

March 18, 1969

R. T. ADAMS ET AL
BIODEGRADABLE DETERGENT ALKYLATE HAVING
IMPROVED DETERGENT PROPERTIES

3,433,846

Filed May 7, 1964

Sheet 1 of 4

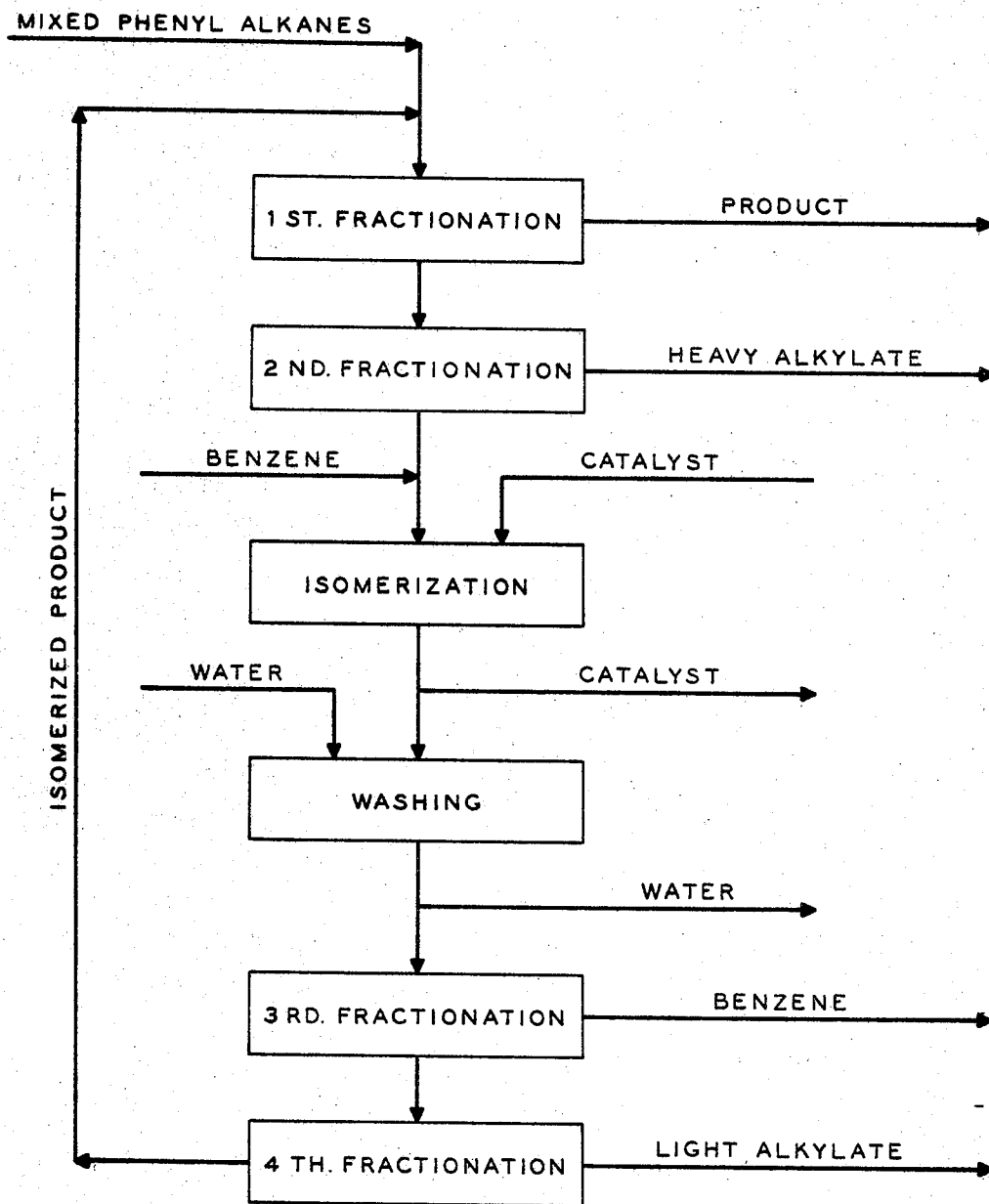


FIG.1

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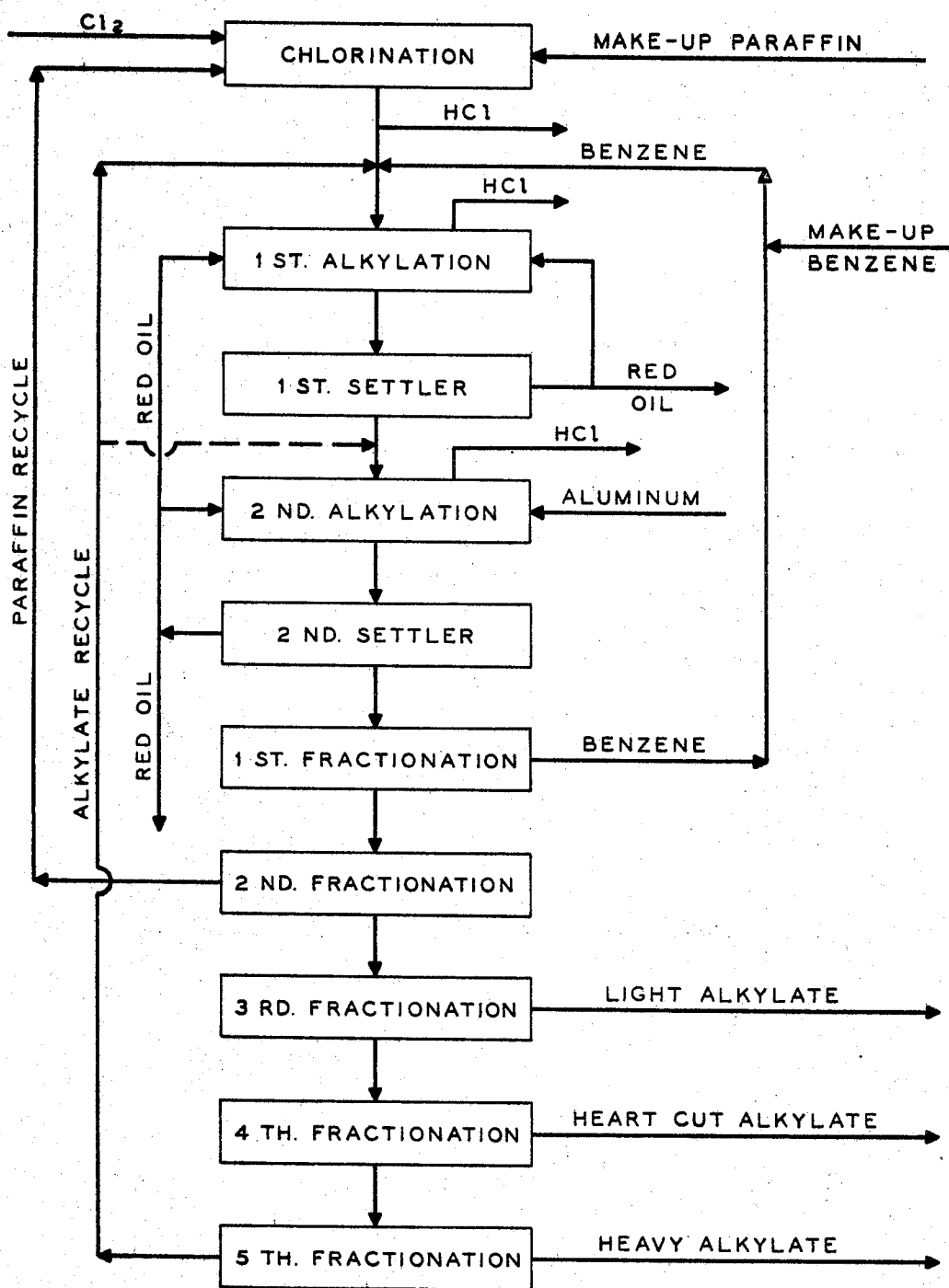


FIG. 2

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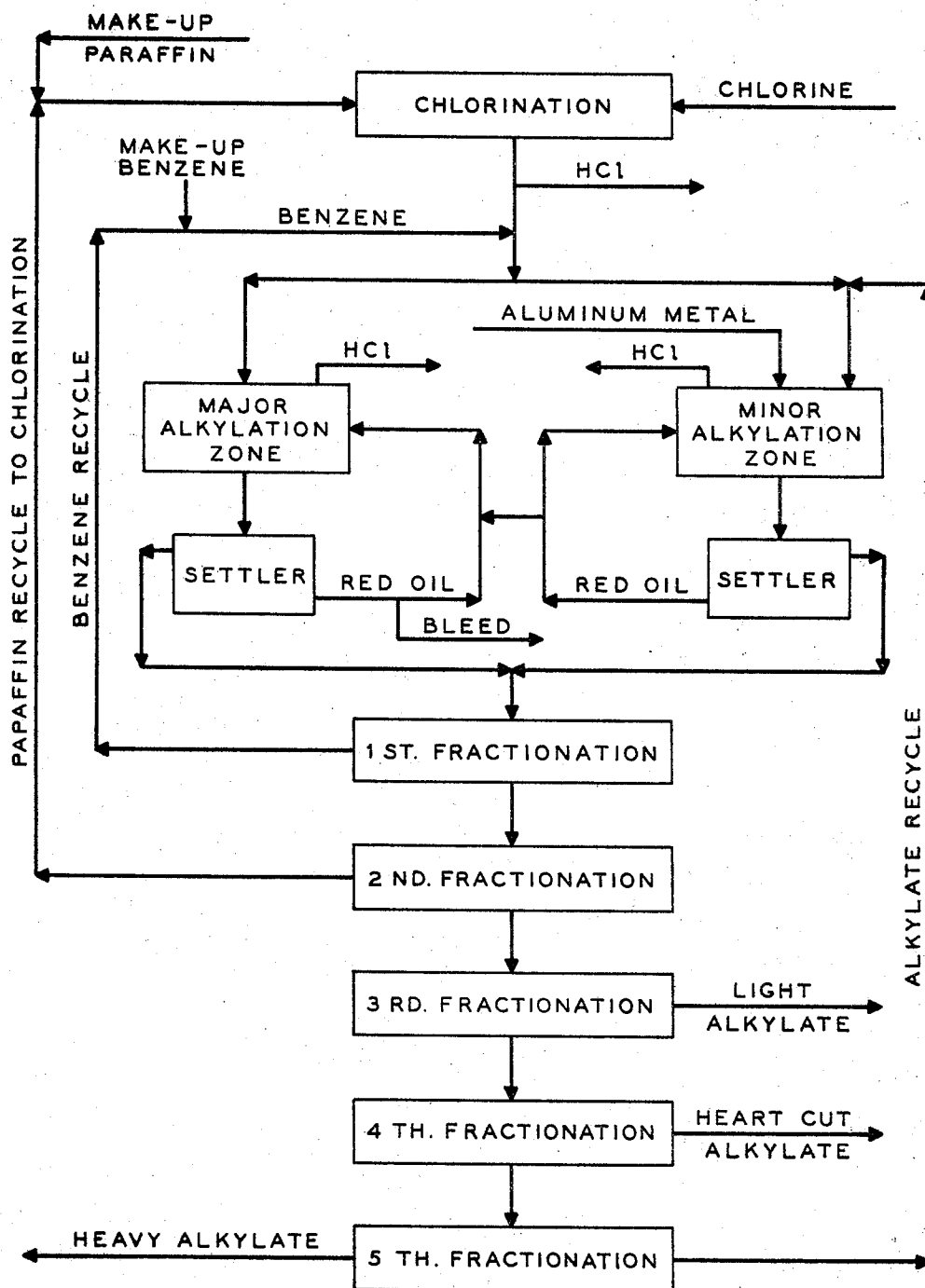


