can then be decomposed in hot water to yield the adducted normal paraffins. It is preferred to carry out the decomposition of the adduct at a temperature in the range of about 80–90° C. Operating at an elevated temperature of this magnitude permits flashing off of any residual hydrocarbon solvent contained by the complex crystals. It is pertinent to mention here that the feedstock can be subjected to a number of adduction procedures. Multistage adduction may in some cases be more efficient than a one-stage process.

CHLORINATION

After a suitable normal paraffin mixture is obtained either by the molecular sieve method or the urea adduction method discussed directly hereinabove, the mixture is

then partially chlorinated so as to produce largely monochlorinated normal paraffins.

Either conventional liquid or vapor phase chlorination of the paraffins can be used. Regardless of which of these particular chlorination techniques is employed, it is necessary that the degree of chlorination not exceed about 35 mole percent in order to attain satisfactory selectivity of mono-chlorinated derivatives. The extent of chlorination should, however, exceed about 10 percent. The preferred degree of chlorination is in the order of about 20 mole percent which provides a product having a selectivity of above about 90 percent mono-chlorinated product with less than 10 percent of di, tri, and poly-chlorinated alkanes.

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 the higher ratios of chlorine to paraffin within the range thereof stated from economical standpoint; for use of very low amounts of chlorine necessitates excessive recycling of the paraffin. After suitably chlorinating the paraffin mixture, the extent of which can be readily determined by GLPC analysis of the hydrocarbon undergoing chlorination, 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. It is preferred to use a temperature of 240–260° C. 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. A preferred thermal chlorination temperature is in the order of about 100–150° C. With photochemical or other catalysis 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 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.

ALKYLATION

The alkylation step contemplated herein essentially corresponds to the prior art method of alkylating benzene to produce ABS detergents except for the presence of large amounts of n-paraffins in the alkylation reaction. Accordingly, it is contemplated that the alkylation step be carried out in the presence of a Friedel-Crafts catalyst. The preferred catalyst is aluminum chloride. The alkylating stock is the chlorination product described in the preceding section, and consequently, as such, contains a high percentage of unhalogenated or pure hydrocarbons. In using such a mixture as an alkylating agent, it was found, contrary to expectations, that the excess normal paraffins were not isomerized during the alkylation of the aryl compound. As mentioned, it is preferred to use a strong alkylating catalyst such as aluminum chloride which is a known catalyst for the isomerizing normal paraffins to isoparaffins. Consequently, this unexpected finding makes the instant process commercially feasible insofar as the normal paraffins present in the alkylation stock can be recovered and reused to prepare additional chlorinated mixtures for use as the alkylating agent. Moreover, it has

also been determined that such recycled normal paraffins from the alkylating step has essentially the same composition as the normal paraffins used in the feed from whence the alkylating stock was derived.

While benzene represents the preferred aryl compound for preparing detergent alkylates, other aromatic compounds such as toluene, xylene, naphthalene, etc., can be used.

The alkylation 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° C.

The ratio of aryl compound, specifically benzene, to the amount of alkyl halide alkylating agent can also be varied over wide limits. For example, such ratios can range from about 1 to 20 parts by weight of the benzene to 1 part 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 content of the alkylating stock. On this basis, from about 1 to 10 percent of aluminum chloride can be used. The use of the aluminum chloride sludge for recycle is advantageous to the process. By recycling the sludge less fresh AlCl_3 needs to be added to the reaction. This amounts to a considerable saving. In addition better product yields are obtained since less of the reactants and product are complexed with the catalyst and lost. Recycle sludge can amount to from 10 to 100 weight percent or more of the chlorinated alkane. Preferred amounts are about 50 to 100 weight percent of the alkyl chlorides.

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 15 to 60 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 employed, temperature, etc.

The alkylation reaction effluent can be introduced into a separator where the catalyst sludge is removed. The resulting substantially catalyst-free effluent is then desirably treated to remove acidic components. This can be readily accomplished by treating with sulfuric acid and washing with a caustic solution, or percolating the effluent through a bed of bauxite.

After preliminarily treating the alkylate reaction effluent in the manner indicated, it is then subjected to fractional distillation. Successive fractions of recycle benzene, recycle n-paraffin, alkylbenzene product, and diphenyl-alkane bottoms are thereby recovered in this manner.

