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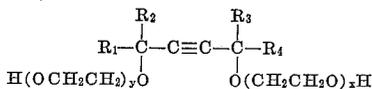
ETHYLENE OXIDE ADDUCTS OF TERTIARY ACETYLENIC ALCOHOLS

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This is a continuation-in-part of our copending application, Serial No. 667,675, filed June 24, 1957, and now abandoned.

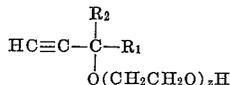
This invention relates to a new class of polyoxyethylene compounds and, more particularly, to ethylene oxide adducts of acetylenic tertiary glycols, acetylenic tertiary carbinols, and mixtures thereof.

The ethylene oxide adducts of the acetylenic tertiary glycols can be structurally represented by the formula



in which R₁ and R₄ are alkyl radicals containing from 3 to 10 carbon atoms, R₂ and R₃ are selected from the group consisting of methyl and ethyl, and x and y have a sum in the range of 3 to 60, inclusive.

The ethylene oxide adducts of the acetylenic tertiary carbinols can be structurally represented by the formula



in which R₁ and R₂ are as previously defined and z is in the range of 3 to 60, inclusive.

The ethylene oxide adducts of the invention possess excellent surfactant or surface-active properties and are particularly useful as wetting agents and detergents and in formulating water-soluble, non-ionic detergents. One indication of the outstanding wetting properties of the adducts of this invention is the rapid and in many cases instantaneous wetting of textiles such as cotton in water containing one of these adducts in solution. We have found that the presence of the acetylenic bond in the hydrophobic chain of the adduct confers increased water solubility and improved surfactant properties especially when compared to the unreacted acetylenic tertiary glycols and carbinols.

The shorter chain adducts of this invention are outstanding low foam surfactants. They may be used as wetting agents in metal plating and cleaning baths, as detergent ingredients in automatic dishwashers, and for other purposes where a low foam surfactant is desired. As the oxyethylene chain length increases, both detergency and amount of foam increase. The longer chain adducts have high detergency and produce some foam although generally much less than the amount produced by conventional non-ionic detergents. These adducts are excellent as detergents and as ingredients in built detergent compositions for laundering machines and hand dishwashing, where both high detergency and the presence of foam are desirable.

The ethylene oxide adducts of this invention are further devoid of objectionable odors and dermal irritations and contribute negligible coloration when used in blending detergent formulations. In general, the adducts are either liquids or low-melting solids.

An outstanding advantage of adducts of this invention is their ability to promote rapid and in many cases instantaneous wetting in aqueous media. The wetting time decreases rapidly with increasing concentration of adduct,

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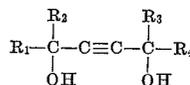
and also decreases with increasing polyoxyethylene chain length. Instantaneous wetting is achieved with preferred adducts such as those of 2,4,7,9-tetramethyl-5-decyne-4,7-diol in concentrations exceeding about 0.2% to about 1%, depending on the polyoxyethylene chain length. The wetting times are substantially shorter than the wetting times obtainable with previously known ethylene oxide adducts of alcohols.

A further advantage of adducts of this invention is their high water solubility, which permits their use in concentrations sufficient for rapid wetting and high detergency.

The preparation of the ethylene oxide adducts of the invention can be accomplished by reacting the acetylenic tertiary glycols, carbinols, or mixtures thereof, together with ethylene oxide in the presence of a basic catalyst.

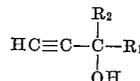
The adducts of this invention are mixtures of ethoxylated acetylenic glycols and carbinols in which the average number of oxyethylene units per mole is in the range of 3 to 60 and preferably 3 to 20.

The acetylenic tertiary glycols which can be condensed with ethylene oxide correspond to the general formula



where R₁, R₂, R₃ and R₄ are as previously defined.

The acetylenic tertiary carbinols which can be condensed with ethylene oxide correspond to the general formula



in which R₁ and R₂ are as previously defined.

The acetylenic tertiary glycols and carbinols can be prepared in various known manners such as those described in the United States patents to Bruson et al., No. 2,250,445, Kreimeier, No. 2,106,180, and Vaughn, No. 2,163,720.

It is advantageous to form the adducts directly from the reaction mixture to form mixed adducts and thus avoid separation procedures where the properties of the pure glycol or carbinol adducts are not desired. Various concentrations of mixed adducts can be formed by forming a mixture from pure adducts in the desired concentration.