FIG. 3

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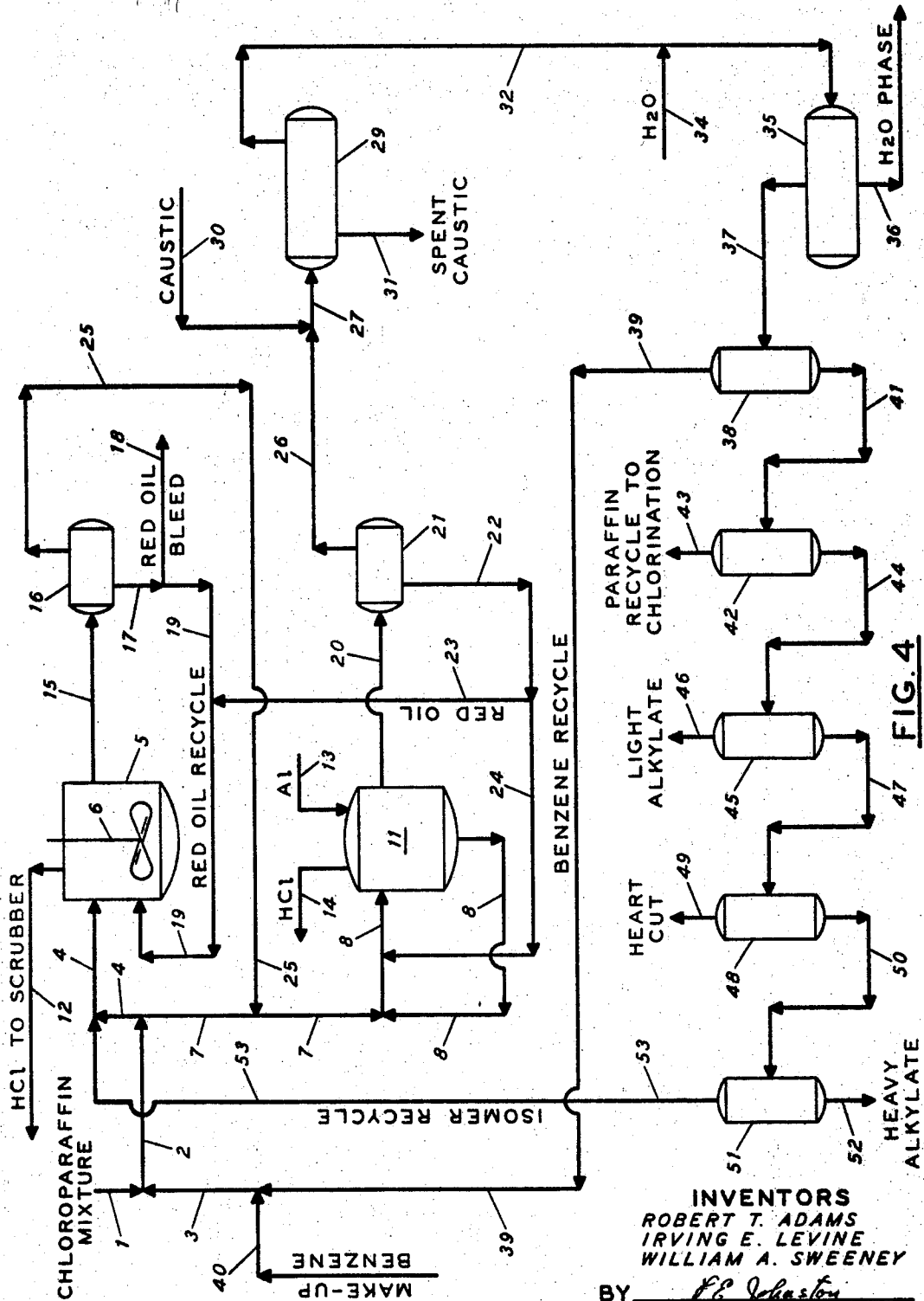


FIG. 4

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3,433,846

BIODEGRADABLE DETERGENT ALKYLATE HAVING IMPROVED DETERGENT PROPERTIES

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14 Claims

Int. Cl. C11d 1/66; C07c 7/04, 5/22

ABSTRACT OF THE DISCLOSURE

A process for producing a biodegradable detergent alkylate having improved detergent characteristics and composed of secondary phenyl-n-alkanes in the range of C₁₀ to C₁₄ and having a higher than equilibrium concentration of centrally attached phenyl isomers. A mixture of phenylalkanes in the C₁₀ to C₁₄ range and having at least 15% and preferably at least 50% by weight of phenylalkanes with 12 or more carbon atoms in the alkane portion of the molecule are subjected to fractional distillation to produce a lower boiling product fraction and a higher boiling fraction consisting predominantly of the terminal 2- and 3-phenylalkanes. This higher boiling fraction is subjected to isomerization, such as with a Friedel-Crafts or AlCl₃ catalyst, to convert the 2- and 3-phenyl isomers to the midchain phenylalkanes and thereafter returning the isomerized product to the aforementioned fractional distillation. Various process modifications and integration with a Friedel-Crafts alkylation process are described.

The present invention relates to a process for preparing a detergent alkylate intermediate convertible into a biologically soft detergent composition having good deterative properties.

For a great number of years, the bulk of detergent alkylate used to make the finished detergent compositions by conversion to the sulfonic acid followed by neutralization has been the monophenyl-substituted propylene polymers, as described, for example, in U.S. Patents Nos. 2,477,382 and 2,477,383 to Lewis. Detergent compositions as thus prepared have been developed and improved to the point that they are regarded as exhibiting optimum deterative performance. Polypropylene-based detergents, however, suffer from a serious disadvantage. Because of the branched-chain nature of the polypropylene precursor used in making the detergent alkylate, they do not meet the recently specified requirements of biodegradability. Therefore, in order to produce a more biodegradable detergent, intensive effort has been and is being expended in order to develop a new type of detergent alkylate or phenyl-substituted alkanes, in which the hydrocarbyl or alkyl radical is a straight-chain radical, sulfonation and neutralization being performed on the alkylate substantially as with the polypropylene-based alkylate.

Detergent alkylate compositions consisting essentially of a mixture of secondary phenyl-substituted, and a small but negligible amount of primary phenyl-substituted n-alkanes of 10 to 14 carbon atoms have excellent biodegradability and can be prepared by a number of reactions. These involve catalytic alkylation of benzene or some other aryl compound, such as toluene or xylene, with either an n-alkene or an n-alkyl halide alkylating agent of the desired molecular weight range, which can be derived from distillate cracking or wax cracking, catalytic dehydrogenation of n-paraffins, chlorination-dehydrochlorination of n-paraffins, ethylene polymerization, and chlorination of n-paraffins. In addition, the raw ma-

terials from which the straight-chain stock is to be derived may be subjected to iso-normal separation processes, such as molecular sieves and urea clathration to produce a more linear product than could otherwise be obtained.

A particularly useful reaction is the well-known Friedel-Crafts condensation reaction using anhydrous aluminum chloride or an aluminum chloride type catalyst, whereby n-alkyl monochlorides of 10 to 14 carbon atoms condense with benzene with the liberation of hydrogen chloride to produce a mixture of phenyl C₁₀-C₁₄ n-alkanes. Following reaction, the phenyl C₁₀-C₁₄ n-alkanes are separated from the catalyst and fractionated to recover the desired detergent alkylate product.

However, while the detergent alkylate produced by any of the above-indicated procedures satisfies the requirement of biodegradability in its finished form, it does not possess the detergency effectiveness of the phenyl-substituted polypropylene-derived detergent compositions. Analysis of the mixture of secondary phenyl n-alkanes indicates it to be of widespread composition, particularly as to the isomer distribution that results when the aromatic compound is alkylated with the straight-chain stock. Taking benzene as illustrative, present in the mixture are terminal, or end-chain, 2- and 3-phenylalkanes, the intermediate 4-phenylalkanes, and the midchain 5-, 6-, and 7-phenylalkanes. Depending on the alkylation process used the 2-phenylalkane content can range by weight based on total isomers, from about 10 to 50%; and combined 2- and 3-phenylalkanes from 20 to 70%.

It has been found that the above mixtures can be treated by a process which modifies the isomer distribution, whereby there is produced a biodegradable alkylate exhibiting a detergent performance as good as polypropylene-based detergent alkylate.

Broadly, the process of the invention involves fractionally distilling in a distillation zone a mixture of secondary phenyl-n-alkanes to obtain a lower boiling fraction and a higher boiling fraction, said mixture having 10 to 14 carbon atoms in the alkane portion of the molecule, at least 15%, usually around 50%, by weight of said mixture being secondary phenyl-n-alkanes containing at least 12 carbon atoms in the alkane portion of the molecule. The lower boiling fraction contains the midchain isomers, and is relatively free of terminal isomers, i.e., has a reduced terminal isomer content. On the other hand, the higher boiling fraction will consist of phenyl-n-alkanes having substantially the same number of carbon atoms, and predominating in 2- and 3-phenylalkanes. The fraction enriched with 2- and 3-phenylalkanes is subjected to Friedel-Crafts alkylation conditions, whereby 2- and 3-phenyl alkanes are isomerized to produce a mixture containing terminal, intermediate and mid-chain isomers in equilibrium, the isomerized mixture after treatment to remove impurities then being passed to the distillation zone.

