

## UNITED STATES PATENT OFFICE

2,596,093

## SURFACE-ACTIVE POLYGLYCOL ETHERS

Peter L. de Benneville, Philadelphia, Pa., assignor  
to Rohm & Haas Company, Philadelphia, Pa., a  
corporation of Delaware

No Drawing. Application March 23, 1950,  
Serial No. 152,520

7 Claims. (Cl. 260—611)

1

This invention relates to non-ionic capillary active compounds which are useful wetting, dispersing, emulsifying, and cleaning agents. It also relates to a process by which these compounds are prepared.

They are represented by the formula



wherein  $R^1$  is an alkyl group of at least six carbon atoms,  $R^2$  and  $R^3$  are hydrogen or the methyl group,  $Ar$  is a hydrocarbon group of the benzene or naphthalene series, and  $n$  is a number of at least six. The process by which these compounds are prepared comprises reacting a halomethylated alkylated aromatic hydrocarbon with about an equimolar amount of a polyethylene glycol in the presence of an alkali metal hydroxide.

Although long-chained alcohols, phenols, carboxylic acids, non-tertiary amines and other compounds having a reactive hydrogen atom have been reacted with ethylene oxide to yield polyether alcohols, there has heretofore been no practical method for the preparation of polyether alcohols having as a terminal ether group a long-chained benzyl naphthylmethyl group. The method by which such compounds are now prepared rests on a novel reaction which permits use of different types of starting material than have hitherto been utilized to provide non-ionic surface-active agents. It also allows some latitude in the choice of the starting materials which provide the hydrophobic portion of the surface-active compounds synthesized therefrom. These compounds differ from previously known phenolic derivatives in avoiding an ether linkage directly to a phenyl ring.

Alkylbenzyl and alkyl naphthylmethyl halides are available from the simple aromatic hydrocarbons, benzene, toluene, xylene, naphthalene, and methylnaphthalene through alkylation followed by haloalkylation. The alkyl group may be obtained from olefins of six or more carbon atoms, alcohols, or alkyl halides. Another method of obtaining an alkyl substituent is through introduction of an acyl group by the Friedel-Crafts reaction followed by reduction. The methods based on use of olefine, alcohol, or alkyl halide are well known. There may, however, be mentioned the method in which hydrocarbon groups can be obtained from petroleum hydrocarbons. For example, kerosene can be chlorinated and the alkyl chlorides obtained condensed with benzene, toluene, xylene, naphthalene, or a methylated naphthalene under the influence of aluminum chloride or the like.

2

The alkylated aromatic hydrocarbons of particular interest are those having an alkyl group of six to eighteen carbon atoms, and preferably eight to twelve carbon atoms, attached to a benzene or naphthalene nucleus. The presence of one or two methyl groups on the ring does not interfere with the reactions. In fact, the presence of such groups in many instances seems to improve the relative ease of the reactions hereinvolved. The exact form of the alkyl group is not of importance. It may be straight or branched, primary, secondary, or tertiary. The relative position of alkyl group and methyl group is not critical. Typical alkylated compounds are hexylbenzene, hexyltoluene, hexylnaphthalene, hexylmethylnaphthalene, (1-methylhexyl)benzene, (1-ethylpentyl)benzene, (1,3-dimethyl-1-propylbutyl)benzene, (1-methylhexyl)toluene, (1-ethylpentyl)toluene, (1-methylhexyl)xylene, (1-ethylpentyl)xylene, (1-methylhexyl)naphthalene, (1-methylhexyl)-dimethylnaphthalene, (1-methylheptyl)benzene, (1-methylheptyl)xylene, (1-methylheptyl)naphthalene, (2-ethylhexyl)toluene, (2-ethyl-1-methylpentyl)toluene, (3,5,5-trimethylhexyl)benzene, (1,2,4,4-tetramethylpentyl)toluene octylmethylnaphthalenes, (1-methylnonyl)-benzene, (1-methylisononyl)naphthalene, decylbenzene, dodecylbenzene, dodecyltoluene, dodecyl naphthalene, tert.-dodecylbenzene, tetradecylbenzenes, tetradecyltoluenes, tetradecylxylenes, tetradecylnaphthalenes, hexadecylbenzenes, hexadecylnaphthalenes, octadecylbenzenes, octadecyltoluenes, etc. The alkylated hydrocarbon may be a single compound or a mixture of isomers or homologues may be used.

The alkylated aromatic hydrocarbon is halo-methylated. A  $-CH_2Cl$  or  $-CHBr_2$  group is introduced by reacting the hydrocarbon with formaldehyde and hydrogen chloride or hydrogen bromide in the presence of a catalyst formed from zinc chloride and a lower monocarboxylic acid, which permits halomethylation under mild conditions such that fairly complete halomethylation is accomplished without production of resins. While the bromomethyl group is satisfactorily introduced and it gives the same reaction as the chloromethyl group, the latter is economically advantageous.