The sulfonation of the detergent alkylate prepared generally in accordance with the above can be carried out by any one of a number of conventional methods using as the sulfonating agent either oleum, SO_3 , mixtures of SO_3 and SO_2 or chlorosulfonic acid. Details with respect to a suitable method for effecting sulfonation and preparing the alkali metal salts thereof will be set forth in one of the specific examples to follow.

In order to illustrate further the details of the process of this invention, and the nature of the compositions obtained in the practice thereof, the following specific examples are given. These examples are presented primarily for the purpose of illustration and any enumeration or details contained therein are not to be interpreted as a limitation on the case except as indicated in the appended claims. All parts referred to in these examples are parts by weight unless otherwise indicated.

Example I

This example illustrates the use of the urea adduction method to segregate from a kerosene fraction normal paraffins for use in preparing the detergent compositions of this invention.

The kerosene used in this example was a distillate cut from a crude topping tower containing approximately 30 percent by weight of iso and normal paraffins and exhibiting the following distillation characteristics:

	° F.
I.B.P. -----	320
50 percent -----	389
E.P. -----	469

Into a suitable mixing vessel equipped with a stirrer were charged 3430 parts urea and 7000 parts methanol. With stirring, the mixture was heated to about 65° C. whereupon 3000 parts of the above-described kerosene fraction was gradually added to the methanol solution while maintaining the temperature of the contents of the vessel at between about 60–65° C. Upon addition of the kerosene, the mixture was allowed to cool to 25° C. with constant stirring. In this cooling cycle (90 minutes) all of the urea-adducted paraffin complex precipitated from solution. The complex was filtered and washed thoroughly with n-pentane. The washed complex was added to a body of hot water maintained at 85° C. in order to effect decomposition thereof. The urea solution was then decanted. The urea can be recovered therefrom for further use in a similar adduction step. The composition of the normal n-paraffins recovered from the above-described adduction process was as follows:

n-Paraffins:	Weight percent
C_9 -----	0.8
C_{10} -----	4.0
C_{11} -----	9.5
C_{12} -----	17.2
C_{13} -----	22.6
C_{14} -----	24.2
C_{15} -----	14.5
C_{16} -----	2.8
Slightly branched C_{11} – C_{15} -----	3.5

Example II

The n-paraffin fraction obtained by the urea adduction process exemplified in Example I was chlorinated in the following manner.

Into a suitable reaction vessel equipped with a stirrer and thermometer were charged 900 parts (5 mole equivalents) of the n-paraffins at 25° C. The contents of the vessel were exposed to the rays of a U.V. lamp. The paraffins were stirred vigorously and at the same time chlorine gas was passed therethrough by means of a sparger at a rate of about 14 parts per hour.

During the passage of the chlorine gas in the initial stage (about 15 minutes) there was no perceptible rise in temperature; however, the paraffins had changed in color from water-white to yellow. After the initial or induction period, the temperature quickly rose from 25° to 36° C. and the color of the solution changed to a lighter shade of yellow. At this point there was a copious evolution of hydrochloric gas. Chlorine gas was continuously passed at the rate indicated for approximately two hours, whereupon the partially chlorinated mixture of normal paraffins was observed to be slightly yellow. The chlorinated mixture was then purged with nitrogen gas for about two hours to remove all traces of hydrochloric acid and unreacted chlorine.

Chemical analysis of the chlorinated mixture indicated 4.77 weight percent chlorine in the total chlorinated product. By statistical distribution, the conversion of n-paraffins to chloro-paraffins was 22.3 mole percent. The selectivity to mono-chlorinated product was ascertained to be 90 percent.

Example III

This example primarily illustrates the alkylation step for preparing the detergent alkylates in accordance with the process of this invention.

Into a suitable reaction vessel equipped with a stirrer and thermometer were charged 850 parts of benzene (10.9 mole equivalents) and 13.1 parts of AlCl_3 . The chlorinated product of Example II in the amount of 937 parts was gradually added to the charged benzene and catalyst mixture in about one hour, during which time of addition the temperature was maintained at 25°–27° C. The weight of the chlorinated n-paraffins present in the charged product was 238 parts. Accordingly, 1.1 mole equivalents of chlorinated material was present in the alkylation reaction mixture. The amount of catalyst was 5.5 percent based on the weight of the chlorinated alkanes present. During the addition of the chlorinated product, HCl gas was continuously evolved and collected. After complete addition of the chlorinated product, the temperature was raised to 45° C. whereupon nitrogen gas was blown through the reaction mixture, same being poststirred for about 35 minutes. Purging with nitrogen gas was continued until about 89.7 percent of the chlorinated material was accounted for as HCl. The alkylate was allowed to cool to room temperature and permitted to stand until the sludge content thereof had completely settled. The alkylate was then separated from the sludge and then was washed with sulfuric acid and base.