In accordance with the invention, the mixture used can be composed of the phenyl-substituted alkanes of a single carbon number fraction (single molecular species), for example, the phenyl isomers of dodecane, or of tridecane or of tetradecane. Advantageously, the alkylate mixture charged to the distillation zone contains at least two homologous carbon fractions, or a mixture of phenyl-substituted decanes, undecanes, dodecanes, tridecanes, and tetradecanes, no homolog being present in a proportion below about 10% by weight of the total mixture. In addition, the highest boiling homolog in this alkylate mixture will preferably be present in a proportion of at least about 20 percent by weight of the mixture. However, for purpose of detergency effectiveness, it has been found that the mixture must contain at least 15% by weight thereof of phenyl alkanes having at least 12 carbon atoms

in the alkane portion of the molecule. Usually the mixture will contain at least about 50% of phenyl alkanes having at least 12 carbon atoms in the alkane portion of the molecule.

Mixtures of homologous fractions as above described are readily obtained by the reaction of alkylation. For example, one convenient way is to effect alkylation of benzene and chlorinated paraffins, or alkanes, in the presence of AlCl_3 catalyst. The paraffin precursor materials obtained from paraffin-containing petroleum oil, and if desired, subjected to a molecular sieve treatment, can be so selected as to correspond to a single carbon number fraction or to a blend of multiple number carbon fractions containing all of the C_{10} – C_{14} homologs.

The terminal 2- and 3-phenyl isomers of a given carbon number, having higher boiling points than the more centrally attached isomers, can easily be separated by fractional distillation. However, the boiling points of the terminal isomers of a given carbon number fraction and of the midchain isomers of the next higher carbon number of homologous fraction overlap.

In carrying out the invention, the higher boiling fraction will consist of phenyl-n-alkanes predominating in terminal 2- and 3-phenylalkanes having substantially the same number of carbon atoms. That is, depending on the efficiency of distillation, the terminal isomer fraction can consist of phenyl alkanes all of which will have the same number of carbon atoms; however, in practice there may be a minor amount of terminal isomers of the next lower homolog in the higher boiling fraction, for example, up to 10% by weight based on the fraction.

As indicated the higher boiling fraction of 2- and 3-phenylalkanes is isomerized, whereby there is produced an equilibrium isomeric mixture of the various position isomers, including the midchain isomers. Isomerization of 2- and 3-phenylalkane to the mid-chain isomers is carried out by subjecting them to Friedel-Crafts alkylation conditions that are customarily used to produce the phenylalkanes, such as the condensation of benzene with chloroparaffins in the presence of AlCl_3 catalyst.

In general, the 2- and 3-phenylalkane fraction can be isomerized by contacting it with AlCl_3 in the presence of benzene at temperatures and for periods of contact time varying with the amount of Friedel-Crafts catalyst used, lower temperatures and shorter reaction times being required as the catalyst concentration increases, and vice versa. In general, molar proportions of AlCl_3 to phenylalkanes varying from 0.03 to 0.20 will be found satisfactory. The benzene is generally present in proportions of about 2 or 3 to 30 or more mols per mol of phenylalkanes.

A convenient way of effecting the isomerization step is to integrate it with the alkylation reaction used to make the phenyl alkanes in the first instance, thus providing an overall process including also, if desired, the chlorination reaction, as will hereinafter be more fully shown.

Therefore, another aspect of the invention involves condensing or alkylating in an alkylation zone benzene and monochlorinated C_{10} – C_{14} n-paraffins, or n-alkanes, in the presence of an aluminum chloride-type catalyst such as AlCl_3 , whereby a mixture of secondary phenyl C_{10} – C_{14} n-alkanes is produced with the liberation of hydrogen chloride. Following the reaction, the phenyl alkanes are separated from the catalyst and fractionated to separate a forecut fraction; a detergent, or heart-cut alkylate of the desired boiling point, or molecular weight; and a higher boiling fraction, the higher boiling fraction being returned to the alkylation zone.

In carrying out the alkylation above indicated, proportions of aluminum chloride catalyst can range from about 0.02 to 0.5, preferably .03 to 0.1 mol per mol of alkyl chloride or chlorinated paraffin. Alkylation temperatures can range from about 45, preferably 100, to 185° F. and higher. As is known in alkylation reactions of the type herein contemplated, greater quantities of catalyst permit

lower reaction times. Similarly, higher temperatures permit the use of lesser amounts of catalyst. Reaction may be continued until hydrogen chloride is no longer evolved, and the time required for this to occur will vary with catalyst concentration and temperature. Lower temperatures and catalyst concentrations require longer reaction times, and higher catalyst concentrations and temperatures, shorter reaction times. An example of a reaction time range being 1 to 30 minutes at a catalyst concentration of .06 to .1 mol catalyst per mol of alkyl chloride and a temperature of 176 to 75° F.

More specifically, taking monochlorinated C_{11} – C_{14} paraffins as illustrative of a preferred fraction, benzene is alkylated with monochlorinated C_{11} – C_{14} paraffins in the presence of an aluminum chloride catalyst under Friedel-Crafts alkylation conditions. Following reaction, the phenyl alkanes are separated from the catalyst and fractionated into a lower boiling fraction boiling below about 545° F., a heart-cut fraction having an initial boiling point of about 545° F., and an end point of about 630° F.; and a heavier or higher boiling fraction having an end boiling point of about 660° F. and an initial boiling point of about 630° F. The said heavier or higher boiling fraction is returned to the alkylation zone and the alkylation reaction performed as before.

In making detergent alkylate, it is desirable that only one hydrogen atom of the aromatic nucleus is replaced with one alkyl group. Accordingly, there is generally used an excess of benzene ranging from 2 to 30 mols per mol of n-alkyl chloride. The excess benzene can be recovered and reused in the process.

The alkylating alkyl chloride component is obtained as a mixture by the chlorination of suitable straight-chain hydrocarbon or paraffin stock, whereby upon alkylation an alkylate is produced, the alkyl group of which corresponds in structure and carbon content to that of the alkyl chloride alkylating agent. Suitable hydrocarbon stocks for chlorination are petroleum distillates which, in the refining of petroleum, generally fall between the gasoline and lubricating oil fractions, i.e., the kerosene fraction. In general, a suitable petroleum distillate will boil in about the range 345° F. to 490° F., corresponding to a carbon content of 10 to 14 carbon atoms. A good source of the petroleum distillate is paraffin-based crude oil, such as the Pennsylvania oils and those obtained from the Minas Fields in Sumatra.

In order to make the n-paraffin material used in the chlorination step to produce chloroparaffin even more desirable for the alkylation step with benzene, i.e., a more linear or straight-chain paraffinic material, it is subjected prior to chlorination to a separation process. In this process the n-paraffins are selectively separated from isoparaffins, aromatics, and cyclic paraffins. Presently favored separation processes involve the use of molecular sieves of natural or synthetic zeolites, for example, calcium aluminosilicates, as described, for example, in the U.S. Patent No. 3,070,542.

Further, in accordance with copending application Ser. No. 292,689, filed July 3, 1963, now U.S. Patent 3,333,014, it is advantageous to subject the pure n-paraffins to the alkylation conditions in the alkylation zone during the condensation of benzene and chloroparaffins, recovering them from the alkylation reaction product mixture and then subjecting them to chlorination.

In addition to the preliminary molecular sieve conditioning treatment of paraffinic feed, the manner of performing the initial chlorination operation and the conditions used for the preparation of the alkyl chloride component are significant.

It is generally desirable to use such conditions in the chlorination step which will maximize the formation of monochloroparaffins and minimize the formation of polychlorides, for example, an alkane in which two hydrogen atoms have been substituted with two chlorine atoms. Accordingly, the chlorination operation is generally con-

ducted under conditions, and with the use of apparatus, as to minimize dehydrochlorination of the resulting alkyl chlorides, which produces hydrogen chloride and olefins, the latter reacting with additional chlorine to form undesirable polychlorides. It has, accordingly, been proposed to use special apparatus such as glass-lined chlorination vessels to inhibit dehydrochlorination. Furthermore, it has been proposed to carry out the chlorination reaction in a manner such as to produce a chlorinated product in which the organically bound chlorine content is far less than would be obtained if chlorine were combined with all of the hydrocarbon molecules on the basis of one chlorine atom per molecule of hydrocarbon. Usually, the degree of chlorination is expressed in terms of mol percent chlorination of the hydrocarbon stock, and conventional chlorination processes are carried out to the extent of converting 10-50%, more usually 15-30%, of the paraffins.

The chlorination product comprising a mixture of unchlorinated paraffins and chlorinated paraffins is then to be used for the alkylation step. In some instances, the chloroparaffins can be separated from unchlorinated paraffins prior to alkylation, the unchlorinated paraffins, if desired, being then reused in the chlorination operation. However, such procedure involves some difficulties. Alkyl chlorides are difficultly separable from closely boiling unchlorinated paraffins. Further, distillation results in the splitting out of hydrogen chloride, thereby producing olefins, which in turn produce undesirable polychlorides. Accordingly, it will often be found advantageous to use the whole of the chlorinated product mixture comprising alkyl chlorides and unreacted hydrocarbons as feed to the alkylation zone.

The process of the present invention is particularly useful when used in connection with the continuous alkylation process described and claimed in Howard N. Moulden copending application, filed July 3, 1963, Ser. No. 292,578, now U.S. Patent 3,355,508.

According to that application, a continuous two-step process is described and claimed, wherein chloroparaffins and an aryl compound, such as benzene, are contacted under alkylation conditions in a first alkylation zone in the presence of unchlorinated paraffins, and red oil catalyst complex produced in a second zone.

Effluent from the first stage alkylation passes into a second stage alkylation zone and therein is contacted under alkylation conditions with aluminum metal. Effluent from the second alkylation zone is treated to separate the red oil catalyst, part of which is used in the first zone.

The red oil-free mixture is then fractionally separated into various fractions, including the alkyl benzenes. In accordance with the present invention, the alkyl benzenes are separated into a fraction containing the desired phenylalkanes, i.e., predominating in midchain isomers, and having a reduced content of terminal phenyl alkanes; and a higher boiling fraction of 2- and 3-phenylalkanes, which is returned to the alkylation zone.

In order to more fully describe the invention reference is now made to the accompanying drawings, wherein:

FIG. 1 is a block flow diagram illustrating fractionation zones to isolate desired product as a lower boiling fraction and terminal isomers as a higher boiling fraction, isomerizing said last mentioned fraction, treating the isomerized mixture, and recycling the treated mixture to a first fractionation zone.