We have found that the ethylene oxide adducts of 3-methyl-1-nonyn-3-ol, 7,10 - dimethyl-8-hexadecyne-7,10-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 4,7-dimethyl-5-decyne-4,7-diol, and mixtures of 7,10-dimethyl-8-hexadecyne-7,10-diol and 3-methyl-1-nonyn-3-ol containing an average of between 3 to 20 oxyethylene moieties possess outstanding surfactant and detergent properties. The ethylene oxide adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol containing from 3 to 30 ethylene oxide units per molecule are particularly outstanding low foam surfactants and detergents.

Various basic catalysts can be used to promote the reaction between the ethylene oxide and the acetylenic tertiary glycols and carbinols in which the hydroxyl groups are attached to a carbon atom in a position alpha to the acetylenic bonds according to this invention. Tertiary aliphatic amines such as trimethylamine, triethylamine, tripropylamine, and the like are particularly advantageous catalysts for the reaction of this invention. Such tertiary aliphatic amines catalyze the condensation reaction at a rapid rate at moderately low temperatures and pressures without inducing cleavage of the acetylenic glycol or carbinol. Trimethylamine is preferred because of its high

catalytic activity, which makes it possible to operate at lower temperatures and pressures and with lower catalyst concentrations than those required when using other tertiary aliphatic amine catalysts.

The use of strongly basic catalysts such as sodium hydroxide, especially at high temperatures of about 150° C., induces cleavage of the acetylenic tertiary glycols and carbinols and for this reason should be avoided. Catalysts of weak basicity such as N,N-dimethylaniline are not sufficiently basic to promote the reaction at a reasonable rate and require the use of very high temperatures and pressures. The tertiary aliphatic amines are ideally suited to promote the reaction of this invention and possess none of the disadvantages of the other catalysts discussed above.

Once the tertiary hydroxyl groups of the acetylenic glycol and carbinol have reacted with ethylene oxide, the resultant adduct exhibits the marked stability of an ether. So stable are the adducts that they can be heated with concentrated base such as sodium hydroxide at elevated temperatures, while comparable treatment of the initial acetylenic glycol is accomplished by extensive degradation. Consequently, strongly basic catalysts, such as the alkali metal hydroxides, can be used to increase the polyoxyethylene chain length once the initial adducts have been formed and protected against decomposition.

At the onset of the condensation reaction, the electro-negativity of the acetylenic bond in the tertiary glycols and carbinols markedly increases the reactivity of the acetylenic glycols and carbinols towards ethylene oxide. Such acetylenic glycols as 4,7-dimethyl-5-decyne-4,7-diol and 2,4,7,9-tetramethyl-5-decyne-4,7-diol react readily with ethylene oxide at atmospheric pressure and moderate temperatures, using trimethylamine or triethylamine as a catalyst.

Using a catalyst of moderate basicity and which does not favor the reverse reaction, the ethylene oxide adduct of the acetylenic glycol can be formed at either atmospheric or moderate to low superatmospheric pressures. The use of moderate to low superatmospheric pressures is preferred since it obviates the necessity of recycling unreacted ethylene oxide and generally proceeds at faster rates than condensations carried out at atmospheric pressures. In addition, those reactions conducted under pressure may be accomplished with ordinary efficient agitation, while reactions conducted at atmospheric pressure often work best when a dispersion-type agitator is provided.

The temperature and pressure at which the reaction is run will depend upon the particular system under reaction and the catalyst concentration. Generally, at higher catalyst concentrations the reactions can be run at lower temperatures and pressures. Most of the reactions involving the glycols can take place at moderate temperature (50–75° C.) using triethylamine as a catalyst. Slightly lower temperatures, down to about 40° C., are operative when trimethylamine is the catalyst. Some reactions require higher temperatures. For example, when forming the ethylene oxide adduct of a glycol containing more than about fourteen carbon atoms, such as a mixture of 7,10-dimethyl-8-hexadecyne-7,10-diol and 3-methyl-1-nonyn-3-ol, it is advantageous to use temperatures of about 150–160° C. with triethylamine as the catalyst, and lower temperatures with trimethylamine as the catalyst. The pressure at which the reaction takes place will be determined to a great extent by the reaction temperature used.