When a benzene hydrocarbon has an alkyl substituent as large as hexyl, conditions of halomethylation must be adopted which will ensure monohalomethylation approaching completion. The difficulty of doing so increases somewhat with increasing size of alkyl group present. With groups of six to eight carbon atoms a fair amount

of halomethylation is obtained by use of zinc chloride as catalyst. Yet a considerable proportion of hydrocarbon remains in the mixture. The addition of a lower aliphatic monocarboxylic acid, such as formic, acetic, chloroacetic, or propionic, brings about a remarkable improvement in the action of the zinc chloride. Acid anhydride can be used in place of or in admixture with the acid. This improvement is probably due to the formation of a complex.

A mixture of one mole of zinc chloride with 1.5 to 8 moles of an aliphatic monocarboxylic acid of not over three carbon atoms is most effective. Under preferred conditions when the alkyl group contains at least ten to twelve carbon atoms a mole ratio of 0.75 to 2.5 parts of zinc chloride per mole part of alkylated aromatic hydrocarbon is used. This ratio may be reduced as the size of the alkyl group diminishes.

For one mole of alkylbenzene, alkyltoluene, alkylxylene, or alkylated naphthalene, one to 2.5 moles of formaldehyde are used. The formaldehyde may be supplied from a revertible polymer. Anhydrous hydrogen chloride or bromide is passed into the reaction mixture. At reaction temperatures of 50° to 100° C. under conditions described, a halomethyl group is introduced without formation of resinous material. In place of formaldehyde polymer and hydrogen halide there may be used a halomethyl ether with good results.

Further details of the preparation of halomethylated alkylated aromatic compounds are given in the following illustrative examples.

#### Example 1

Hexylbenzene, prepared by the alkylation of benzene with propylene dimer, was mixed in an amount of 60 parts by weight with 25 parts of zinc chloride and 25 parts of acetic acid and heated to 50° C. Thereto over a period of an hour 40 parts of dichloromethyl ether was added with stirring. The reaction mixture was stirred and held at 55° C. to 60° C. for an hour. It was then cooled. Layers were allowed to form and the upper layer was taken. This was washed with water and sodium bicarbonate solution and then distilled under reduced pressure. The fraction collected at 120° C.-130° C./0.2 mm. corresponded in composition to hexylbenzyl chloride. It was chiefly the para isomer.

#### Example 2

Commercial 3-heptanol was dehydrated at 400° C. on an alumina catalyst and the heptene therefrom redistilled. A mixture was made with 125 parts by weight of this olefine, 198 parts of benzene, and 196 parts of sulfuric acid cooled to 5° C. The mixture was stirred for three hours, allowed to form layers, and separated. The organic layer was washed with water and a small amount of a soda ash solution, dried, and distilled under reduced pressure to yield 167 parts of heptylbenzene.

A mixture was made from 160 parts of this product, 90 parts of anhydrous zinc chloride, and 138 parts of glacial acetic acid. Thereto 106 parts of dichloromethyl ether were added with stirring while the temperature of the reaction mixture was kept at 60° C. The reaction mixture was stirred for five hours while this temperature was maintained. The mixture was cooled, allowed to form layers, and separated. The product layer was washed, dried, and fractionally distilled. Pure heptylbenzyl chloride was collected at 127°-132° C./0.2 mm.

#### Example 3

A mixture of 95 parts by weight of octylbenzene (chiefly 2-octylbenzene with some 3-octylbenzene), 30 parts of paraformaldehyde, 54 parts of anhydrous zinc chloride, and 120 parts of glacial acetic acid was stirred at 50° C. while hydrogen chloride was passed in for two hours at a fairly rapid rate. The reaction mixture was allowed to stratify and the upper layer was taken, washed with hot water, with a 10% sodium bicarbonate solution, and with hot water, dried over sodium sulfate and distilled. The forerun of 30 parts consisted of octylbenzene. There was then obtained at 119°-121° C./1 mm. 71 parts of octylbenzyl chloride.

#### Example 4

To a mixture of 46.5 parts of octylbenzene (chiefly 2-octylbenzene), 17 parts of anhydrous zinc chloride, and 40 parts of glacial acetic acid there was added dropwise 50 parts of bisbromomethyl ether. The mixture was stirred and heated at 70° C. for four hours in all. Layers were allowed to form and were separated. The upper layer was washed with hot water, with 10% sodium bicarbonate solution, and with water. It was dried over sodium sulfate and distilled. At 155°-174° C./2 mm. there was obtained a fraction corresponding in composition to octylbenzyl bromide. It contained by analysis 28.8% of bromine. Theory for this product is 28.3%.