FIG. 2 is a block flow diagram illustrating an integrated process involving chlorination; a series two-stage alkylation; fractionation into a lower boiling fraction containing desired product, a high boiling fraction containing terminal isomers that are recycled to a first alkylation zone.

FIG. 3 is a block flow diagram illustrating a modified version of the process of FIG. 2 according to which alkylation occurs in two separate parallel major and minor zones, and terminal isomers are passed to the said minor zone.

FIG. 4 is a schematic flow diagram illustrative of apparatus useful in a modified version of the process of FIG. 2.

Referring to FIG. 1, a mixture of phenyl C₁₀-C₁₄ alkanes obtained, for example, from the AlCl₃ alkylation of appropriate chloroparaffins, or by other appropriate process such as HF catalyzed alkylation of n-olefins, is fractionated as by distillation in a first fractionation zone to recover a desired product relatively free of terminal isomers in a lower boiling fraction. The higher boiling fraction enriched in terminal isomers is fractionated in a second fractionation zone to remove from it high boiling alkylate which is rejected.

The fraction of terminal 2- and 3-phenylalkanes next passes into the isomerization zone and there mixed with an isomerization catalyst, such as AlCl₃, BF₃, AlBr₃, or SbCl₅, and benzene. Typical isomerization conditions are a temperature of 160° F., 0.11 mol of catalyst per mol of phenylalkanes, 25 mols benzene per mol of phenylalkanes, and a reaction time of 13 minutes.

Following isomerization the catalyst is removed, as by simple decantation. If desired, this catalyst may be recycled to the isomerization zone. The catalyst-free mixture is washed with water. The washed and dried mixture then passes to a third fractionation zone. Here the benzene is removed and, if desired, recycled to the isomerization zone. The benzene-free phenylalkanes then enter a fourth fractionation zone. In this zone, light alkylate is separated from the equilibrium mixture of phenylalkanes, the latter being passed into the first fractionation zone.

FIG. 2 illustrates that the process of the present invention is particularly useful when used in connection with the continuous two-step alkylation process of Howard N. Moulden copending application, filed July 3, 1963, Ser. No. 292,578, hereinabove described.

Accordingly, chlorination is effected in a chlorination zone into which chlorine and paraffins are continuously charged. The resulting chloroparaffins and benzene in an amount of 2 to 30 mols per mol of chloroparaffins, are contacted in a first alkylation zone in the presence of unchlorinated paraffins and red oil catalyst complex produced in a second alkylation zone. The mixture of chloroparaffins and unchlorinated paraffins is conveniently the product obtained from chlorinating paraffins to 15-30% chlorination. Contact is effected at a temperature in the range of 45° F., preferably 100 to 185° F., and for a period of time to effect 85-95% conversion of the chloroparaffins.

Effluent from the first stage alkylation is then treated in a first settler to separate a phase comprising catalyst material and a phase comprising alkylbenzenes, paraffins, benzene, and dissolved hydrogen chloride.

This latter phase then passes into the second stage of the alkylation zone and is therein contacted with aluminum metal, the amount of metal used being in the range of 0.02 to 0.1 gram atom per mol of chloroparaffin in the original feed. Contact is effected at a temperature in the range of 45° F., preferably 100 to 185° F. for a period of time of 0.3 to 15 minutes to convert substantially all of the chloroparaffin material entering the second stage alkylation zone.

Effluent from the second alkylation zone now comprising paraffins, benzene, alkylbenzenes, and red oil catalyst is treated in a second settler to separate the red oil catalyst. Part of the red oil catalyst is then sent to the first stage alkylation zone as the red oil catalyst for that zone, in quantities such as to effect the desired degree of chloroparaffin conversion in that zone, and corresponding to that withdrawn as spent catalyst after reaction in the first alkylation zone. Part of the red oil is sent to the second alkylation zone and part of it may be bled from the system. In general, the red oil in the first alkylation zone can range from about 0.5 to 30%, preferably 1 to 10%; and 5 to 80%, preferably 10 to 60%, often around 35%, in the second alkylation zone. Percentages are based on volume of the contents of each zone.

The red oil-free mixture is then fractionally separated. Benzene is recovered in a first fractionation zone and re-used in the first alkylation zone, together with make-up benzene. Paraffins are recovered in a second fractionation zone and sent to chlorination, together with makeup paraffin corresponding in quantity on a molar basis to that used in the chlorination operation; or preferably, according to copending application Ser. No. 292,689, filed July 3, 1963, makeup paraffins are fed to the first alkylation zone, together with the chlorination product before chlorination. The mixture of phenylalkanes free of benzene and paraffin is then distilled to remove light alkylate and heart-cut alkylate. Finally, in a fifth fractionation zone a heavy or high boiling fraction undesirable for detergent manufacture is separated from a fraction predominating in desired 2- and 3-phenyl alkane, the latter being recycled to the first alkylation zone or optionally to the second alkylation zone, or to both.

As noted above, FIG. 3 represents a modification of the process illustrated by FIG. 2.

According to FIG. 3, following chlorination and mixing with benzene in the manner described for FIG. 2, the partial chlorinated product is divided into portions. A major proportion, i.e., about 75 to 95%, preferably 85 to 90%, by volume, is sent to the major alkylation zone; and a minor proportion, i.e., about 5 to 25%, preferably 10 to 15% by volume, to the minor alkylation zone.

Alkylation is effected in the major alkylation zone by subjecting the chloroparaffin and benzene to alkylation temperatures of about 45° F., preferably 100° F. to 185° F., more preferably around 150° F. to 170° F., in the presence of red oil catalyst obtained from the minor alkylation zone.

The residence time in the major alkylation zone required to effect alkylation, i.e., substantially complete conversion of the chloroparaffin to phenyl alkanes, will vary depending on the amount of red oil catalyst. Accordingly, the amount of red oil catalyst can vary from 5 to 80 volume percent of the contents, preferably from 10 to 40%. The residence time can vary from 6 to 60 minutes, preferably 20 to 45 minutes. During alkylation, hydrogen chloride is formed and is vented from the alkylation zone. In the minor alkylation zone, alkylation is effected by contacting the minor proportion of the chloroparaffin and benzene in the presence of aluminum metal at a temperature ranging from 45° F., preferably 100° F. to 185° F. The amount of aluminum metal introduced will range from 0.02 to 0.1 gram atom per mol of chloroparaffin. As in the major alkylation zone, residence time will vary depending on volume of red oil catalyst which may range from 5 to 80%, preferably 10 to 60%, based on the volume of the contents. At these concentrations of catalyst, residence time can vary from 60 minutes at the lower red oil concentration to 0.3 minute at the higher red oil concentration.

The alkylation reaction product mixtures from the two alkylation zones are each separated into a red oil catalyst phase and a hydrocarbon phase. The red oil phase from the major alkylation zone is recycled, except for a small bleed portion. The red oil from the minor alkylation zone is also recycled, except for a small portion which passes to the major alkylation zone in a quantity substantially equivalent to that withdrawn as bleed.

The hydrocarbon phases are combined, subjected to fractionation, and the terminal phenylalkane recycled, as described for the process illustrated by FIG. 2.

According to FIG. 4, a chlorination mixture, from a source not shown, obtained by partial chlorination of, for example, C₁₁-C₁₄ paraffins, present in about equimolar proportions, and containing a minor proportion of monochloroparaffins, e.g. 15-30%, and a major proportion of unchlorinated paraffins, e.g., 70-85%, is introduced through line 1 into line 2. Benzene is introduced from line 3 into line 2, the proportion of benzene varying from 2 mols to 30 mols per mol of chloroparaffins.

A major proportion, i.e., about 75 to 95%, preferably about 85 to 90%, by volume of the chloroparaffin mixture is sent through line 4 into first stage alkylator 5, which may be a stirred tank reactor provided with stirrer 6. The minor proportion of chloroparaffin mixture, i.e., 5 to 25%, preferably 10 to 15%, by volume is introduced through line 7 and pumparound loop 8 into second stage alkylator 11.

Alkylation is effected in alkylator 5 by subjecting the chloroparaffins and benzene to alkylation temperatures of about 45° F., preferably 100 to 185° F., more preferably around 150° F. to 170° F. in the presence of red oil catalyst obtained from the second stage alkylation zone 11, as hereinafter more fully described. The residence time in alkylator 5 required to effect alkylation, i.e., substantially complete conversion of the chloroparaffins to phenyl alkane, will vary depending on the amount of red oil catalyst. Accordingly, the amount of red oil catalyst can vary from about 5 to 80 volume percent of the contents, preferably around 10-40 volume percent, and the residence time from 6 to 60 minutes, preferably 20 to 45 minutes. During alkylation hydrogen chloride is formed and is vented from the alkylator through vent line 12.

In the second stage alkylator 11, alkylation is effected by contacting the minor proportion of the chloroparaffin and benzene in the presence of aluminum metal introduced through line 13 at a temperature ranging from 45° F., preferably 100° F. to 185° F. The amount of aluminum metal introduced will range from 0.02 to 0.1 gram atom per mol of chloroparaffin entering through line 2. As in the first alkylation zone, residence time will vary depending on volume of red oil catalyst which may range from 5 to 80%, preferably 10 to 60%, based on the volume of the contents. At these concentrations of catalyst, residence time can vary from 60 minutes at the lower red oil concentration to 0.3 minute at the higher red oil concentration. Hydrogen chloride formed during reaction is vented through vent line 14.

Returning to alkylator 5, alkylate effluent is withdrawn through line 15 and introduced into settler 16, wherein an alkylate-containing phase and a catalyst-containing phase are formed. The catalyst phase is withdrawn through line 17, a part of it being discarded through line 18, and a portion recycled through line 19 into reactor 5. Similarly, effluent from alkylator 11 is withdrawn through line 20 and sent to settler 21, wherein an alkylate-containing phase and a catalyst phase are formed. The catalyst phase is withdrawn through line 22. A portion, corresponding in amount withdrawn through bleed line 18, is sent through lines 23 and 19 into alkylator 5, and a portion recycled through line 24 and pumparound loop 8 to alkylator 11.

Amounts of red oil discarded through line 18, and passed through lines 19, 23, and 24 are such as to maintain the desired concentration of catalyst in the alkylators.

The alkylate-containing phase of settler 16, withdrawn through line 25, is combined with the minor proportion of the chloroparaffin mixture in line 7, and is charged to the second stage alkylator 11 via the pumparound loop 8.