The reaction of the acetylenic tertiary carbinols with ethylene oxide require slightly higher temperatures and pressures in order to promote the reaction at a reasonable rate. It is thus advantageous to react the carbinols at temperatures of about 150° C. and at pressures between about 150 to 200 p.s.i.g. when using triethylamine as a catalyst. Although higher and lower temperatures and pressures can be used depending upon the particular carbinol being reacted and the other reaction conditions such as the type and amount of catalysts being used, it is ad-

vantageous to react such acetylenic tertiary carbinols as 3-methyl-1-nonyn-3-ol at temperatures above 150° C. and at pressures above 200 p.s.i.g. since the reaction of these carbinols proceeds rather slowly at or below these temperatures and pressures.

To prepare the ethylene oxide adducts of the invention, the acetylenic glycol or carbinol is liquefied by melting and the catalyst added with stirring. No warming is required if the initial glycol or carbinol is a liquid. To this mixture is added liquid ethylene oxide with stirring, and the reaction concluded when the desired polyoxyethylene chain length is achieved. No solvents are necessary during the reaction, but inert solvents may be used when the initial acetylenic glycol or carbinol employed is moderately high melting (greater than 80° C.).

In adding the liquid ethylene oxide to the acetylenic tertiary glycol and the catalyst, care should be taken to avoid the presence of an excess of ethylene oxide in the reaction mixture since the reaction is a powerful exothermic one which might prove to be very hazardous. We have found that the danger of an uncontrollable reaction can be avoided by adding the ethylene oxide in a manner and at a rate such that it is absorbed as rapidly as it is introduced into the reaction mixture.

The condensation reaction between the acetylenic tertiary glycols or carbinols and ethylene oxide is a non-selective one and the progress of the reaction can be followed by various means to determine at which point the reaction is to be terminated. The reaction can be followed, for example, by observing the cloud point of the reaction mixture, by continuously weighing it, by observing changes in the refractive index, and the like. We have found that the reaction can be more advantageously followed by observing the cloud point which is more accurate in determining the average polyoxyethylene chain length during the course of the reaction. As the average polyoxyethylene chain length increases, the cloud point correspondingly increases. After the reaction has been stopped and the adduct isolated, an accurate determination of the average polyoxyethylene chain length can be made by determining the gain in weight of the resulting adduct over the original glycol or carbinol reacted and by a carbon, hydrogen analysis. Once it has been determined that a particular average polyoxyethylene chain length is obtained under set reaction conditions, the adducts can be reproduced without the necessity of following the reaction to determine at which point it should be terminated.

Generally, the polyoxyethylene chain lengths corresponding to about 3 to 10 oxyethylene units are clear, soluble, amber-colored oils. Increasing the polyoxyethylene chain length to about 15 to 30 oxyethylene moieties increases the viscosity of the resultant adduct, while at chain lengths corresponding to about 30 to 60 oxyethylene units, the adducts are low melting solids. The adducts were found to possess optimum surfactant properties when the polyoxyethylene chain length averaged between 3 and 20 oxyethylene units.

The effect of the acetylenic bond on the surfactant properties of the adducts is particularly striking. By way of illustration, a 0.1% aqueous solution of an ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol containing a molar ratio of 1:6.8 of glycol to oxyethylene moieties, has an index of wetting of 14.5 seconds, measured by the Draves-Clarkson wetting test. A low index of wetting, as determined by this test, is indicative of a high degree of wetting ability.

The following examples are illustrative of the preparation and properties of the ethylene oxide adducts of the invention.

In Examples I and II, ethylene oxide was reacted with 2,4,7,9-tetramethyl-5-decyne-4,7-diol using triethylamine as a catalyst to form an adduct having a molar ratio of 1:8.0 of glycol to ethylene oxide units. Low pressures were used in the first example, and atmospheric pressure in Example II.

EXAMPLE I

Adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol

Low pressure method.—To a one-gallon autoclave was added 904 g. (4.0 moles) of 2,4,7,9-tetramethyl-5-decyne-4,7-diol and 20 g. of triethylamine as a catalyst. After purging all lines in the autoclave system with nitrogen, the mixture was warmed at temperatures of 55° to 60° C., with stirring, until all of the glycol had melted. The nitrogen pressure in the autoclave was then adjusted to zero gauge pressure at 55° C., and 1231 g. (28.0 moles) of liquid ethylene oxide slowly added to the surface of the

maximum of 120°–125° C. The reaction was discontinued when the reaction adduct contained a molar ratio of 1:8.0 of glycol to ethylene oxide units.