#### Example 5

To a mixture of 184 parts of toluene and 103 parts of sulfuric acid there was added 112 parts of octene while the mixture was stirred and held at 5°-13° C. The octene had been prepared by dehydration of capryl alcohol on an alumina catalyst. (Cf. Komarewsky, Ulick, and Murray, J. Am. Chem. Soc. 67, 557 (1945).) The reaction mixture was stirred for three hours at room temperature, and the product layer was separated. It was washed twice with concentrated sulfuric acid and distilled. The fraction taken at 93°-95° C./0.3 mm. corresponded in composition to sec-octylmethylbenzene.

To a mixture of 81 parts of this product, 47.5 parts of anhydrous zinc chloride, and 65 parts of glacial acetic acid there was added 46 parts of dichloromethyl ether while the mixture was stirred and held at 50°-60° C. for an hour. It was stirred at 70°-75° C. for four hours and allowed to form layers. The upper layer was separated, washed with water and sodium bicarbonate solution, and distilled. The fraction taken at 130°-150° C./0.3 mm. amounted to 43.8 parts and corresponded in composition to methyl-octylbenzyl chloride.

#### Example 6

To a mixture of 70 parts of 2-ethylhexylbenzene (prepared according to the method of Sulzbacher and Bergmann, J. Org. Chem. 13, 303 (1948)), 50.3 parts of anhydrous zinc chloride, and 60 parts of glacial acetic acid there was added with stirring 42.5 parts of dichloromethyl ether over the course of an hour, while the reaction mixture was maintained at 60° C. Stirring was continued for another two hours with the temperature held at 60° C. Layers were then allowed to form and separated. The product layer was washed with sodium bicarbonate solution and distilled at 110°-125° C./0.07 mm. The distillate corresponded in composition to 2-ethylhexylbenzyl chloride.

## Example 7

To a mixture of 138 parts by weight of toluene and 90 parts of anhydrous hydrogen fluoride, contained in a copper flask and held at 0°-10° C., there was added 336 parts of mixed octenes, boiling at 123°-134° C., at such a rate that the temperature did not rise above 10° C. The reaction mixture was stirred for an hour and then poured upon ice. The organic layer was separated, washed with water, with 5% sodium bicarbonate solution, and again with water, dried over calcium chloride, and finally distilled. Unreacted toluene and octene were removed and the organic liquid stripped by heating to 115° C./35 mm. There was then obtained a fraction between 135° C./35 mm. and 155° C./0.5 mm. which consisted essentially of octyltoluenes.

A mixture was made in the reaction vessel equipped with a stirrer of 32 parts of octyltoluene, 25 parts of anhydrous zinc chloride, and 60 parts of glacial acetic acid. With the temperature kept at 50° to 60° C. there was added thereto 20 parts of dichloromethyl ether. The temperature of the mixture was then raised to 90° C. for three hours. The reaction mixture was then separated into layers. The product layer was washed with water, with a 5% sodium bicarbonate solution, and again with water. Upon distillation a fraction was obtained at 133°-148° C./0.3 mm. which corresponded in composition to 2-methyl-5-octylbenzyl chloride.

## Example 8

(a) Commercial diisobutyl carbinol was dripped slowly over a bed of alumina at 400° C. The vapors were taken off and condensed. Therefrom nonene was separated and distilled at 72°-75° C./100 mm. The product, containing by analysis 85.7% of carbon and 14.3% of hydrogen, was 2,6-dimethyl-3-heptene, for which the theoretical content of carbon is 85.8% and of hydrogen is 14.3%.

There was added 135 parts by weight of this product to a stirred mixture of 159 parts of benzene and 147 parts of sulfuric acid. The temperature was held between 0° and 10° C. After the mixture had been stirred for three hours, it was allowed to form layers. The upper layer was distilled and the distillate redistilled at 102°-106° C./3 mm. This distillate had a molecular weight of 203 (theory 204) and corresponded in composition to nonylbenzene. The yield was 95 parts.

To a mixture of 80 parts of nonylbenzene, 40 parts of zinc chloride, and 59 parts of glacial acetic acid there was added at room temperature 45 parts of dichloromethyl ether. The mixture was stirred and heated at 70° C. for three hours. It was then allowed to stand and form layers. The upper layer was separated, washed with hot water, and with sodium bicarbonate solution, dried over sodium sulfate, and distilled. The fraction distilling at 141°-142° C./2 mm. was nonylbenzyl chloride.