The alkylate-containing phase of settler 21, withdrawn through line 26, is combined with caustic from line 30 and introduced through line 27 into caustic washer 29. In washer 29, contact of the combined hydrocarbon phase is made with caustic to remove suspended and dissolved catalyst. Spent caustic is discharged through line 31.

The caustic-treated mixture is withdrawn from caustic washer 29 through line 32 and washed with water introduced through line 34. The mixture is then allowed to settle in settler 35, to form a hydrocarbon phase and a water phase, the water phase being discharged through line 36.

The hydrocarbon phase is then withdrawn from water settler 35 through line 37 and is sent to the distillation

section. Accordingly, it is sent through line 37 into benzene still 38, wherein benzene is taken overhead through line 39 and joined with makeup benzene introduced through line 40, for recycle to the alkylation zones through line 3 joining line 2.

The benzene-free mixture is removed from still 38 through line 41 and introduced into paraffin still 42. Taken overhead are the paraffins which may be recycled to chlorination zone, not shown, through line 43.

The bottoms of still 42 are withdrawn through line 44 and introduced into light alkylate still 45, wherein light alkylate unsuitable for detergent manufacture is withdrawn through line 46. The remaining alkylate is withdrawn through line 47 and charged to heart-cut alkylate still 48. The heart-cut fraction, i.e., desired product relatively free of terminal 2- and 3-phenyl alkanes, is withdrawn through line 49. A higher boiling fraction is withdrawn through line 50 and charged to still 51. In still 51 high boiling alkylate unsuitable for detergent manufacture is removed through line 52, while a fraction predominating in 2- and 3-phenylalkanes is taken from the still 51 through line 53 and sent through line 4 into first alkylator 5.

A significant test for determining the deterative effectiveness of a detergent, and the one used in obtaining the data below with the biodegradable detergent alkylate of the present invention, is the so-called "hand dishwashing test."

According to this test, dinner dishes or plates having a diameter of nine inches are washed under conditions simulating home dishwashing, the total number of plates washed before the foam collapses being determined.

In this test the dishes are smeared with molten, partially hydrogenated vegetable oils, melting point of 110–115° F. ("Crisco"), treated with a dye, such as Sudan Red dye to impart a uniform appearance to the grease. Using a syringe, 2.2 cc. of the molten soil is placed in the center of each clean, dry dinner plate. With the fingers, the soil is spread over a space of about 6.5 inches in diameter on each plate.

Six liters of washing water adjusted to the desired hardness and at a temperature of 117° F. are placed in an 8,000 ml. container having a faucet outlet in the base (Scientific Glass, item P-2350). Samples of the built detergent to be tested are made up into 6% solutions, and 15.33 cc. of each solution is added to a dishpan 13.5 inches in diameter and 5.75 inches deep, thereby giving a final concentration of 0.15% by weight.

The water container is then placed above the dishpan in such a position that the distance between faucet outlet and bottom of the dishpan is 18 inches. Further, the dishpan is so placed that the stream of water strikes the center of the dishpan with the water faucets fully open. This requires about 45–60 seconds. When the dishpan is completely charged, washing of the dishes is begun.

Five soiled plates and a clean dishcloth are placed in the dishpan. The dishes are washed in a circular manner to remove the grease from the front of the plate, then turned over and the grease clinging to the back is removed in the same way. During the washing, each plate is held at an angle so that almost one-half of the plate is kept under the washing solution. This is repeated until the five plates are washed. Another set of five plates is then placed in the dishwasher and washing continued, this procedure being repeated until the foam collapses in the dishpan. At this point the surface is nearly devoid of foam.

The following examples illustrate how the invention can be practiced.

EXAMPLE 1

n-Tetradecane was chlorinated to produce a chlorination product having a chlorine content of 3.29% by weight. This product, containing monochlorotetradecane alkyl chloride, and 30 mols of benzene per mol of chlorination product, were charged to an alkylation zone in the presence of 0.07 mol of aluminum chloride per mol

of alkyl chloride. Alkylation was carried out at a temperature of 162° F. over a period of two hours. Following alkylation, the catalyst was removed and the hydrocarbon layer washed with water and distilled to remove unreacted benzene and n-tetradecane. The remaining alkyl benzene was fractionally distilled to separate a light fore-run cut (1.6 weight percent) boiling in about the range 495–615° F., a heart-cut fraction (91.8%) boiling in the range 615–660° F., and a heavier bottom fraction (6.6%) boiling above 660° F. The heart-cut alkyl benzene fraction analyzing 24% 2-phenyl-, 15% 3-phenyl-, 11% 4-phenyl-, and 50% 5-, 6-, and 7-phenylalkanes was sulfonated with oleum, neutralized with sodium hydroxide, and then combined with heavy-duty detergent builders, so as to give the following composition: 25% sodium alkylbenzene sulfonate, 40% sodium tripolyphosphate, 1% carboxymethyl cellulose, 7% sodium silicate, 8% water, and 19% sodium sulfate. This composition washed 16 plates, in accordance with the dishwashing test hereinbefore described.

EXAMPLE 2

Example 1 was repeated except that the heart-cut material boiling in the range 615–660° F. was fractionated into two fractions, one boiling in the range 615–630° F. (34% by weight) and a second fraction boiling in the range 630–660° F. (66% by weight). The higher boiling fraction was then added to a second batch alkylation performed as in Example 1, using the same reactants and proportions, except for the addition of said higher boiling fraction. Following alkylation, a fraction boiling in the range 615–630° F. and analyzing 1% 2-phenyl-, 6% 3-phenyl-, 15% 4-phenyl-, and 79% 5-, 6-, and 7-phenylalkanes was isolated, sulfonated, neutralized and compounded into a built detergent formulation as in Example 1. This detergent composition washed 25 plates.

EXAMPLE 3

Example 2 was repeated, except that twice the amount of aluminum chloride catalyst, namely, 0.14 mol per mol of alkyl chloride, was used in the alkylation reaction. A built detergent composition prepared from the heart-cut fraction boiling in the range 618–628° F. washed 26 plates.

EXAMPLE 4

Following a procedure similar to that illustrated in FIG. 1, a mixture of phenyltetradecanes boiling between 615° F. and 660° F. and containing 24% 2-phenyl-, 15% 3-phenyl-, 11% 4-phenyl-, and 50% 5-, 6-, and 7-phenyltetradecanes was continuously fed into a first fractionation or distillation zone. From this zone, heart-cut alkylate boiling in the range 615–630° F. was recovered. The alkylate boiling above 630° F. was sent to a second fractionation zone. From this second zone, there was recovered an intermediate fraction boiling in the range 630–660° F. and a heavy alkylate fraction boiling above 660° F. The intermediate fraction containing 52% 2-phenyl-, 27% 3-phenyl-, and 21% 4-, 5-, 6-, and 7-phenyltetradecanes, was charged to an isomerization zone, together with benzene and aluminum chloride in an amount of 30 mols of benzene and 0.14 mol of aluminum chloride per mol of phenylalkane charged. Isomerization was carried out by heating to 120° F. and stirring for hour. At the end of this time the catalyst was removed from the reaction mixture and the organic phase was washed with water. After separation of water, the organic material was charged to a third fractionation zone. In this zone, unreacted benzene was separated and recycled to the isomerization zone. The organic phase free of benzene was charged to a fourth fractionation zone wherein a light alkylate having a boiling point below 615° F. was removed and discarded. The remaining material was combined with fresh phenyltetradecanes and recharged to the first fractionation zone. The above process was conducted as indicated until steady state conditions were reached.

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At steady state and based on 100 pounds of phenyltetradecane charged, the heart-cut alkylate from the first distillation zone was 96.6 pounds; the intermediate fraction from the second distillation zone, 130 pounds; the heavy alkylate reject from the second zone, 2.8 pounds; and the light alkylate reject from the fourth fractionation zone, 0.6 pound.

After steady state was reached a sample of heart-cut product having a boiling point of 615–630° F. was taken for conversion to alkyl benzene sulfonate. It was sulfonated, neutralized, and formulated with builders as in Example 1 to yield a detergent composition capable of washing 26 plates.

EXAMPLE 5

Substantially the same continuous procedure was followed as in Example 4, except that a mixture of phenyltridecanes boiling in the range 590–625° F. and containing 28% 2-phenyl-, 17% 3-phenyl-, 12% 4-phenyl-, and 43% 5-, 6-, and 7-phenyltridecanes was continuously distilled and isomerized. With this feed stock the heart-cut material had a boiling range of 590–600° F.; the intermediate fraction sent to isomerization, containing 51% 2-phenyl-, 28% 3-phenyl-, and 21% 4-, 5-, 6-, and 7-phenyltridecanes, had a boiling range of 600–625° F.; the heavy reject material boiled above 625° F. and the light alkylate boiled below 590° F. At steady state, and based on 100 pounds of phenyltridecane feed stock, the heart-cut alkylate product amounted to 96.8 pounds; the intermediate fraction, 118 pounds; the heavy alkylate reject, 2.7 pounds; and the light alkylate reject, 0.5 pound.

Sulfonation, and neutralization of a steady state heart-cut sample followed by compounding into a detergent composition, as in Example 1, gave a material capable of washing 29 plates.

The original unfractionated and unisomerized phenyltridecanes were also sulfonated, neutralized, and formulated in like manner. This material washed only 18 plates.

EXAMPLE 6

A mixture of phenyldodecanes boiling in the range 565–600° F. and containing 32% 2-phenyl-, 19% 3-phenyl-, 15% 4-phenyl-, and 34% 5-, and 6-phenyldodecanes was processed as described in Example 4. In this case, the heart-cut product boiled in the range 565–570° F.; the intermediate fraction containing 52% 2-phenyl-, 28% 3-phenyl-, and 20% 4-, 5- and 6-phenyldodecanes, had a boiling range of 570–600° F.; the heavy reject boiled above 600° F., and the light alkylate boiled below 565° F. At steady state and based on 100 pounds of phenyldodecanes charged to the process, the heart-cut alkylate material amounted to 96.3 pounds; the intermediate recycle fraction, 166 pounds; the heavy alkylate reject, 3.1 pounds; and the light alkylate reject, 0.6 pound.

After steady state was reached, a sample of heart-cut alkylate was isolated, sulfonated, neutralized, and compounded to a detergent composition which was capable of washing 26 plates.

A detergent composition prepared from the undistilled and unisomerized phenyldodecane feed material washed only 17 plates.

EXAMPLE 7

A blend of phenylundecanes, dodecanes, tridecanes and tetradecanes having a weight distribution of 10, 30, 32, and 28 weight percent, respectively, and a boiling point range of 545–660° F. was subjected to a process similar to that illustrated by FIG. 1.

