

1

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**DETERGENT ALKYLATE COMPOSITION OF
SECONDARY PHENYL-SUBSTITUTED n-
ALKANES**

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The present invention relates to a unique composition of aryl-substituted n-alkanes. More particularly, the invention is concerned with detergent alkylate intermediate convertible into biologically soft detergent having, in addition, good deterative properties.

For a great number of years the bulk of detergent alkylate used to make the finished detergent composition by conversion to the sulfonic acid, followed by neutralization, has been the monophenyl-substituted polypropylene 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 alkyl 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 aryl-substituted alkanes in which the hydrocarbyl or alkyl radical is derived from straight-chain or normal hydrocarbons.

Detergent alkylate compositions consisting essentially of a mixture of secondary phenyl-substituted n-alkanes of 11-14 carbon atoms have excellent biodegradability and can be prepared in known fashion by a number of reactions. Conventional reactions involve catalytic alkylation of benzenes 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 materials 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.

By whatever method the detergent alkylate is prepared, its finished form meets the requirements of biodegradability, but does not possess the detergency effectiveness of the phenyl-substituted polypropylene derived detergents. It has now unexpectedly been found that the deficiency in deterative power is due to the widespread composition, particularly as to the isomer distribution that results when the aryl or aromatic compound is alkylated with the straight-chain stock. Mixtures of phenyl-substituted n-alkanes are produced upon alkylation of benzene with a C₁₁-C₁₄ alkyl chloride or olefin mixture. These include the terminal or end-chain 2- and 3-phenyl alkanes, the intermediate 4-phenyl alkanes and the mid-chain 5-, 6-, and 7-phenyl alkanes.

Broadly, the invention is based on the discovery that the presence of the terminal 2- and 3-phenyl alkanes impairs the deterative effectiveness of the alkylate mixture, and that by increasing the proportion of the mid-chain 5-, 6- and 7-phenyl alkane isomers, detergency is enhanced.

Accordingly, in one embodiment of the invention, a

2

detergent alkylate composition is contemplated consisting essentially of secondary phenyl-substituted n-alkanes having 11 to 14 carbon atoms in the alkane portion of the molecule. At least 50% by weight of the composition consists of phenyl-substituted n-alkanes having 12 to 14 carbon atoms in the alkane portion of the molecule, a major proportion of which is mid-chain phenyl-substituted alkanes; 5 to 30%, preferably 5 to 15%, by weight, of intermediate 4-phenyl alkane; and a minor proportion of 2- and 3-phenyl alkane below about 35%, generally below 20%, and preferably below 10%, by weight, of the C₁₂-C₁₄ phenyl alkanes.

Surprisingly, the 2- and 3-phenyl undecanes, as well as the 4-phenyl and mid-chain phenyl undecanes, can be tolerated in relatively large amounts. Indeed, these terminal phenyl alkanes manifest better detergency properties than the mid-chain 5- and 6-phenyl undecanes. Therefore, satisfactory detergent alkylate compositions can contain up to 50% by weight, generally below 30%, and often 5-10% by weight of phenyl-substituted undecanes, the remainder of the detergent alkylate having the characteristics described above.

In accordance with the invention, the detergent alkylate compositions can be composed of the phenyl-substituted alkanes of a single number carbon fraction, for example, the phenyl isomers of dodecane, or of tridecane or of tetradecane, again the proportions of the various isomers being as specified above.

Most conveniently, the alkylate mixture can be prepared from a mixture of at least two homologous carbon fractions, for example, a mixture of phenyl-substituted tridecanes and tetradecanes, again the proportions of the various position isomers and the content of phenyl-substituted n-alkanes being as specified above.

Homologous mixtures as above described are readily obtained by the process of alkylation. For example, one convenient way is to effect alkylations of benzene and chlorinated paraffins, or alkanes, in the presence of AlCl₃ 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 number carbon fraction or to a blend of multiple number carbon fractions containing all of the C₁₁-C₁₄ homologs, the various homologs being present in approximately equal molar proportions.