(b) A portion of 3,5,5-trimethylhexyl alcohol was dehydrated as in Example 8a and 125 parts of the nonenes therefrom reacted with 200 parts of xylene and 125 parts of sulfuric acid at about 0° C. for four hours. The reaction mixture was allowed to stand. Layers formed and were separated. The organic layer was washed, dried, and distilled at low pressure. One hundred parts of the main fraction was mixed with 50 parts of zinc chloride and 70 parts of glacial acetic acid. Thereto was added 50 parts of dichloro-

methyl ether. The reaction mixture was gradually warmed to about 75° C. and stirred for four hours. The mixture was allowed to stand. It formed layers, which were separated. The organic layer was washed with water, sodium bicarbonate solution and again with water, and dried over calcium sulfate. The product obtained gave an analysis which corresponded closely to that for nonyldimethylbenzyl chloride.

## Example 9

(a) The procedure of Example 8b was applied to naphthalene in place of xylene. There was obtained nonylnaphthylmethyl chloride of good purity.

(b) A mixture was made from 100 parts of propylene dimer, 150 parts of dimethylnaphthalene, and 150 parts of sulfuric acid, which had been chilled to about 0° C. The mixture was stirred at 0°-5° C. for two hours and then for two hours without cooling. The reaction mixture was left standing until layers formed. They were separated. The organic layer was washed with water, with soda ash solution, and with water again, was dried over calcium sulfate, and heated under low pressure to remove unreacted starting material. The product remaining had the correct composition for hexyldimethylnaphthalene.

A mixture was made from 120 parts of this product, 50 parts of zinc chloride, 75 parts of acetic acid, 15 parts of acetic anhydride, and 25 parts of paraformaldehyde. Hydrogen chloride was passed into the mixture while it was stirred. Reaction began and carried the temperature to about 80° C., where it was controlled by rate of addition of hydrogen chloride and by cooling. After three hours the mixture was left standing. Layers formed and were separated. The upper layer was washed with water, with 10% sodium bicarbonate solution, and with water. It was dried over calcium sulfate and heated under low pressure. The product was essentially hexyldimethylnaphthylmethyl chloride.

(c) There were mixed 156 parts of a crude methylnaphthalene and 156 parts of sulfuric acid, both of which had been chilled to 0° C. The mixture was stirred and 212 parts of propylene tetramer was slowly added, maintaining the temperature below 20° C. The reaction mixture was stirred for three hours at room temperature and the organic layer was then separated and distilled. There was thus obtained 122 parts of dodecylmethylnaphthalene boiling over the range of 160°-220° C. at 0.65 mm. of mercury.

A mixture of 155 parts of this product, 75 parts of zinc chloride, and 100 parts of acetic acid was stirred and thereto was added 105 parts of chloromethyl ether over a period of an hour with the temperature at 70° C. The temperature was maintained at this level and stirring was continued for three hours. The layers were separated as in previous examples and dodecylmethylnaphthylmethyl chloride obtained as a residue.

(d) To a mixture of 96 parts of naphthalene and 60 parts of 96% sulfuric acid cooled below 10° C. there was added over a period of 40 minutes 101 parts of propylene polymer which averaged four propylene units. The reaction mixture was stirred for three hours. Layers were allowed to form and were separated. The organic layer was treated with a little lime and distilled. After a forerun of naphthalene, there was obtained a dark-colored oil distilling at 165°-

263° C./5 mm. and amounting to 108 parts by weight. This oil was redistilled, a fraction of 83 parts being taken at 185°–225° C./3 mm. which corresponded closely in composition to dodecyl-naphthalene. The molecular weight determined ebullioscopically was 305 (theory, 296).

There were mixed 65 parts of this product, 13.5 parts of paraformaldehyde, 30 parts of anhydrous zinc chloride, and 100 parts of glacial acetic acid. Into this mixture at 50°–70° C. hydrogen chloride was passed for five hours. Layers were formed and separated. The upper layer was washed with water and with dilute sodium bicarbonate solution. It was stripped under low pressure to yield 63 parts of a light brown, viscous oil which was essentially dodecyl-naphthylmethyl chloride. It contained by analysis 10.8% of chlorine (theory, 10.4%).

#### Example 10

To a mixture of 312 parts of benzene and 180 parts of sulfuric acid was added dropwise at 10°–20° C. 281 parts of decene, which was freshly prepared by dehydration of n-decanol on alumina. The mixture was stirred for five hours at room temperature. It was then allowed to form layers. The upper layer was separated, washed with concentrated sulfuric acid twice, and distilled. The fraction distilling at 115°–127° C./1.3 mm. was identified as sec.-decylbenzene.

