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2,903,485

ALKYLPHENOXYPOLYETHOXYALKANOLS

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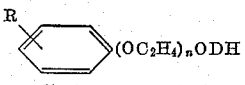
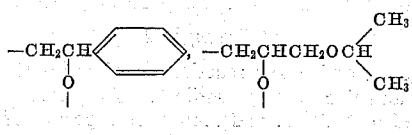
10 Claims. (Cl. 260—613)

This invention deals with specific alkylphenoxypolyethoxyalkanols as new compositions of matter. It further concerns a method for the preparation of these compositions.

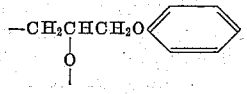
The compounds of this invention may be represented by the formula



in which R is an alkyl group of six to twelve carbon atoms, D is one of the groups —$C_8H_{16}O$—,



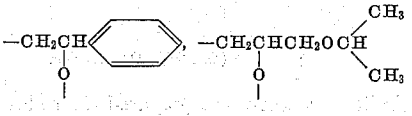
or



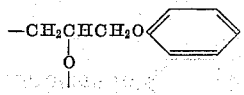
and *n* is an integer of ten to thirty-five.

R may represent a hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl group in any of the known spatial configurations such as normal, iso, tertiary, and the like. R may occupy any possible ring position with a para location with respect to the ether chain preferred.

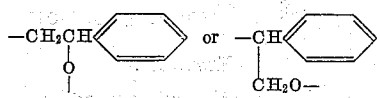
The groups represented by the symbol D may be represented by the formulas —$C_8H_{16}O$—,



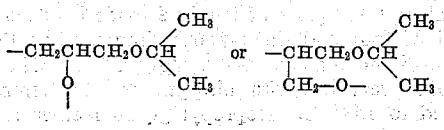
and



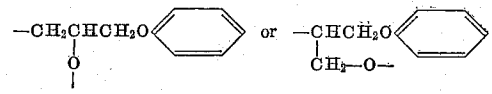
and are derived from octylene oxide, styrene oxide, isopropyl glycidyl ether, and phenyl glycidyl ether, respectively. Actually, the spatial representations of the D groups are those that are most likely, based on the best analytical and theoretical considerations. It may be possible that the D group derived from styrene oxide, for instance, may be represented as either



with the former formula more probable. Also, the D groups derived from isopropyl glycidyl ether and phenyl glycidyl ether may be represented by either



or either



respectively, with the former representations more probable. The group —$C_8H_{16}O$— as a representation of D may have the oxygen atom positioned at any possible chain location although the terminal location is more readily obtained. The foregoing and following formulas containing the defined D groups must be construed in the light of the above discussion in that the more likely formula is given. Nevertheless the other spatial possibilities are encompassed within this invention.

The number of ethylene oxide groups in the above compound varies from ten to thirty-five. It is important in the present compounds that, while the number of ethylene oxide units varies within the defined range, only a single unit of D is employed. While it is possible to have a second unit of D in the present compound, such is not desirable or advantageous because, it is difficult to attach the second unit of D and, even with the second unit of D, results obtained are no better or possibly worse than with a single unit of D. Only by strict adherence to the structure just defined can the desirable results of this invention be obtained.

The products of this invention are generally pale yellow liquids, although some approach colorlessness. These products exhibit excellent detergency, particularly on glass, plastic, metal, wool, and cotton. They also have satisfactory cloud points and exhibit very slight or no foam especially at normal temperatures of use. They also possess the valuable properties of low solidification temperature and stability in built formulations. Surprisingly, the compounds of this invention possess all of the above properties to a highly advantageous degree which makes them available for many important applications, particularly commercial and residential automatic dishwashing and textile cleansing, unavailable to compounds that otherwise have some structural similarities.

It is known in the art that various alkylene oxides can be added to compounds having reactive hydrogen atoms to form compounds that are surface active. The known compounds generally suffer from one or more deficiencies with regard to the above-enumerated properties, the absence of any one of which can act as a bar to many practical applications. For instance, many otherwise acceptable detergents exhibit high foam which bars their use in many applications. others are unstable in built formulations and become discolored in an unsightly way frequently with concurrent diminution of detersive properties; others tend to become very viscous even to the point of solidification even in the range of normal room temperatures which bars their use in automatic dispensing units; others have unsatisfactory cloud points under normal storage conditions. The unique compounds of this invention suffer no such limitations and, hence, have a wide range of valuable applications not available to the known compounds.