The terminal 2- and 3-phenyl isomers of a given carbon number, because of their higher boiling point, are separable from more centrally attached phenyl alkane isomers by simple distillation. Therefore, mixtures of phenyl alkanes can be prepared having the desired 2- and 3-phenyl alkane content by separating the 2- and 3-phenyl isomers from one fraction and the 2- and 3-phenyl alkane content from another fraction, the fractions remaining having a higher proportion of the more centrally phenyl attached isomers being combined. For example, a fraction containing phenyl undecanes and phenyl dodecanes is treated by distillation to lower the 2- and 3-phenyl dodecane content, and the resulting mixture combined with a mixture of phenyl tridecanes and tetradecanes, from which also the 2- and 3-phenyl tetradecanes have been removed. As can readily be appreciated when proceeding in this manner, the proportions of the various homologs can vary. In general, however, in any mixture of homologs, any one homolog will be present in a proportion of at least 25% by weight of the homologous mixture.

Accordingly, in a particular useful embodiment of the invention, a detergent alkylate composition of a mixture of phenyl-substituted alkanes is contemplated, substantially all of said mixture consisting of phenyl-substituted alkanes containing 11 to 14 carbon atoms in the alkane portion of the molecule. The said mixture is further characterized in that 5 to 30%, by weight, of the mixture

is phenyl undecanes, while the remainder of the mixture consists of phenyl alkanes having 12 to 14 carbon atoms in the alkane portion of the molecule, and contains at least 25%, based on said remainder, each of phenyl dodecanes, phenyl tridecanes and phenyl tetradecanes. Moreover, said remainder consists of at least about 45% of phenyl-substituted alkanes other than the 2-, 3- and 4-phenyl alkanes, the aggregate content of 2- and 3-phenyl tetradecanes being less than 4 percent.

The detergency effectiveness of the alkylate compositions of the present invention is manifested by mixtures of the sulfonate derivative, obtained in conventional fashion, with so-called heavy duty detergent builders, in which the sulfonate can be present in proportions of 10 to 30% by weight of the finished composition. As is known in the art, these detergent builders are principally condensed inorganic phosphate detergent salt builders, used in conjunction with nonsoap synthetic surfactants to produce heavy duty detergent compositions. They can be used in their commercially available anhydrous form, obtained by the high temperature dehydration of the orthophosphates-tripolyphosphates, from a mixture of disodium orthophosphate and monosodium orthophosphate; tetrasodium pyrophosphates, from disodium orthophosphate; and sodium polymetaphosphates, from orthophosphate. The various condensed phosphates can be used singly or in admixture. As is known in the detergent art, the proportions of the various phosphates are frequently altered in practice, and similar practice can prevail here. Generally, good results are obtained when tripolyphosphate is essentially the sole condensed phosphate, or is admixed with the other condensed phosphates, for example, 80% tripolyphosphate and 20% pyrophosphate.

Other compatible optional ingredients which are particularly useful in the preparation of the compositions herein contemplated are those customarily present in heavy duty detergent formulations. These include, in weight amounts, based on the composition: an anticorrosion and stabilizing agent, such as sodium silicate, wherein the SiO_2 -to- Na_2O ratio can range from $\frac{1}{2}$ to $\frac{3}{4}$, in proportions of, for example, 5%; an antiredeposition agent, such as sodium carboxymethyl cellulose, as described, for example, in U.S. Patent No. 2,568,334, proportions of about 1 to 3% being cited as illustrative; a foam modifier, such as a mono- or diethanolamide of a fatty acid, such as lauric isopropanolamide, in proportions, for example, of 5%; a chemical bleaching agent, such as sodium perborate or sodium percarbonate, for example, in an amount of 2 to 5%; optical whiteners, in amounts of the order of 0.1 to 0.2%, such as the triazinyl and aroylstilbenes, benzidinesulphones, bisbenzimidazoles, triazoles, and amino coumarins; sequestering agents, in amounts, for example, of the order less than 1%, such as tetrasodium ethylene diamine; finally, certain inorganic

salts, up to about 30%, such as inorganic sulfate, carbonate, or borate.

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." This test is based on a procedure presented at the ASTM D-12 Subcommittee on Detergents, March 10, 1959, New York, N.Y.