A mixture of 54.5 parts of this sec.-decylbenzene, 27.3 parts of zinc chloride, and 60 parts of glacial acetic acid was stirred and heated to 70°–75° C. while 28.8 parts of dichloromethyl ether was slowly added. Stirring was continued at 70°–80° C. for five hours. Layers were allowed to form. The upper layer was separated, washed with water and sodium bicarbonate solution, dried, and distilled. At 155°–175° C./1.8 mm. there was obtained a fraction of 30 parts which corresponded in composition to sec.-decylbenzyl chloride.

#### Example 11

Dodecyltoluene was prepared by mixing 344 parts of toluene and 294 parts of concentrated sulfuric acid and, while the mixture was stirred and the temperature maintained below 10° C., dodecylene was slowly added. The dodecylene used was a propylene tetramer. After 506 parts of dodecylene were added, the mixture was allowed to come to room temperature and stirring was continued for 24 hours. After separation from the acid layer, the product was washed with concentrated sulfuric acid and distilled in vacuo. Five hundred fifty-five parts of a colorless liquid boiling at 110°–160° C. at 1.2–2.2 mm. of mercury was obtained.

A mixture of 450 parts of dodecyltoluene with 105 parts of formaldehyde, 175 parts of anhydrous zinc chloride, and 250 parts of glacial acetic acid was stirred at 60°–70° C. while hydrogen chloride was passed in rapidly for two hours. Absorption was rapid and the reaction was accompanied by a rise of temperature. The lower catalyst layer was drained off and the product washed with water, 10% sodium carbonate solution, and again with water, then dried in vacuo on a steam-bath. Four hundred ninety parts of a yellow liquid having a chlorine content of 11.2% was obtained. The theoretical chlorine content of dodecylmethylbenzyl chloride is 11.5%. This material distills almost completely at 145°–185° C. at 0.5–1 mm. of mercury. It may, however, be used without further purification.

#### Example 12

To a mixture of 156 parts of benzene and 110 parts of anhydrous hydrofluoric acid at 0°–5° C. was added 252 parts of octadecylene at such a rate that the temperature did not exceed 10° C. The mixture was then stirred for three and one-half hours at 5°–10° C. and after it had stood overnight at room temperature the mixture was poured on ice, washed with water, then with 10% sodium bicarbonate and water, dried, and distilled. The product was collected between 195° and 210° C. at 1.5–2 mm. mercury, amounting to 225 parts.

To a mixture of 30 parts of octadecylbenzene, 35 parts of anhydrous zinc chloride and 80 parts of glacial acetic acid was added 16 parts of bis-chloromethyl ether dropwise at 55° C. The mixture was then stirred for two and one-half hours, allowed to stand overnight and the upper product layer separated, dissolved in benzene and washed with water, 10% sodium bicarbonate and water, and dried over anhydrous calcium chloride. The benzene was stripped to yield 32 parts of a straw-colored liquid containing 9.02% chlorine (theory, 9.37%). This was essentially octadecylbenzyl chloride.

#### Example 13

Hydrogen chloride was passed into a mixture of 104 parts of dodecyltoluene, 24 parts of paraformaldehyde, 53.3 parts of zinc chloride and 59.2 parts of propionic acid for two hours at 70° C. The reaction product was worked up as in the preceding example. One hundred eighteen parts of methyl-dodecylbenzyl chloride was obtained.

#### Example 14

To a mixture of 138 parts of toluene and 150 parts of sulfuric acid at about 0° C. there was slowly added with stirring 196 parts of an olefine fraction which contained olefines from C<sub>12</sub> to C<sub>15</sub> and averaged C<sub>14</sub>. The mixture was stirred at 0°–10° C. for three hours and then separated. After the organic layer had been washed with water and soda ash solution, it was dried and distilled. A fraction obtained between 120° and 160° C. at 2 to 0.5 mm. consisted of alkylated methylbenzene.

It was mixed with zinc chloride and acetic acid as in previous examples and chloromethylated with chloromethyl ether. When tests showed that the product was essentially a monochloromethylated material, the reaction was stopped. The product was washed and dried to yield alkylmethylbenzyl chlorides in which the alkyl group on the average contained fourteen carbon atoms.

#### Example 15

For the preparation of alkylbenzenes from relatively inexpensive materials kerosene or close-cut naphthas may be taken. For instance, an aliphatic type distillate having a distillation range of 190° to 250° C. and having an average molecular weight of about 190 was chlorinated until one equivalent of chlorine was taken up per average molecular unit. The alkylchlorides thus formed were reacted with toluene in the presence of 10% of its weight of aluminum chloride. The resulting alkyltoluenes were stripped free of reactants and distilled at low pressures from 100°–160° C./2–0.5 mm.