The washed alkylate fraction was then distilled to yield the following cuts:

Benzene ----- Up to 130° C. at atmospheric pressure.
Cut No. 1 ----- Up to 155° C. at 20 mm. Hg.
Cut No. 2 ----- 153–225° C. at 20 mm. Hg.

The yield of normal paraffins (Cut No. 1) was 91.8 mole percent of theoretical. Yield of alkylate was 64.5 mole percent of theoretical.

The recovered detergent alkylate was sulfonated in the following manner.

On a basis of 62.5 parts of the alkylate were added 78 parts of 20 percent oleum at a constant rate so that the temperature of the sulfonation mixture did not exceed 25° C. Cooling is effected by maintaining an ice bath about the sulfonation mixture. After complete addition of the oleum, the sulfonation mixture was then raised to a temperature of 38° C. at which temperature the mass was held for about one hour. Thereafter, sufficient quantity of ice was added to the sulfonation mass so as to cool same to 30° C. The sulfonation reaction mixture was decanted from the spent sulfuric acid and the sulfonated alkyl benzene was then slowly neutralized with a dilute solution of caustic.

Example IV

This example primarily describes a modification of the alkylation procedure used in Example III whereby improved yield of alkylate is obtained.

A fraction of C_{11} – C_{15} normal paraffins was chlorinated, employing substantially the identical procedure described in Example II thereby effecting about 25 mole percent conversion of the normal paraffins to chloro-paraffins. The selectivity to mono-chlorinated product was 85.5 percent. The composition of the fraction employed will be listed hereinbelow in comparison with the analysis obtained for the paraffins recovered after alkylation.

Benzene was alkylated with the above-described chlorination product following substantially the reaction conditions shown in Example III. The mole ratio of benzene to alkyl chlorides present in the halogenation product was 9.4. The weight of aluminum chloride catalyst, based on the alkyl chlorides present in the halogenation product, was 1.4 percent. In addition to this catalyst there was added to the alkylation reaction mixture 61.3 parts of the sludge recovered from the alkylation reaction of Example III, said percent based on the weight

of alkyl chlorides present in the alkylation reaction mixture.

Following the alkylation reaction, the product thereof was purified in the manner shown in Example III and then distilled. The unreacted normal paraffins were recovered almost quantitatively by distilling between 95–167° C. at 20 mm. Hg. The comparative analysis of the recovered paraffins and the original paraffin fraction is as follows.

	n-Paraffins Before Alkylation, Wt. Percent	n-Paraffins After Alkylation, Wt. Percent
C_{11} -----	5.10	5.41
C_{12} -----	23.09	25.88
C_{13} -----	24.24	26.53
C_{14} -----	20.98	18.89
C_{15} -----	20.59	18.89
(Unidentified)-----	5.99	4.71

The alkylate was recovered by distilling between 168–232° C. at 20 mm. Hg. The yield of alkylate was 89.3 mole percent. The alkylate was colorless and used as such for sulfonation. The color of the sulfonate so prepared was excellent and had no undesirable odor.

Example V

This example primarily serves to illustrate the complex chemical constitution of detergent compositions prepared in accordance with the instant invention. More specifically, in this example a pure grade of dodecane was subjected to chlorination in accordance with the process of the invention, whereupon the chlorination product was used to alkylate benzene. The detergent alkylates so prepared were then structurally characterized.

Into a suitable reaction vessel equipped with a thermometer and stirrer were charged 2000 parts of n-dodecane. The charged alkane was exposed to a suitable source of U.V. light consisting of two U.V. lamps and one mercury arc lamp. With the charged material at room temperature, chlorine gas was passed therethrough by means of a sparger at a rate of about 120 parts per hour.

After an induction period of 10 minutes, the temperature rose to 90° C. Chlorine gas was continuously introduced at the above indicated rate for approximately 100 minutes, after which time the chlorine flow was stopped and thereupon nitrogen blown through the chlorinated mixture in order to expel the presence of hydrochloric gas and unreacted chlorine in the mixture.