The unusual characteristics and concurrent advantageous uses of the present compounds are apparently based on the critical hydrophobic-hydrophilic balance caused by the relationship between the R group, the D group, and the remainder of the molecule. This is a surprising result in the light of the teaching of the art.

The foam characteristics of the present compounds were evaluated by employing 1.0% by weight of a selected instant compound in a constant volume of constant temperature water (135° F.) in a standard commercial dishwasher, observing the speed of the rotor spray arm, and comparing the speed of the rotor spray arm when the

same volume of same temperature of water was used as a blank. The speed of the rotor spray arm in revolutions per minute for water alone was 100. For a detergent to be commercially acceptable it must give a value of about 75 and preferably 80 or above. The present compounds consistently give values ranging between 90 and 100. On the other hand, similar alkylphenoxypolyethoxyalkanols not having the single unit of the defined D groups gave values below 30 down to the point of stalling the motor, with concurrent serious diminution of cleansing powers reduced to the range of unacceptability.

Dishwashing detersive characteristics were determined by the Fineman dynamic hard surface detergency test in which the compound under test was evaluated against glass, steel, and plastic substrates. The present compounds gave excellent results on all three substrates both as to cleansing efficiency and prevention of redeposition of soil. These compounds are also effective textile detergents, particularly for removal of oily carbon from cotton and wool.

It is important in most practical applications that a detergent have a cloud point appreciably above the normal temperature at which it is to be stored. This is even more significant where automatic dispensing units are contemplated. If the cloud point of a detergent is too low, undesired stratification occurs from its aqueous solutions so that, especially on prolonged storage, the concentration of any given portion of the stratified aqueous detergent system is unpredictable and, therefore, highly undesirable. Under such circumstances it is highly problematical what detersive effects will be realized. As a general rule it is advantageous for a detergent to have a cloud point at least above normal room temperatures. The instant compounds have cloud points that are entirely acceptable, usually ranging from about 50° C. and up as determined in 1% distilled aqueous systems by a standard method.

The compounds of this invention have very low solidification temperatures. This is significant in that the present compounds may be stored in containers in cooled temperatures and still be pourable and, therefore, readily transferable and usable. Many alkylphenoxypolyethoxyalkanols lacking the exact formula of the present compounds are at least semi-solids at room temperatures and, therefore, must be stored with care or reheated in order to restore pourability.

If desired, the compounds of this invention may be built into desirable formulations by employing borates, carbonates, silicates, phosphates, and the like, in known ways. These formulations are effective and stable.

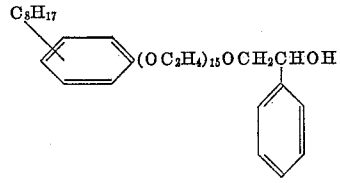
The compounds of this invention are prepared by reacting an alkylphenol with ethylene oxide in the temperature range of 130° to 200° C., preferably, 170° to 195° C., in the presence of a strong basic catalyst such as sodium, potassium, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium ethoxide, and the like. Pressures from atmospheric to about thirty pounds per square inch gauge may be advantageously employed. Following the ethylene oxide addition there is added, in a similar way and under similar reaction conditions, either phenyl glycidyl ether, styrene oxide, octylene oxide, or isopropyl glycidyl ether. The product is isolated in yields consistently above 85% by neutralizing the catalyst, steam stripping if necessary until residual oxide odors disappear, and then by stripping off water, preferably under reduced pressure. If desired, the product may be filtered to remove minor amounts of colored bodies but such is not usually necessary.

The compounds of this invention and the method of their preparation may be more fully understood from the following illustrative examples in which parts by weight are used throughout.

Example 1

There are added to a reaction vessel 153 parts of octylphenol and one part of powdered potassium hydroxide. The system is flushed out with nitrogen and the temperature raised to 185° C. Ethylene oxide is slowly introduced over a period of three hours, while the reaction temperature is heated at 195° to 200° C. A total of 495 parts of ethylene oxide is added.