The blend was distilled in a first fractionation zone to recover the desired heart-cut product boiling in the range 545–630° F. Material boiling above 630° F. was charged to a second fractionation zone and an intermediate fraction boiling between 630° F. and 660° F. was separated and charged to the isomerization zone. This fraction analyzed as 50% 2-phenyl-, 26% 3-phenyl-, and

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24% 4-, 5-, 6-, and 7-phenyltetradecane. Material boiling above 600° F. was rejected.

In the isomerization zone, in addition to the intermediate fraction there were present 30 mols of benzene and 0.20 mol of aluminum chloride per mol of phenyltetradecane charged. Reaction was continued for one hour at 120° F. At the end of this time, the catalyst was separated and the reaction product mixture was washed with water and then charged to the third fractionation zone. In this zone benzene was removed and recycled to the isomerization zone. That material boiling above 175° F. was charged to a fourth fractionation zone in which a small amount of light alkylate having a boiling range of 175 to 545° F. was removed and discarded. The remainder, boiling above 545° F., was mixed with fresh feed and charged to the first fractionation zone. This process was continued until all units reached steady state.

At steady state, and based on 100 pounds of feed stock, the heart-cut alkylate product amounted to 98.7 pounds; the intermediate recycle cut, 30 pounds; the heavy alkylate reject, 1.1 pounds; and the light alkylate reject, 0.2 pound.

Steady state heart-cut material was converted to detergent as previously described and found to wash 23 plates. The untreated mixed phenyl C₁₁–C₁₄ alkanes upon conversion to detergent washed only 18 plates.

EXAMPLE 8

A blend of phenyldecanes, undecanes, dodecanes, and tridecanes, having a weight distribution of 17, 29, 30, and 24 weight percent, respectively, and a boiling point range of 520–625° F. was subjected to a process substantially as represented by FIG. 1. It was distilled in a first fractionation zone to recover the desired heart-cut alkylate product boiling in the range 520–600° F. That material boiling above 600° F. was charged to a second fractionation zone wherein an intermediate fraction boiling between 600 and 625° F. was separated and charged to the isomerization zone. This fraction analyzed as 51% 2-phenyl-, 28% 3-phenyl-, and 21% 4-, 5-, 6-, and 7-phenyltridecane. That material boiling above 625° F. was rejected. In the isomerization zone, in addition to the intermediate fraction there were present 30 mols of benzene and 0.14 mol of aluminum chloride per mol of phenyltridecane. Reaction was continued for one hour at 120° F. At the end of this time, the catalyst was separated and the reaction product mixture was washed with water and then charged to the third fractionation zone. In this zone benzene was removed and recycled to the isomerization zone. That material boiling above 175° F. was charged to a fourth fractionation zone in which a small amount of light alkylate having a boiling range of 175° F. to 520° F. was removed and discarded. The remainder, boiling above 520° F., was mixed with fresh feed and recharged to the first fractionation zone. This process was continued until all units reached steady state.

At steady state and based on 100 pounds of feed stock, the heart-cut alkylate product amounted to 98.7 pounds; the intermediate recycle cut, 28 pounds; the heavy alkylate reject, 1.1 pounds; and the light alkylate reject, 0.2 pound.

Steady state heart-cut material was converted to detergent as previously described and found to wash 18 plates. The untreated mixed phenyl C₁₀–C₁₃ alkanes upon conversion to detergent washed only 13 plates.

EXAMPLE 9

A blend of phenyldodecanes, tridecanes, and tetradecanes, having a weight distribution of 32, 38, and 30 weight percent, respectively, had a boiling point range of 565 to 660° F. This material was treated by a process as represented by FIG. 1. It was distilled in a first fractionation zone to recover the desired heart-cut alkylate product boiling in the range from 565–630° F. That material boiling above 630° F. was charged to a second fractionation zone, wherein an intermediate fraction boil-

ing between 630° F. and 660° F. was separated and charged to the isomerization zone. This fraction analyzed as 52% 2-phenyl-, 27% 3-phenyl-, and 21% 4-, 5-, 6-, and 7-phenyltetradecane. That material boiling above 660° F. was rejected. In the isomerization zone, in addition to the intermediate fraction, there were present 30 mols of benzene and 0.14 mol of aluminum chloride per mol of phenyltetradecane. Reaction was continued for one hour at 120° F. At the end of this time, the catalyst was separated, and the reaction product mixtures was washed with water and then charged to a third fractionation zone. In this zone benzene is removed and recycled to the isomerization zone. That material boiling above 175° F. was charged to a fourth fractionation zone in which a small amount of light alkylate having a boiling range of 175° F. to 565° F. was removed and discarded. The remainder, boiling above 565° F., was mixed with fresh feed and recharged to the first fractionation zone. This process was continued until all units reached steady state.

At steady state and based on 100 pounds of feed stock, the heart-cut alkylate product amounted to 98.3 pounds; the intermediate recycle cut, 36.8 pounds; the heavy alkylate reject, 1.4 pounds; and the light alkylate reject, 0.3 pound.

Steady state heart-cut material was converted to a detergent formulation as previously described in Example 1. The composition washed 22 plates. The untreated mixed phenyl C₁₂-C₁₄ alkanes upon conversion to a built detergent washed only 17 plates.

EXAMPLE 10

A blend of phenylundecanes, and dodecanes, having a weight distribution of 24 and 76 weight percent, respectively, had a boiling point range of 545 to 600° F. This material was subjected to a process substantially as represented by FIG. 1. It was distilled in a first fractionation zone to recover the desired heart-cut alkylate product boiling in the range 545-570° F. That material boiling above 570° F. was charged to a second fractionation zone, wherein an intermediate fraction boiling between 570° F. and 600° F. was separated and charged to the isomerization zone. This fraction analyzed as 52% 2-phenyl-, 28% 3-phenyl-, and 20% 4-, 5-, 6-, and 7-phenyl-dodecane. That material boiling above 600° F. was rejected. In the isomerization zone, in addition to the intermediate fraction, there was present 30 mols of benzene and 0.14 mol of aluminum chloride per mol of phenyldodecane. Reaction was continued for one hour at 120° F. At the end of this time, the catalyst was separated, and the reaction product mixture was washed with water and then charged to the third fractionation zone. In this zone benzene is removed and recycled to the isomerization zone. That material boiling above 175° F. was charged to a fourth fractionation zone in which a small amount of light alkylate having a boiling range of 175° F. to 545° F. was removed and discarded. The remainder, boiling above 545° F., was mixed with fresh feed and recharged to the first fractionation zone. This process was continued until all units reached steady state.

At steady state and based on 100 pounds of feed stock, the heart-cut alkylate product amounted to 96.6 pounds; the intermediate recycle cut, 123 pounds; the heavy alkylate reject, 2.8 pounds; and the light alkylate reject, 0.6 pound.

Steady state heart-cut material was converted to a built detergent composition as described in Example 1; it washed 20 plates. The untreated mixed phenyl C₁₁-C₁₂ alkanes upon conversion to a built detergent composition washed only 16 plates.

EXAMPLE 11

A blend of phenyltridecanes and tetradecanes having a weight distribution of 52 and 48 weight percent, respectively, had a boiling point range of 590 to 660° F. This material was treated by a process substantially as represented by FIG. 1. It was distilled in a first frac-

tionation zone to recover the desired heart-cut alkylate product boiling in the range from 590-630° F. That material boiling above 630° F. was charged to a second fractionation zone, wherein an intermediate fraction boiling between 630° F. and 660° F. was separated and charged to the isomerization zone. This fraction analyzed as 52% 2-phenyl-, 27% 3-phenyl-, and 21% 4-, 5-, 6-, and 7-phenyltetradecane. That material boiling above 660° F. was rejected. In the isomerization zone, in addition to the intermediate fraction, there were present 30 mols of benzene and 0.14 mol of aluminum chloride per mol of phenyltetradecane. Reaction was continued for one hour at 120° F. At the end of this time, the catalyst was separated, and the reaction product mixture was washed with water and then charged to a third fractionation zone. In this zone benzene is removed and recycled to the isomerization zone. That material boiling above 175° F. was charged to a fourth fractionation zone in which a small amount of light alkylate having a boiling range of 175° F. to 590° F. was removed and discarded. The remainder, boiling above 590° F., was mixed with fresh feed and recharged to the first fractionation zone. This process was continued until all units reached steady state.

At steady state and based on 100 pounds of feed stock, the heart-cut alkylate product amounted to 97.8 pounds; the intermediate recycle cut, 61.3 pounds; the heavy alkylate reject, 1.8 pounds; and the light alkylate reject, 0.4 pound.

Steady state heart-cut material was converted to a built detergent composition as previously described in Example 1, and found to wash 23 plates. The untreated mixed phenyl C₁₃-C₁₄ alkanes upon conversion and formulation washed only 18 plates.

The isomerized product from Example 10, 40 parts, was combined with the isomerized product from Example 11, 60 parts, to give a C₁₁-C₁₄ alkylate mixture having a boiling range of 545° to 630° F. and essentially the weight distribution of homologs as the product of Example 7. In this mixture, essentially all of the 2- and 3-phenyl isomers of both C₁₂ and C₁₄ have been removed. A built detergent prepared from this blend washed 25 plates, compared to 23 plates and 18 plates for the product and feed stock, respectively, of Example 7.

EXAMPLE 12

Following a procedure substantially as represented by FIG. 2, a mixture of normal undecane, dodecane, tridecane, and tetradecane in a weight ratio of 10, 30, 31, and 29 percent, respectively, and having a boiling range of 385-490° F. was obtained by a typical molecular sieve separation process from a paraffinic feed stock having the same boiling point range. These hydrocarbons were chlorinated at 190° F. with gaseous chlorine to about 4.25% weight chlorine content.

The resulting chloroparaffins were charged to a first alkylation zone (a stirred tank reactor), along with benzene (10 mols per gram atom combined chlorine). At the same time red oil (from the second alkylation reactor) was fed at such a rate as to maintain 1 volume percent red oil in the first zone. The average residence time in this zone was maintained at 31 minutes at 162-167° F.

The reaction mixture from the first zone was passed into a settler, wherein the red oil phase separated and was removed. A portion of the red oil was discarded and the remainder was recycled back to the first reaction zone to maintain a constant catalyst volume in that vessel, more particularly described below. The red oil-free reaction product from this first settler was then passed into the second alkylation zone (a pump and time tank reactor) along with aluminum metal in proportions of .078 gram atom of aluminum metal per mol of chloroparaffin introduced into the first alkylation zone, respectively. In this zone the average residence time was 7 minutes at 155-162° F. The red oil in this vessel was maintained at 20-30 volume percent.