To illustrate the ease of addition of varying molar amounts of ethylene oxide to the acetylenic tertiary glycols, Table 1 summarizes the conditions and results achieved when several ethylene oxide adducts were prepared with ratios of glycol to ethylene oxide units ranging from 1:4.0 to 1:3.0. In each case, the glycol was reacted with ethylene oxide using the low pressure method described above. Triethylamine was used as the catalyst.

TABLE 1.—ADDUCTS OF 2,4,7,9-TETRAMETHYL-5-DECYNE-4,7-DIOL

Moles of Glycol	Average Reaction Conditions			Grams of Ethylene Oxide	Ethylene Oxide Adduct	
	Pressure (p.s.i.)	Temp. (° C.)	Time (hrs.)		Molar Ratio	Solubility (25° C.)
0.5	35–158	42–151	4	200	1:4.0	Soluble-cloudy.
4.0	25–125	25–135	4.5	2,110	1:6.8	Do.
4.0	32–130	28–125	4.75	2,270	1:7.8	Do.
0.5	37–80	30–160	4	309	1:9.0	Soluble.
0.5	40–280	72–160	9	477	1:16.2	Do.
0.45	30–240	25–240	2.5	312	1:30.0	Do.

molten glycol, during which addition the temperature was maintained between 55° and 100° C. After the addition of about 75% of the total amount of ethylene oxide at 55° to 100° C., the absorption rate diminished and the pressure began to rise. At this point the average number of ethylene oxide units per mole of diol is about 5. The reaction temperature was then gradually lowered to about 25° to 40° C. to control the autoclave pressure and to allow the remainder of the ethylene oxide to be added at a pressure of 35–50 p.s.i.g.

The residual ethylene oxide in the lines was then blown into the autoclave with slight nitrogen pressure, the autoclave sealed, and the reaction mixture heated to 125° C. for about one hour, during which time a maximum pressure of 100 to 150 p.s.i.g. was generated. The resultant product was a mobile, light, orange-brown oil having a molar ratio of glycol to ethylene oxide of 1:7.0. The oil was cleansed of any unreacted ethylene oxide and triethylamine by vacuum topping at 120°–130° C./25 mm. The amine catalyst was removed from the product which altered its color to a light amber shade. If further purification is required, the product can be treated with several drops of concentrated hydrochloric acid, and decolorized with charcoal.

The adduct was freely soluble in water, and was usable without further purification in blending a detergent mixture. The conversion to the desired adduct was 98.2% of theory, based on the ethylene oxide consumed. The use of triethylamine as a catalyst in the reaction effectively prevented alkali cleavage of the starting glycol to methyl isobutyl ketone, via the reverse-Favorski reaction.

EXAMPLE II

Adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol

Atmospheric pressure method.—This method was the same as the preceding low pressure method except that the liquid ethylene oxide was added at atmospheric pressure. The rate of the reaction at atmospheric pressure was found to be noticeably slower than at low to moderate pressures. By way of comparison, reactions concluded at atmospheric pressure generally required from three to five times as long as the corresponding reaction carried out at low pressures.

Using substantially the same apparatus as described for the low pressure method of Example I, 1231 g. (28.0 moles) of liquid ethylene oxide was added to a mixture containing 904 g. (4.0 moles) of 2,4,7,9-tetramethyl-5-decyne-7,9-diol and 20 g. of triethylamine. The reaction temperature was initially 55°–75° C., and after the addition of between 2 to 3 moles of ethylene oxide per mole of glycol, the temperature was gradually increased to a

EXAMPLE III

Adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol

Using trimethylamine catalyst.—Two moles (452 g.) of 2,4,7,9-tetramethyl-5-decyne-4,7-diol was charged to a one-gallon autoclave equipped with an internal heating and cooling coil and a stirrer. The autoclave was sealed, purged with nitrogen, and heated to a temperature of 50 to 55° C. To the autoclave was added 2.67 g. (0.59 percent based on the weight of 2,4,7,9-tetramethyl-5-decyne-4,7-diol) of trimethylamine as a liquid under pressure. The last traces of trimethylamine were driven in with nitrogen gas under pressure. Six hundred ml. (529 g., 12 moles) of ethylene oxide was introduced into the autoclave over a period of 1.5 hours while the temperature was maintained at 40 to 50° C. by circulation of cooling water through the internal coil. After the addition of ethylene oxide was completed, the reaction mixture was maintained at a temperature of 50 to 65° C. for an additional 2 hours. During this time the pressure varied from 40 to 68 p.s.i.g. The reaction mixture was then cooled to below room temperature. Unreacted ethylene oxide was removed in vacuo. The product ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol contained an average of 5 moles of ethylene oxide per mole of glycol.