A portion of the distillate in an amount of 75 parts was mixed with 12 parts of paraformaldehyde.

hyde, 30 parts of zinc chloride, 30 parts of acetic acid, and 30 parts of acetic anhydride. The mixture was heated to about 60° C. and hydrogen chloride was passed in. The temperature increased to about 85° C. After three hours the mixture was cooled. Layers formed and were separated. The organic layer was washed with water, with 10% sodium bicarbonate solution and again with water. The product was dried over calcium sulfate.

Polyethylene glycols, the second type of reactant needed in the process of this invention, are well known. They can be prepared from ethylene oxide over a wide range of molecular sizes. While it may happen that a polyglycol preparation which has an apparent molecular weight of 550, 600, 800, 1200, 1500, 1800, or the like may in fact be a mixture of glycols, this does not alter the reaction or yield compounds which are any less useful because of utilization of a mixture. The polyethylene glycol should supply a chain of at least six  $-\text{OC}_2\text{H}_4-$  units and enough such units to give to the final product dispersibility or solubility in water. There is no fixed upper limit to the number of such units which may be present in polyethylene glycol or final product. The properties gradually change as more and more such units are used, but a practical upper limit is about forty.

A polyethylene glycol,  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ , where  $n$  has a value of about six to forty, is reacted with an alkylated benzyl or naphthylmethyl halide in about an equal molar amount in the presence of about an equal molar amount of an alkali metal hydroxide. Theoretically, the polyethylene glycol, halide, and hydroxide react in equimolecular proportions, but strict adherence to this proportion is not absolutely essential as the presence of a little of the bis alkylbenzyl polyether derivative, formed when an excess of halide is used, does not lessen the utility of the product. Excess of the hydroxide gives no difficulty.

The reaction is carried out by heating the mixture of polyethylene glycol, hydroxide, and halide between 80° and 150° C. The reaction is usually complete in one to five hours. The reaction mixture can then be cooled and diluted with a volatile organic solvent such as toluene, petroleum ether, isopropanol, or the like. Salt formed in the reaction can then be removed by filtering. It is usually preferred to effect the separation of salt, although it is not essential. Free halomethylated alkyl aromatic hydrocarbon may be removed by dissolving the reaction mixture in an aqueous medium and extracting the solution with a water-immiscible organic solvent.

There follow examples of typical preparations of compounds of this invention.

#### Example 16

There were mixed 4.4 parts by weight of sodium hydroxide and 30 parts of a polyethylene glycol having an average molecular weight of about 300 and containing, therefor, about six  $-\text{OC}_2\text{H}_4-$  units. The mixture was heated to 80° C. and 21 parts of hexylbenzyl chloride was slowly added. The mixture was stirred and heated for four hours with the temperature carried up to 140° C., cooled, and extended with toluene. The solution was filtered and the filtrate was evaporated to leave a straw-colored oil. This has the composition  $\text{C}_6\text{H}_{13}\text{C}_6\text{H}_4\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}$  where  $n$  has a value of six or a little more on average. The product is water-soluble and surface-active. Its

solutions have low surface and interfacial tensions.

#### Example 17

A mixture of 4.4 parts of sodium hydroxide and 30 parts of polyethylene glycol having an apparent molecular weight of 300 was heated at 80° C. and 26 parts of hexylnaphthylmethyl chloride slowly added thereto. Stirring was continued at temperatures gradually increased to 140° C. for a period of four hours. The reaction mixture was cooled, diluted with toluene, and filtered. The filtrate was evaporated to leave a yellow oil. This product was water-soluble and gave solutions of low surface tension. It dispersed carbon black and other fine particled solids.

#### Example 18

A mixture of 40 parts of polyethylene glycol having a molecular weight of about 400 and 6.4 parts of potassium hydroxide was heated to 90° C. and thereto was slowly added with good stirring 28 parts of octylmethylbenzyl chloride. After addition was complete, the reaction mixture was stirred and heated to 150° C. over the course of three hours. The reaction mixture was cooled, diluted with toluene, and filtered. The solvent was evaporated to leave an amber oil, which was water-soluble and surface-active, having wetting, emulsifying, and dispersing actions.

#### Example 19

A mixture of 50 parts of a polyethylene glycol having a molecular weight of 500 and 8.4 parts of potassium hydroxide was heated to 90° C. and 24 parts of an octylbenzyl chloride was slowly added. The reaction mixture was stirred and heated up to 150° C. for three hours. It was cooled, diluted with toluene, and filtered. The filtrate was evaporated to yield a light brown oil, which was water-soluble. Its solutions were capillary active. A 0.5% solution had a surface tension of 30.5 dynes/cm., for example, and an interfacial tension against a white mineral oil of 4.5 dynes/cm. The composition of this product was  $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{CH}_2(\text{OCH}_2\text{CH}_2)_{11}\text{OH}$ . It was found an effective detergent.