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The reaction mixture from the second zone was then passed into a second settling zone. In this zone, the red oil separated and was removed. A portion was recycled to the second reaction zone, another portion was recycled back to the first reaction zone, and a third portion was withdrawn and discarded.

The amount of red oil passed from the second settler to the first reactor was adjusted to maintain a constant catalytic activity in the first reactor. Thus, as more of the second stage red oil was fed to the first stage reactor, catalyst activity increased. The series of runs shown in Table I were carried out at several levels of catalytic activity in the first alkylation zone.

The hydrocarbon phase from the second alkylation zone was washed with water and then distilled in the first fractionation zone to remove a benzene fraction boiling below 385° F. This fraction was recycled back to the first alkylation zone. The benzene-free bottoms from the first distillation zone were then fed to a second fractionation zone in which unreacted paraffins, boiling point 385–490° F., were separated and recycled back to the chlorination zone. The undistilled material was charged to a third fractionation zone in which a light alkylate, boiling point 490–541° F., was removed and discarded. The bottoms from this zone were then fed to a fourth fractionation zone in which the heart-cut alkylate product, boiling point 541–628° F., was separated and recovered. The bottoms from this zone were then distilled in the fifth fractionation zone in which an intermediate alkylate, boiling point 630–660° F., was separated and recycled back to the first alkylation along with fresh chloroparaffin feed stock.

In each of the runs in Table I the reaction process described above was continued until all units were at steady state, at which time samples were taken for analysis and for conversion to alkylbenzene sulfonates.

As previously described the red oil activity in the first alkylation zone was adjusted by the quantity of red oil recycled from the second settler. In the tabulated runs, the quantity of recycle was adjusted and then the activity was determined at steady state conditions by determining the extent of conversion in the first alkylation zone. The results from a series of three runs is given in Table I.

TABLE I

Run No.	1	2	3
Percent conversion of alkyl chloride, first alkylation zone	59	84	97
Percent conversion of alkyl chloride, second alkylation zone	99.5+	99.5+	99.5+
Quantity of alkylate streams based on 100 pounds of phenylalkane fed to the first fractionation zone:			
(1) Light alkylate	1.3	1.4	1.2
(2) Heart-cut alkylate	91.4	91.1	91.8
(3) Heavy alkylate	7.3	7.5	7.0
(4) Recycle alkylate	42.3	32.8	62.5
Analysis of recycle alkylate:			
2-phenyltetradecane	56	52	60
3-phenyltetradecane	27	26	26
4-, 5-, 6-, 7-phenyltetradecane	17	22	14
Dishes washed by built detergent from—			
(1) Heart-cut alkylate (boiling point 545–630° F.)	22	23	20
(2) Alkylate without isomerization		18	

EXAMPLE 13

A mixture of paraffins consisting essentially of 10% undecane, 32% dodecane, 32% tridecane, and 26% tetradecane (percent by weight) was chlorinated to produce a chlorination mixture having 22 mol percent chloroparaffins. This mixture was admixed with benzene (10 mols per mol of chloroparaffin) and then divided into two portions. The larger portion (90 volume percent) was sent to a single stage alkylation reactor where it was contacted with a red oil catalyst (20 volume percent based on the chloroparaffinbenzene mixture) for an average reaction time of 28 minutes at 160° F.

The remaining 10 volume percent of the chloroparaffinbenzene mixture was fed to a second alkylation zone

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together with a 2-phenyl- and 3-phenyltetradecane mixture recycled from previous operation. Red oil was recycled to the reactor to maintain 30 volume percent red oil in the reaction zone. Hydrocarbon residence time was 39 minutes at 160° F. The degree of isomerization¹ of the 2-phenyl- and 3-phenyl isomers was a 72 percent approach to equilibrium.

Distillation of the combined products from the first and second reaction zones yielded the following fractions (after removal of benzene and paraffin):

Cut	Boiling point range, ° F.	Weight percent (on paraffin free basis)
Lt. alkylate	405–545	1.4
Heart cut	545–630	66.4
Recycle cut	630–660	24.5
Hvy. alkylate	> 660	7.7

Isomer distribution of the C₁₄ component was:

	Heart cut (vol. percent)	Recycle isomer (vol. percent)
2-phenyl	0	53
3-phenyl	4	26
4-phenyl	12	14
5, 6, 7-phenyl	84	7

When the volume of the red oil phase was changed in the isomerization stage while maintaining a constant hydrocarbon feed rate, the degree of isomerization was changed as follows:

Run No.	Hydrocarbon res. time (minutes)	Red oil in reactor (volume percent)	Degree of isomerization percent approach to equilibrium
1	39	35	73
2	25	60	77
3	55	10	53
4	12	80	84

Effluents from both alkylation zones were combined and sent to neutralization, washing, and distillation. The alkylate from Run No. 2 was sulfonated, neutralized, and compounded into a detergent which washed 23 plates.

EXAMPLE 14

In this example a procedure substantially as illustrated by FIG. 4 was followed. The feed stock consisted essentially of a mixture of C₁₁–C₁₄ paraffins and chloroparaffins in a mol ratio of 5.72 to 1, the carbon distribution by weight being 14% C₁₁, 32% C₁₂, 31% C₁₃, and 23% C₁₄. The process was carried out continuously. At steady state conditions, 37.3 mols of feed stock was combined with 62.7 mols of benzene to give an alkylation mixture, 85% of which was charged along with 2.7 mols of recycle phenyltetradecanes to the first stage alkylation reactor at a rate to maintain an average residence time in this reactor of 38 minutes. The reactor contents contained 10% by volume of red oil and were at a temperature of 160° F. After the reaction mixture had phase separated in the first settler, the hydrocarbon phase was removed and charged along with the remaining 15% of the alkylation mixture to the second stage alkylation reactor at a rate to maintain an average residence time of 6.7 minutes. The second reactor contents contained 35% by volume of red oil and were at 160° F. Aluminum metal was charged to this reactor at 0.039 gram atom per mol of chloroparaffin charged to the process. After separation in the second settler, the hydrocarbon phase was fractionally distilled to give benzene and paraffin for recycle to the alkylation and the chlorination zones, respectively; a light alkylate (B.P. 385–545° F.) which was discarded, a heart-cut alkylate (B.P. 545–630° F.), a recycle al-

¹ Degree of isomerization refers to the percent of the material isomerized, based on the material that could have isomerized at complete equilibrium; that is, degree of isomerization refers to the fractional approach to equilibrium which was achieved at steady state. A mixture of isomers has a definite composition; i.e., the ratio of isomers at equilibrium is always the same.

kylate containing phenyl tetradecanes (B.P. 630–660° F.), and a heavy alkylate (boiling above 660° F.) which was also discarded.

The heart-cut alkylbenzenes were sulfonated, neutralized, and compounded into a detergent formulation which was washed 23 plates.

Analysis of the recycle alkylate and heart-cut alkylate indicated that a 40% degree of isomerization was reached in the above experiment.

Other runs were carried out in which the volume of red oil in the second alkylation reactor was varied from 31–49% and the degree of isomerization varied from 28–50%, respectively.

We claim:

1. Continuous process for producing a biodegradable detergent alkylate having improved detergent characteristics by the alkylation in an alkylation zone of benzene by an $n\text{-C}_{10}\text{--C}_{14}$ alkyl chloride alkylating agent, at least 15% of said alkylating agent being alkyl chloride containing at least 12 carbon atoms in the alkyl group, said alkylation zone including a first reaction zone and a second reaction zone, which comprises contacting in a first reaction zone said alkyl chloride alkylating agent in the presence of a red oil alkylation catalyst complex at alkylation temperatures for a period of time sufficient to convert a major portion of the alkyl chloride, thereby producing a reaction product mixture comprising red oil catalyst, secondary phenyl-n-alkanes, alkyl chloride, benzene and hydrogen chloride, separating the red oil, and passing the red oil-free product into a second reaction zone and therein contacting it with aluminum metal at alkylation temperatures, for a period of time to convert substantially all of the alkyl chloride, separating from the effluent from the second reaction zone a red oil alkylation catalyst complex phase and an organic phase comprising a mixture of secondary n-phenylalkanes, said mixture containing terminal 2- and 3-phenyl-n-alkanes and midchain phenyl-n-alkanes, passing the red oil alkylation catalyst complex phase into the first reaction zone to supply substantially all of the red oil alkylation catalyst complex used in that zone, fractionating the mixture of secondary n-phenylalkanes into fractions, including a lower boiling fraction predominating in the midchain secondary phenyl-n-alkanes, and a higher boiling fraction consisting of phenyl-n-alkanes, having substantially the same number of carbon atoms and predominating in the terminal 2- and 3-phenyl-n-alkanes, and passing said last-mentioned fraction to the alkylation zone.

2. Process according to claim 1, wherein alkylation temperatures range from about 45° F. to 185° F., the benzene is used in an excess of 2 to 30 mols per mol of alkyl chloride alkylating agent, and at least 50% of said alkylating agent being alkyl chlorides containing at least 12 carbon atoms.

3. Continuous process for the production of superior detergent alkylate by the alkylation of benzene with alkyl chloride in a first alkylation zone followed by alkylation in a second alkylation zone, which comprises subjecting a stoichiometric excess of benzene and a mixture of $\text{C}_{10}\text{--C}_{14}$ alkyl chlorides consisting predominantly of secondary alkyl chlorides and a minor portion of primary alkyl chlorides to alkylating conditions in a first alkylation zone in the presence of a red oil catalyst complex obtained from the second alkylation zone, said red oil catalyst complex constituting about 0.5 to 30 percent by volume of the contents of said first alkylation zone, continuing alkylation in the first alkylation zone until about 85–95% of the alkyl chlorides have been converted, passing the effluent from the first alkylation zone to a first settling zone to form a first red oil phase and a first organic phase comprising secondary phenyl-n-alkanes, alkyl chlorides, benzene and hydrogen chloride, recycling a portion of the red oil catalyst phase to the first alkylation zone, discharging a portion of the red oil phase corresponding in amount to that supplied from the second

alkylation zone, so as to maintain the specified volume of red oil catalyst complex in the first alkylation zone, passing the first organic phase into a second alkylation zone, and therein contacting it with aluminum metal under alkylation conditions, continuing the alkylation until substantially all of the alkyl chloride has been converted, thereby producing a second reaction product mixture comprising benzene, red oil catalyst complex, and secondary phenyl-n-alkanes, including 2- and 3-phenyl-n-alkanes and midchain phenyl-n-alkanes, passing the effluent from the second alkylation zone to a second settler to form a second organic phase and a second red oil catalyst phase, recycling a portion of said second red oil catalyst to the second alkylation zone to maintain the specified red oil volume and passing the remainder of said second red oil catalyst to the first alkylation zone, fractionating said second organic phase into a lower boiling fraction relatively free of 2- and 3-phenyltetradecanes and a higher boiling fraction predominating in midchain phenyl-n-alkanes, then adding said higher boiling fraction to further quantities of benzene and alkyl chloride, and subjecting the resulting mixture to alkylation.