Analysis of the chlorinated mixture showed that 4.34 weight percent of chlorine was combined in the product. By statistical distribution, the conversion of n-paraffins to chloro-paraffins was 19.9 mole percent. The selectivity to mono-chlorinated product was 90.5 percent.

Benzene was alkylated with the dodecyl chlorides-dodecane product described above in the same general manner employed in Example III.

The mole ratio of benzene/chlorinated product was 10:1. The amount of catalyst (AlCl_3) was 7.8 percent based on the weight of the dodecyl chloride content of the chlorinated product. The HCl formed during the alkylation reaction was suitably collected. Following the period of purging with nitrogen, the total weight of HCl collected equalled 84.5 percent of theory. The alkylate mixture was allowed to settle for a period of about 12 hours after which time the sludge was separated therefrom.

The alkylate mixture rid of sludge was then stirred with 100 parts of concentrated sulfuric acid for 20 minutes and allowed to settle for 20 minutes. The acid was drained and the mixture stirred with a solution consisting of 400 parts of 5 percent aqueous caustic solution and 100 parts of ethanol for 20 minutes. After permitting the mixture to stand for about 30 minutes, the total mixture consisting of benzene, dodecane and alkylated

dodecane was then distilled at atmospheric pressure followed by further distillation at reduced pressures. The benzene was removed at atmospheric pressure at a vapor temperature of 130° C. and pot temperature of 221° C. The amount of benzene recovered was 868 parts. The dodecane content of the mixture was then recovered at a vapor temperature of 222° C. and a pot temperature of 270° C. at atmospheric pressure. The weight of dodecane recovered amounted to 719 parts. The residue fraction was then distilled to yield the following cuts:

Cut No. 1—44.8 parts (up to 164° C.) dodecane
Cut No. 2—203 parts (165–205° C.) dodecylbenzene product

Bottoms—20.9 parts

Cut No. 2 on Apezon column at 274° C. indicated the following isomer distribution:

5 and 6 phenyl dodecane isomers	35.52
4 phenyl dodecane	9.37
3 phenyl dodecane	17.72
2 phenyl dodecane	29.77
1 phenyl dodecane	4.40
x isomer	3.21
	99.99

The above data show that a relatively small amount of primary alkyl linkages are contained in detergent alkylate compositions prepared as taught herein. Furthermore, these data serve to illustrate the complex isomeric mixtures represented by the compositions of this invention.

Example VI

In this example the detergency and dishwashing foam characteristics of the detergent compositions prepared in accordance with Examples III and V were compared with that of a conventional ABS detergent consisting of dodecylbenzene sulfonate prepared by alkylating benzene with a branched-chained C₁₂ olefin derived by polymerizing propylene.

Detergency was determined on the Tergotometer using Testfabrics soiled cotton. Washing temperature was 100–120° F. and water hardness at 50 and 250–300 p.p.m. The various sulfonates were combined in a heavy duty formulation consisting of 20 percent sulfonate, 40 percent sodium tripolyphosphate, 5–10 percent sodium silicate and 28–38 percent sodium sulfate. The percent soil removed is calculated in the difference in reflectance before and after washing for 10 minutes.

The dishwashing foam stability test consists of washing plates soiled with a greasy type soil in detergent solution. The number of plates which can be washed before the detergent solution becomes ineffective is measured. The destruction of the foam is used as the end point.

The results observed are tabulated in the following Table I:

TABLE I.—EVALUATION OF BIODEGRADABLE SULFONATES

	Detergency, Percent Soil Removed		Dishwashing Foam Stability	
	50 p.p.m.	250 p.p.m.	.045 Percent Active, No Salt, 100 p.p.m. Hardness (Average)	.025 Percent Active, 650 p.p.m. Salt, 100 p.p.m. Hardness (Average)
n-Alkylbenzene Sulfonate (Example III)	32	30	11	20
Dodecylbenzene Sulfonate (Example V)	29	30	8	16
Dodecylbenzene Sulfonate (Commercial ABS from Propylene Tetramer)	26	25	8	10

Example VII

This example illustrates the principal test method by which the n-alkylbenzene sulfonate of Example III was compared with a commercial grade of dodecylbenzene sulfonate (Table I) for determination of biodegradable characteristics. The bacteria used in this test was a laboratory culture of *Escherichia coli*. This particular

culture was observed to be stable in its ability to decompose sulfonates, and the rate of decomposition induced thereby was found to be representative of other cultures obtained from soil, activated sludge sewage plants and rivers. Both of the sulfonates tested were used at 30 mg./l. concentrations calculated on an active basis. The medium in which these substrates were exposed to the microorganism consisted of the following ingredients:

10	Ammonium chloride	g--	3.0
	Dipotassium phosphate	g--	1.0
	Magnesium sulfate	g--	0.25
	Potassium chloride	g--	0.25
	Ferric sulfate		Trace
15	Yeast extract	g--	0.3
	Deionized water	ml--	1,000
	Substrate (sulfonate)	mg--	30

The above medium was added in 1-liter amounts to 2-liter Erlenmeyer flasks and sterilized by autoclaving 15 minutes at 20-pound steam pressure.

After cooling to room temperature, the flasks were inoculated with 1 ml. of a 48-hour old culture that had been growing in the presence of normal dodecylbenzene, NaSO₃. The flasks were then placed on a gyratory shaker and allowed to shake for 30 minutes, following which time, 10-ml. aliquots in triplicate were removed from each flask and transferred to 50-ml. flasks. These samples served as controls, indicating starting sulfonate concentrations in each flask. The 10-ml. samples were made acid by adding 2 ml. of concentrated HCl. This ceased microbial activity in the samples. The shaker flasks were replaced on the shaker and allowed to shake for seven days.

After the seven-day incubation period on the shaker, the flasks were made acid with 80 ml. of concentrated HCl to stop further biological degradation. Triplicate 10-ml. aliquots were then again removed for colorimetric analysis.

The method of assaying the amount of unaltered sulfonate contained in the samples over the period of the test was by means of a colorimetric method utilizing methyl green dye. This particular colorimetric procedure involves the formation of a complex in water between the basic methyl green dye and an anionic detergent. The complex, being organic soluble, is removed from the aqueous reaction medium by extraction with benzene. Excess dye, being water soluble, remains in the water phase and does not interfere.

The optical density of the extracted complex is then read in a spectrometer and compared with a standard. Thus, the degree of degradation can be readily determined. In using the above procedure, it was noted that the n-alkylbenzene sulfonate of Example III was completely decomposed in seven days, whereas the dodecylbenzene

sulfonate was only 25 percent degraded in this length of time.

Example VIII

This example illustrates the use of the molecular sieve method for fractionating kerosene to obtain a normal paraffin fraction suitable for the use in preparing the compositions of this invention. The kerosene used as a

feedstock herein had the following distillation characteristics:

I.B.P. -----	° F.	
50 percent -----		395
I.P. -----		431
		576

A 5-Angstrom pore size run molecular sieve was contacted with the kerosene feedstock to effect a sieve loading of approximately 8 percent observing the following conditions:

Pressure -----	375 p.s.i.g.
Temperature -----	500° F.
Space velocity -----	1.0 v./v.-r.

The loaded sieve was then desorbed with normal heptane observing the pressure and temperature conditions used for the sorption phase of the process. After the sieve contents had been eluted, the sorbed fraction and heptane were separated in a conventional fractionation tower. The distribution of normal paraffins observed for the sorbed fraction was as follows:

Less than C ₁₁ -----	0.4	
C ₁₁ -----	34.3	
C ₁₂ -----	25.5	
C ₁₃ -----	18.1	
C ₁₄ -----	10.9	
C ₁₅ -----	8.9	
Greater than C ₁₅ -----	1.8	
	99.9	

A detergent prepared from the above mixture of n-paraffins in accordance with the procedure exemplified in Examples II and III was noted to be completely biodegradable and to have excellent deterative properties comparable to that shown for the n-alkylbenzene sulfonate composition used in Table I.

We claim:

1. A detergent alkylate obtained by the aluminum chloride catalyzed alkylation of an aryl compound selected from the group consisting of benzene, a lower alkyl substituted benzene and mixtures thereof with a chlorination product prepared by partially chlorinating a petroleum derived hydrocarbon fraction consisting essentially of C₁₀ to C₁₈ straight chain paraffins to the extent whereby from about 10 to 35 mole percent of the paraffins are chlorinated, said fraction further characterized as comprising a predominant amount of component paraffins of 11 to 15 carbon atoms.

2. A biodegradable water-soluble surfactant comprising the alkali metal sulfonate salt of the detergent alkylate of claim 1.

3. A detergent alkylate in accordance with claim 1 wherein said aryl compound is benzene.

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