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.

Five thousand eight hundred fifty ml. of washing water adjusted to the desired hardness and at a temperature of 117° F. are placed in an 8000 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 150 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. The water from the container is drained into 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 dishwater and washing continued, this procedure being repeated until the foam collapses in the dishpan. At this point the surface is nearly devoid of foam. A detergent formulation capable of washing at least twenty plates and preferably at least twenty-four plates is regarded as suitable.

The following tabulated examples illustrate the practice of the invention, the column headed "Plates" indi-

Ex. No.	Plates	Percent C_{11}	Percent C_{12} - C_{14}				Based on the C_{12} - C_{14} Portion											
							Percent Mid-Chain				Percent 4 ϕ				Percent 2 plus 3 ϕ			
			C_{12}	C_{13}	C_{14}	Total	C_{12}	C_{13}	C_{14}	Total	C_{12}	C_{13}	C_{14}	Total	C_{12}	C_{13}	C_{14}	Total
1	18	16	32	32	20	84	13.1	16.4	11.9	41.4	5.7	4.5	2.6	12.8	19.4	17.1	9.3	45.8
2	19	9	37	41	13	91	14.3	19.3	12.4	46	6.3	5.4	1.4	13.1	20.1	20.4	0.4	40.9
3	24	9	31	34	26	91	12	15	22.8	49.8	5.1	4.8	4.3	14.2	17.1	17.5	1.4	36
4	24	8	13	35	44	92	4.8	16.4	41.4	62.6	2.1	4.6	4.9	11.6	7.3	17.1	1.4	25.8
5	29	10	30	39	21	90	29.2	42	22.3	93.5	4.1	1.2	0.8	6.1	0.4	0	0	0.4
6	18	0	0	100	0	100	43	0	0	43	0	12	0	12	45	0	0	45
7	24.5	0	0	100	0	100	0	63	0	63	0	12	0	12	0	25	0	25
8	29	0	0	100	0	100	85	0	0	85	0	10	0	10	5	0	0	5
9	16	0	0	0	100	100	50	0	0	50	0	11	0	11	0	39	0	39
10	20	0	0	0	100	100	66	0	0	66	0	13	0	13	21	0	0	21
11	26.5	0	100	0	0	100	84	0	0	84	14	0	0	14	2	0	0	2
12	18	0	48	52	0	100	16.3	22.4	0	38.7	7.2	6.2	0	13.4	24.5	23.5	0	47.9
13	24	0	48	52	0	100	16.3	44.2	0	60.5	7.2	5.2	0	12.4	24.5	2.6	0	27.1
14	5	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
15	30	0	35	36	29	100	26	29.2	23	78.2	7.6	5	4.1	16.7	1.3	2.3	1.5	5.1
16	24.5	47.5	0	0	52.5	52.5	0	0	87	87	0	0	10	10	0	3	0	3
17	25	0	0	100	0	100	0	53	0	53	0	31	0	31	0	16	0	16
18	31	0	0	100	0	100	0	96	0	96	0	4	0	4	0	0	0	0

cating the number of plates washed in accordance with the previously described test.

In the examples the sulfonate is produced by sulfonating the detergent alkylate intermediate, followed by neutralization with sodium hydroxide and drying. The resulting sulfonate product is compounded into a built detergent composition analyzing as follows, by weight: 25% sodium alkylbenzene sulfonate, 40% trisodium polyphosphate, 7% sodium silicate, 1% carboxy methyl cellulose, 19% sodium sulfate, and 8% water.

Referring to the table, Experiment 1 represents a phenyl alkane mixture obtained by the alkylation reaction of benzene and chlorinated paraffins having 11 to 14 carbon atoms. The sulfonate of the alkylate when compounded into a heavy duty detergent composition as described above washes eighteen dishes. It will be noted that the 2- and 3-phenyl C_{12} - C_{14} alkanes content is 45.8%. Progressively lowering the 2- and 3-phenyl alkane content gives increasingly better results as shown in Experiments 2-5.