#### Example 20

A mixture of 50 parts of a polyethylene glycol having a molecular weight of 500 and 8.4 parts of potassium hydroxide was heated to 90° C. Thereto was slowly added 28.5 parts of octylbenzyl bromide. The reaction mixture was stirred and heated to 150° C. for three hours. It was then cooled, extended with toluene, and filtered. The filtrate was evaporated to yield a light brown oil, which was soluble in water and had properties almost identical with those of the product of Example 19.

#### Example 21

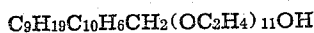
A mixture of 60 parts of a polyethylene glycol having an apparent molecular weight of 600, 80 parts of toluene, and 5.6 parts of potassium hydroxide was heated on a steam-bath and thereto over a one hour period 26 parts of nonylbenzyl chloride was added. Heating of the mixture was continued for 3.5 hours and the mixture was filtered to remove the salt. The toluene was distilled off and the resulting oil was dissolved in equal parts of water and methanol. This solution was twice extracted with 80 parts of heptane. The solution was then stripped of solvents. A yield of 69 parts of an oil was obtained. It had

## 11

the composition  $C_9H_{19}C_6H_4CH_2(OC_2H_4)_{11}OH$ . Its solutions were capillary active. The wetting times of canvas patches were determined as follows: At 0.5% of the product 25.9 seconds, at 0.2% 73 seconds, and at 0.1% 132 seconds. The solutions had fairly good foaming power. The product was a dispersing and emulsifying agent and had good cleaning power.

## Example 22

By the method of Example 21 there were mixed 60 parts of the polyethylene glycol with a molecular weight of 600, 80 parts of toluene, and 5.6 parts of potassium hydroxide. Thereto 30 parts of monynaphthylmethyl chloride was added and reacted therewith. Purification was accomplished in the same way. The product obtained had the composition

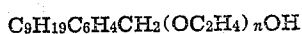


Its solutions were capillary active but gave less rapid wetting-out than the product of Example 21. Nevertheless it had marked emulsifying and dispersing actions.

The above preparation was repeated without the use of toluene and the reaction mixture was heated to 150° C. during the course of three hours. The product was freed of salt by diluting with toluene and filtering. The extraction step was then carried out. There was thus obtained 81 parts of an oil which had the above composition and which had the same properties.

## Example 23

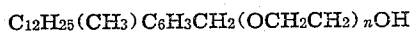
A mixture of 40 parts of a polyethylene glycol having a molecular weight of 400 and 5.8 parts of potassium hydroxide was heated at 90°–100° C. and 25.7 parts of nonylbenzyl chloride was slowly added. The reaction mixture was then heated for four hours with the temperature carried to 140° C. Purification was accomplished by solution in isopropanol followed by filtration. The filtrate was extended with water and the solution extracted with toluene. A yield was obtained of 57 parts of



where  $n$  averages 8.7. The product was water-soluble and gave surface-active solutions. A 0.5% solution gave a wetting time by the canvas patch method of 16 seconds.

## Example 24

A mixture of 80 parts of a polyethylene glycol having a molecular weight of about 800 and 6 parts of potassium hydroxide was heated to about 100° C. while 31 parts of dodecylmethylbenzyl chloride was slowly added. Heating was continued for four hours while the temperature was raised to 140° C. The reaction product was purified by filtration of its solution in toluene and extraction with heptane of a solution in 50% aqueous isopropanol. The product was a viscous oil, which was water-soluble. It had the composition



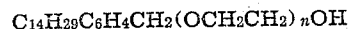
when  $n$  had an average value of almost 18. The water solutions were capillary active as shown by low surface and interfacial tensions. The product had emulsifying, dispersing, and cleansing properties.

## Example 25

A mixture of 125 parts of a polyethylene glycol

## 12

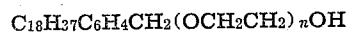
having a molecular weight of 1250 and 6 parts of potassium hydroxide was reacted at 90°–100° C. with 32 parts of tetradecylbenzyl chloride. The reaction mixture was heated for five hours up to 140° C. and purified as in the previous examples. The product obtained had the composition



where  $n$  had a value of 28. This product was water-soluble and had emulsifying and dispersing actions.

## Example 26

A mixture of 90 parts of a polyethylene glycol of a molecular weight of about 1800 and 2 parts of sodium hydroxide was heated to about 100° C. and 19 parts of octadecylbenzyl chloride slowly added. The reaction was continued by heating for five hours at 140°–150° C. The reaction product was purified as in the previous example and, when it was cooled, it became waxy. It dispersed in water to give solutions having reduced surface tension. It had emulsifying and dispersing actions. The composition of this product corresponds to the formula



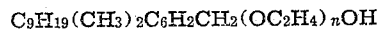
where  $n$  has a value of about 40.