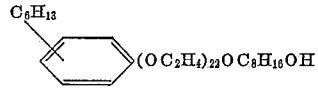
Into another reaction flask there is charged 200 parts of the above octylphenoxypolyethoxyalkanol. The system is swept out with nitrogen and then 33.4 parts of styrene oxide is added over a 60-minute period, while the temperature of the reaction mixture is heated at 178° to 183° C. The temperature is maintained at that level for six hours after the styrene oxide addition. The product is neutralized with aqueous 96% sulfuric acid, then washed with water in toluene. The water layer is discarded and the mixture of toluene and product is stripped to 120° C. under water vacuum to remove the toluene. The product is filtered and identified as the compound apparently having the formula



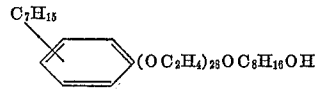
In a similar way, there are prepared the corresponding products having 10, 24, 32, and 35 ethylene oxide units.

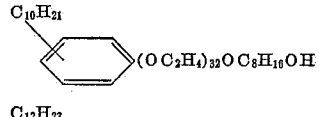
Example 2

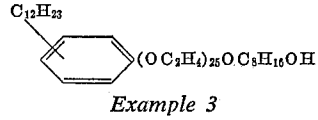
There are added to a reaction vessel 356 parts of hexylphenol and five parts of sodium. The reaction mixture is heated to 145° C. and then over a period of two and one-half hours, 1,936 parts of ethylene oxide is introduced while the temperature is heated at 160° to 188° C. The system is flushed out with nitrogen and there is then added over a 50-minute period 256 parts of octylene oxide during which time the temperature is maintained at 176° to 187° C. The temperature is maintained at this level for two hours after the octylene oxide addition. The product is neutralized with sulfuric acid, then washed with water and toluene. The water layer is discarded and the toluene then stripped off under water vacuum at 120° C. The product is filtered and is identified as the compound having the formula



In a similar way there are prepared the following compounds:



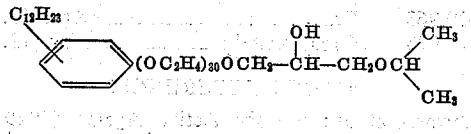




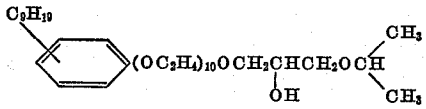
Example 3

Into a reaction vessel there are added 262 parts of dodecylphenol and three parts of sodium methoxide. The system is swept with nitrogen and the reaction is heated to 154° C. at which time ethylene oxide is introduced. A total of 1,320 parts of ethylene oxide is added over a period of four and three-quarter hours, while the temperature is maintained at 170° to 195° C. The system is again swept out with nitrogen and the temperature adjusted to 158° C. Isopropyl glycidyl ether is slowly

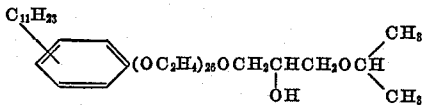
added and the temperature raised to 185° to 192° C. A total of 115 parts of isopropyl glycidyl ether is added over a period of one and one-half hours. The reaction mixture is neutralized with sulfuric acid and steam stripped. Water is removed by heating the mixture up to 148° C. under water vacuum. The mixture is filtered and the product is collected as the filtrate. The product corresponds to the compound having the formula



In like manner, there are prepared the following compounds:

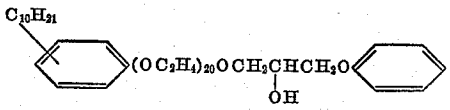


and

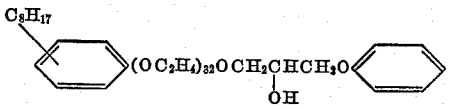


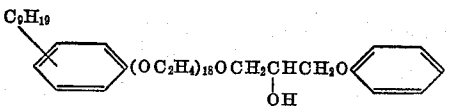
Example 4

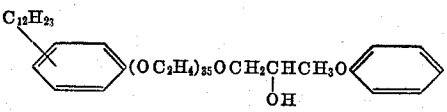
There are added to a reaction vessel 187.2 parts of decylphenol and two parts of sodium hydroxide. The temperature of the reaction mixture is raised to 170° C. and then ethylene oxide is introduced. A total of 704 parts of ethylene oxide is added over a period of four hours while the temperature is maintained at 172° to 190° C. The system is swept out with nitrogen and there is then added over a period of four hours 120 parts of phenyl glycidyl ether while the temperature is heated at 190° to 198° C. The product is neutralized with aqueous sulfuric acid and washed with water and toluene. The water layer is discarded and the toluene is removed by steam stripping under water vacuum at 100° C. The mixture is filtered and the product is collected as the filtrate. The product corresponds to the compound having the formula



In an analogous way there are prepared compounds having the following formulas:

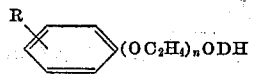




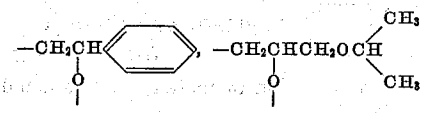


We claim:

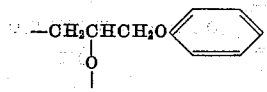
1. As a composition of matter the compound having the formula



in which R is an alkyl group of six to twelve carbon atoms, *n* is an integer of ten to thirty-five, and D is a member from the class consisting of —$C_8H_{16}O$—,

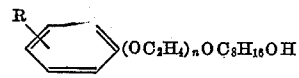


and



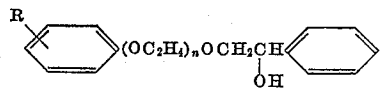
in which the terminal hydrogen atom of the said ODH-group is attached to the free oxygen valence of the said D-group.

2. As a composition of matter the compound having the formula



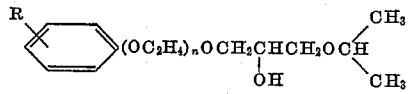
in which R is an alkyl group of six to twelve carbon atoms and *n* is an integer of ten to thirty-five.

3. As a composition of matter the compound having the formula



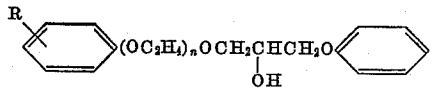
in which R is an alkyl group of six to twelve carbon atoms and *n* is an integer of ten to thirty-five.

4. As a composition of matter the compound having the formula



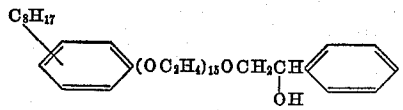
in which R is an alkyl group of six to twelve carbon atoms and *n* is an integer of ten to thirty-five.

5. As a composition of matter the compound having the formula

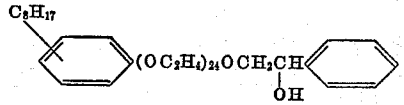


in which R is an alkyl group of six to twelve carbon atoms and *n* is an integer of ten to thirty-five.

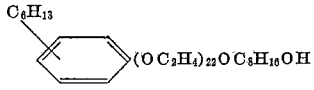
6. As a composition of matter the compound having the formula



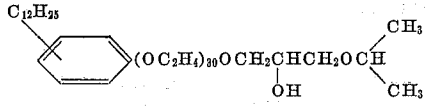
7. As a composition of matter the compound having the formula



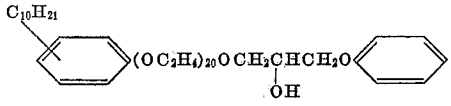
8. As a composition of matter the compound having the formula



9. As a composition of matter the compound having the formula



10. As a composition of matter the compound having the formula



References Cited in the file of this patent

UNITED STATES PATENTS

2,213,477	Steindorff et al.	Sept. 3, 1940
2,596,091	Benneville	May 13, 1952
2,596,092	Benneville	May 13, 1952
2,609,344	Johnson	Sept. 2, 1952

FOREIGN PATENTS

1,120,963	France	Apr. 23, 1956
770,073	Great Britain	Mar. 13, 1957

OTHER REFERENCES

Schwartz et al.: Surface Active Agents (1949), pp. 17, 18, 19, 202, 203, 204.