Substantially the same effect is noted using a single carbon number fraction, that is, one in which the phenyl alkanes have the same number of carbon atoms, as shown in Experiments 6-8 (C_{13}); Experiments 9-10 (C_{14}); and Experiment 11 (C_{12}).

In Experiments 12 and 13, mixtures of two homologous fractions (phenyl C_{13} and C_{14} alkanes) are shown the effects of decreasing 2- and 3-phenyl alkane content.

On the other hand, a mixture consisting of phenyl undecanes gives poor results, as shown in Experiment 14. Although no phenyl undecanes need be present, as indicated in Experiment 15, up to 50% phenyl undecanes can be tolerated as shown in Experiment 16.

Finally, the 4-phenyl content of mixtures contemplated by the present invention can vary widely as shown in Experiments 17 and 18.

What is claimed is:

1. A detergent alkylate composition consisting essentially of secondary phenyl-substituted n-alkanes, 5 to 50% by weight of said phenyl-substituted n-alkanes having 11 carbon atoms in the alkane portion of the molecule, the remainder of said phenyl-substituted n-alkane having 12 to 14 carbon atoms in the alkane portion of the molecule, said remainder consisting of a major proportion of mid-chain substituted phenyl alkanes, from 5 to 30% by weight of 4-phenyl alkanes, and a minor proportion of 2- and 3-phenyl alkanes not exceeding about 35% by weight.

2. Composition according to claim 1, wherein the C_{12} - C_{14} 4-phenyl alkanes range from 5 to 15 percent.

3. Composition according to claim 2 wherein the phenyl-substituted n-alkane having 11 carbon atoms is present in an amount of 5 to 10 percent.

4. A detergent alkylate composition consisting essentially of secondary phenyl-substituted n-alkanes having 11 to 14 carbon atoms in the alkane portion of the molecule, at least 50% by weight of said composition being a mixture of secondary phenyl-substituted n-alkanes of

at least two homologous fractions selected from the group consisting of C_{12} , C_{13} and C_{14} n-alkane homologous fractions, a major proportion of said mixture consisting of mid-chain phenyl-substituted n-alkanes, from 5 to 30% by weight of 4-phenyl-substituted alkanes and a minor proportion of 2- and 3-phenyl alkanes not exceeding 35% by weight.

5. A composition according to claim 4 wherein the 4-phenyl-substituted n-alkanes are present in an amount of 5 to 15%, and the 2- and 3-phenyl alkanes do not exceed 20 percent.

6. Composition according to claim 5, wherein the composition contains 5 to 50% by weight of phenyl-substituted alkanes containing 11 carbon atoms in the alkane portion.

7. A detergent alkylate composition consisting essentially of a mixture of phenyl-substituted alkanes, substantially all of the mixture consisting of phenyl-substituted alkanes containing 11 to 14 carbon atoms in the alkane portion of the molecule, 5 to 30% of the mixture consisting of phenyl undecanes, substantially all of the remainder of the mixture consisting of phenyl alkanes containing 12 to 14 carbon atoms in the alkane portion of the molecule and containing at least 25% each of phenyl dodecanes, phenyl tridecanes and phenyl tetradecanes, said remainder consisting of at least 45% of phenyl-substituted alkanes other than the 2-, 3- and 4-phenyl alkanes, and said remainder having an aggregate content of 2- and 3-phenyl tetradecanes less than 4 percent.

8. A detergent alkylate composition consisting essentially of secondary phenyl-substituted n-alkane within the range of 11 to 14 carbon atoms in the alkane portion of the molecule with at least 50% by weight of said composition composed of secondary phenyl-substituted n-alkanes wherein the alkane portion contains 12, 13 and 14 carbon atoms and in which the phenyl attachment to said n-alkane is predominantly in the 4, 5, 6 and 7 position and a minor proportion of 2- and 3-phenyl alkanes in the phenyl-substituted C_{12} - C_{14} n-alkane portion of said composition which does not exceed 35% by weight.

9. Composition according to claim 8 wherein the 2- and 3-phenyl alkanes of the phenyl-substituted C_{12} - C_{14} n-alkane portion of said composition does not exceed 20 percent.

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