## Example 27

A mixture of 151 parts of a polyethylene glycol having a molecular weight in excess of 1500 and 6.4 parts of potassium hydroxide was heated to 90° C. and 36 parts of dodecylmethyl-naphthylmethyl chloride slowly added. The reaction was continued at 140°–150° C. for four hours. The product was purified by removal of salt through filtration of its toluene solution and extraction of a solution in 50% aqueous isopropanol with the aid of heptane. The product obtained as a residue on evaporation of solvents was an unctuous waxy material which was dispersible in water. Its solutions were capillary active. It had dispersing and emulsifying actions. This product contained about 34 ethoxy groups.

## Example 28

A mixture of 100 parts of a polyethylene oxide having a molecular weight of about 1000 and 6 parts of potassium hydroxide was heated to 90° C. and 28 parts of nonyldimethylbenzyl chloride added thereto. Heating was continued for four hours with the temperature being carried to 150° C. The product was purified as in previous examples. A viscous oil was obtained which was water-soluble and capillary active. Its composition corresponds to the formula



where  $n$  has a value of about 23. This product had good dispersing, emulsifying, and cleansing properties.

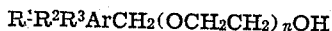
The compounds of this invention, obtained by the reaction of an alkylbenzyl or alkynaphthylmethyl halide and polyethylene glycol in the presence of an alkali metal hydroxide, are useful surface-active materials of the non-ionic type. They supply effective dispersing and emulsifying actions and can be used in conjunction with either anionic or cationic surface-active agents. They may also be used in conjunction with alkaline detergents, supplying wetting, dispersing, and emulsifying actions. An example of an efficient cleaning and sanitizing

13

composition is one combining sodium phosphates and a long-chained quaternary ammonium salt along with one of the compounds of this invention. On the other hand, these compounds can be used to enhance the value of carboxylic soaps of long-chained sulfates or sulfonates.

I claim:

1. A process for preparing a compound of the formula



which comprises reacting at 80° to 150° C. about one mole of a polyglycol of the formula



and about one mole of a halide of the formula



in the presence of about one mole of an alkali metal hydroxide,  $R^1$  being an alkyl group of 6 to 18 carbon atoms,  $R^2$  and  $R^3$  being members of the class consisting of hydrogen and the methyl group,  $Ar$  being a member of the class consisting of benzene and naphthalene groups,  $n$  being a number from 6 to 40 and at least of sufficient size to ensure the dispersibility of the compound in water, and  $X$  being a halogen from the class consisting of chlorine and bromine.

2. A process for preparing a compound of the formula



which comprises reacting at 80° to 150° C. about one mole of a polyglycol of the formula



and about one mole of a halide of the formula



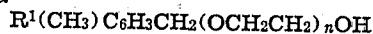
in the presence of about one mole of an alkali metal hydroxide,  $R^1$  being an alkyl group of 8 to 12 carbon atoms and  $n$  being a number from 6 to 40 and at least of sufficient size to ensure the dispersibility of the compound in water.

14

3. A process of claim 2 in which  $R^1$  is an octyl group.

4. A process of claim 2 in which  $R^1$  is a nonyl group.

5. A process for preparing a compound of the formula



which comprises reacting at 80° to 150° C. about one mole of a polyglycol of the formula



and about one mole of a halide of the formula



15 in the presence of about one mole of an alkali metal hydroxide,  $R^1$  being an alkyl group of 8 to 12 carbon atoms and  $n$  being a number from 6 to 40 and at least of sufficient size to ensure the dispersibility of the compound in water.

20 6. The process of claim 5 in which  $R^1$  is a nonyl group.

7. The process of claim 5 in which  $R^1$  is a dodecyl group.

PETER L. DE BENNEVILLE.

# REFERENCES CITED

The following references are of record in the file of this patent:

## UNITED STATES PATENTS

| Number    | Name                   | Date          |
|-----------|------------------------|---------------|
| 2,209,911 | Bruson et al. ....     | July 20, 1940 |
| 2,213,477 | Steindorff et al. .... | Sept. 3, 1940 |
| 2,459,526 | Heckenbleikner ....    | Jan. 18, 1949 |

## FOREIGN PATENTS

| Number  | Country       | Date          |
|---------|---------------|---------------|
| 202,352 | Germany ..... | Oct. 3, 1908  |
| 422,948 | Germany ..... | Dec. 16, 1925 |
| 655,871 | France .....  | Dec. 22, 1928 |