4. Process according to claim 3, wherein the red oil catalyst is present in the second alkylation zone in an amount of 5 to 80 percent by volume based on the contents of said second alkylation zone, aluminum metal is continuously fed into the second alkylation zone at a rate of 0.02 to 0.1 gram atom per gram atom of chlorine in the feed entering the first alkylation zone, and the alkylation reaction in the first and second alkylation zones is carried out at a temperature in the range of 100° to 185° F.

5. Continuous process for producing a superior detergent alkylate, which comprises reacting normal paraffinic hydrocarbons containing 10 to 14 carbon atoms per molecule with elemental chlorine in a chlorination zone to produce a chlorination product mixture consisting essentially of 10 to 50 mol percent chlorinated paraffins and 50 to 90 mol percent of unchlorinated paraffins, passing the chlorination product, and a substantial molar excess relative to the chlorinated paraffins of benzene into a first alkylation zone and therein contacting them with a red oil alkylation catalyst complex at a temperature in the range 45°–185° F. for a period of 3 to 15 minutes, to form a reaction product mixture comprising phenyl-n-alkanes, hydrogen chloride, benzene, unchlorinated paraffins and chlorinated paraffins, passing said last-mentioned reaction product mixture into a second reaction zone and therein contacting them with aluminum metal at a temperature of 45°–185° F. until substantially all of the chlorinated paraffins have reacted, separating from the effluent from the second reaction zone a red oil alkylation catalyst complex phase and an organic phase comprising unreacted benzene, unchlorinated paraffins, and phenyl-n-alkanes, including terminal 2- and 3-phenyl-n-alkanes and midchain phenyl-n-alkanes, passing the red oil alkylation catalyst complex phase into the first reaction zone to supply substantially all of the red oil alkylation catalyst complex used in that zone, distilling the organic phase to remove benzene, unchlorinated paraffins, a midchain phenyl-n-alkane fraction, and a terminal 2- and 3-phenyl-n-alkane fraction, recovering said midchain phenyl-n-alkanes, and passing said terminal 2- and 3-phenylalkanes to the first alkylation zone.

6. Process according to claim 5, wherein the benzene is present in proportions of 5 to 15 mols per mol of chlorinated paraffins, the paraffinic hydrocarbons boil in the range 345° to 490° F.; the midchain phenyl-n-alkane fraction, in the range 520° to 630° F.; and the terminal 2- and 3-phenyl-n-alkane fraction, in the range 630° to 660° F.

7. Process for producing a superior detergent alkylate, which comprises forming a mixture of benzene and a chlorination reaction product consisting essentially of 10

to 50 mol percent monochloro C_{10} - C_{14} paraffins and 50 to 90 mol percent unchlorinated C_{10} - C_{14} paraffins, at least 15% by weight, of said monochloroparaffin containing at least 12 carbon atoms in the molecule, said benzene being present in proportions of 2 to 30 mols per gram atom of chlorine in said mixture, passing a major proportion of said mixture into an alkylation zone and therein contacting it with red oil catalyst, passing a minor proportion of said mixture into a second alkylation zone and therein contacting it with aluminum metal, maintaining alkylation temperatures in said alkylation zones to convert substantially all of the monochloroparaffin to phenyl- C_{10} - C_{14} n-alkanes, including terminal 2- and 3-phenyl-n-alkanes and midchain phenyl-n-alkanes, separating the alkylation reaction product mixtures into a red oil catalyst phase and a hydrocarbon phase comprising said phenyl- C_{10} - C_{14} n-alkanes, benzene and unchlorinated paraffins, passing the red oil catalyst phase obtained from the second alkylation zone to the first-mentioned alkylation zone to supply substantially all of the red oil catalyst complex used in that zone, combining the hydrocarbon phases obtained from the alkylation zones, fractionally distilling the combined hydrocarbon phases to separate benzene, unchlorinated paraffins and a phenyl-n-alkane fraction, fractionally distilling said fraction into a lower boiling fraction of midchain phenyl-n-alkanes relatively free of terminal 2- and 3-phenyltetradecanes, and a higher boiling fraction predominating in 2- and 3-phenyltetradecanes, and passing said higher boiling fraction to the second alkylation zone.

8. Process for producing a superior detergent alkylate, which comprises forming a mixture of benzene and the product resulting from the chlorination of C_{11} - C_{14} n-paraffins boiling in the range 385° to 490° F., said product consisting essentially of 15-30 mol percent monochlorinated C_{11} - C_{14} n-paraffins and 70-85 mol percent unchlorinated C_{11} - C_{14} n-paraffins, said benzene being present in proportions of 2 to 30 mols per gram atom of chlorine in said chlorination product, passing a major proportion of said mixture into an alkylation zone maintained at a temperature in the range 150-170° F., and in the presence of red oil catalyst in proportions of 10 to 40 volume percent based on the contents of said alkylation zone, passing a minor proportion of said mixture into a second alkylation zone at a temperature in the range 150-170° F., and therein contacting it with aluminum metal at a rate of 0.02 to 0.1 gram atoms per gram atom of chlorine in said chlorination product, maintaining a red oil catalyst concentration of 10 to 60 percent by volume of the contents in the second alkylation zone, the residence times in the alkylation zones being, respectively, 20 to 45 minutes and 10 to 25 minutes, withdrawing effluent from the alkylation zones, settling said effluents to form a red oil catalyst phase and a hydrocarbon phase comprising benzene, unchlorinated paraffins, and secondary phenyl-n-alkanes boiling in the range 545° to 660° F., recycling a portion of the red oil catalyst phase from the first-mentioned alkylation zone back to said alkylation zone and discarding a portion as spent catalyst, recycling a portion of the catalyst phase from the second alkylation zone and passing the remainder to the first-mentioned alkylation zone in quantities sufficient to maintain the aforesaid red oil catalyst concentrations, combining the hydrocarbon phases from the alkylation zones, fractionally distilling the combined hydrocarbon phase to obtain a fraction boiling in the range 545° to 630° F. and another fraction boiling in the range 630° to 660° F., and passing said last-mentioned fraction to the second alkylation zone.

9. Process for producing a superior detergent alkylate, which comprises forming a mixture of benzene and a chlorination reaction product consisting essentially of 10 to 50 mol percent monochloro C_{10} - C_{14} paraffins and 50 to 90 mol percent unchlorinated C_{10} - C_{14} paraffins, at

least 15% by weight, of said monochloroparaffin containing at least 12 carbon atoms in the molecule, said benzene being present in proportions of 2 to 30 mols per gram atom of chlorine in said mixtures, passing a major proportion of said mixture into an alkylation zone and therein contacting it with red oil catalyst, passing a minor proportion of said mixture into a second alkylation zone and therein contacting it with aluminum metal, maintaining alkylation temperatures in said alkylation zones to convert substantially all of the monochloroparaffin to phenyl- C_{10} - C_{14} n-alkane alkylation reaction product mixtures, including terminal 2- and 3-phenyl-n-alkanes and midchain phenyl-n-alkanes, separating the alkylation reaction product mixtures into a red oil catalyst phase and a hydrocarbon phase comprising phenyl- C_{10} - C_{14} n-alkanes, benzene and unchlorinated paraffins, passing the red oil catalyst phase obtained from the second alkylation zone to the first-mentioned alkylation zone to supply substantially all of the red oil catalyst complex used in that zone, passing the hydrocarbon phase obtained from the first alkylation zone to the second alkylation zone, fractionally distilling the hydrocarbon phase of the second alkylation zone to separate benzene, unchlorinated paraffins and a phenyl-n-alkane fraction, fractionally distilling said fraction into a lower boiling fraction of midchain phenyl-n-alkanes relatively free of terminal 2- and 3-phenyl-n-alkanes, and a higher boiling fraction predominating in 2- and 3-phenyl-n-alkanes, and passing said higher boiling fraction into the first-mentioned alkylation zone.

10. Process according to claim 9, wherein in the first-mentioned alkylation zone the red oil catalyst forms 5 to 80 volume percent of the contents of that zone, the residence time is 6 to 60 minutes; and in the second alkylation zone, aluminum metal is introduced at a rate of 0.02 to 0.1 gram atom per mol of total chloroparaffin fed to the two reaction zones, the red oil catalyst forms 5 to 80 volume percent of the contents, and the residence time is 0.3 to 60 minutes, the alkylation temperatures ranging from 45° to 185° F.

11. Process according to claim 9, wherein the first-mentioned alkylation zone the red oil catalyst forms 10 to 40 volume percent of the contents; and in the second alkylation zone, 10 to 60 volume percent of the contents.

12. The cyclic process for preparing a biodegradable detergent alkylate having improved detergent properties which comprises alkylating benzene with monochlorinated C_{10} - C_{14} n-alkanes, at least 15% by weight of said monochlorinated n-alkanes having at least 12 carbon atoms in the molecule, in the presence of a Friedel-Crafts catalyst in an alkylation zone to produce a mixture of secondary phenyl-n-alkanes, fractionating the resulting mixture of secondary phenyl-n-alkanes into fractions including a lower boiling fraction predominating in the midchain secondary phenyl-n-alkanes and a higher boiling fraction predominating in the 2- and 3-phenyl-n-alkanes, recycling said higher boiling fraction predominating in the 2- and 3-phenyl-n-alkanes to the alkylation zone and recovering as the improved detergent alkylate the fraction predominating in the midchain phenyl-n-alkanes.

13. Process according to claim 12 wherein benzene is present in proportions of 2-30 mols per mol of chloroalkane, at least 50% of the monochlorinated n-alkane having at least 12 carbon atoms in the molecule, and the Friedel-Crafts catalyst is an $AlCl_3$ catalyst.

14. Process according to claim 13, wherein said lower boiling fraction has an initial boiling point of about 545° F., and an end point of about 630° F.; and said higher boiling fraction has an end boiling point of about 660° F., and an initial boiling point of about 630° F.

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