EXAMPLE IV

Adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol

Using trimethylamine catalyst.—Four moles (904 g.) of 2,4,7,9-tetramethyl-5-decyne-4,7-diol was charged to a one-gallon autoclave equipped with an internal heating and cooling coil and a stirrer. The autoclave was sealed, purged with nitrogen, and heated to a temperature of 50 to 55° C. To the autoclave was added 5 g. (1 percent based on the weight of 2,4,7,9-tetramethyl-5-decyne-4,7-diol) of trimethylamine as a liquid under pressure. The last traces of trimethylamine were driven in with nitrogen gas under pressure. Eight hundred and fifty ml. (748 g., 17 moles) of ethylene oxide was introduced into the autoclave over a period of 3 hours while the temperature was maintained at 40 to 50° C. by circulation of cooling water through the internal coil. After the addition of ethylene oxide was completed, the reaction mixture was maintained at a temperature of 50 to 64° C. for an additional 2 hours. During this time the pressure varied from 45 to 75 p.s.i.g. The reaction mixture was then cooled to below room temperature. Unreacted ethylene oxide was removed in vacuo. The product ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol contained an average of 4 moles of ethylene oxide per mole of glycol.

EXAMPLE V

Adducts of 7,10-dimethyl-8-hexadecyne-7,10-diol

To a one-liter autoclave was added a solution of 141 g. (0.5 mole) of 7,10-dimethyl-8-hexadecyne-7,10-diol dissolved in 160 ml. xylene. After adding 5 g. of triethylamine to the solution, the autoclave lines were flushed with nitrogen at 25 p.s.i.g., the nitrogen adjusted to zero gauge pressure, and the mixture warmed to about 55° to 60° C. At this temperature, 301 g. (6.8 moles) of liquid ethylene oxide were slowly added to the surface of the glycol solution, and the temperature slowly increased to about 100° C. After about 70 percent of the ethylene oxide had been added, the temperature was decreased to about 40° C. by cooling, and the balance of the ethylene oxide added.

Upon the addition of all the liquid ethylene oxide, the autoclave was closed, and the reaction mixture heated to 156° C., which temperature generated a maximum pressure of 285 p.s.i.g. The temperature was maintained for about an hour, or until there was no further pressure drop.

The resultant adduct, after cooling, consisted of an amber oil which contained a ratio of 1:7.3 of glycol to oxyethylene moieties. The adduct readily dissolved in water in all proportions, yielding a cloudy to turbid solution.

EXAMPLE VI

Mixed adducts of 7,10-dimethyl-8-hexadecyne-7,10-diol and 3-methyl-1-nonyn-3-ol

A mixture comprising by weight about 84% of 7,10-dimethyl-8-hexadecyne-7,10-diol and about 16% of 3-methyl-1-nonyn-3-ol was prepared. Upon cooling, the glycol-carbinol mixture solidified to a light cream solid, which was used without further purification for the reaction with ethylene oxide.

The glycol-carbinol mixture was liquefied by warming and 133.5 g. of the molten glycol-carbinol (corresponding to 0.4 mole glycol and 0.133 mole carbinol) transferred to a liter autoclave. After adding 5 g. of triethylamine, the autoclave was sealed and purged with nitrogen at 25 p.s.i.g., and the nitrogen pressure adjusted to zero gauge pressure. A total of 354 g. (8.04 moles) of liquid ethylene oxide was added to the reaction mixture in two stages.

In the first stage, 218 g. of ethylene oxide was added to the reaction mixture in the autoclave, and the entire charge was heated for five hours at an average temperature of 150° C. The pressure during this period varied from an optimum of 268 to a minimum of 231 p.s.i.g. and then remained essentially unchanged. The autoclave was then cooled to 25° to 30° C., and the remaining 136 g. of ethylene oxide added. After heating the charge for an additional five hours at 150° C., the autoclave was again cooled to room temperature, opened, and the product warmed to 120° C. to free it of unreacted ethylene oxide (88.5 g.). The product was vacuum topped at 120–150° C./25 mm. to eliminate the last traces of ethylene oxide and triethylamine, yielding 229 g. of a light amber oil which had a 1:10.4 glycol to ethylene oxide ratio and which possessed excellent surfactant properties.

EXAMPLE VII

Adducts of 4,7-dimethyl-5-decyne-4,7-diol

To a one-liter autoclave were added 99 g. (0.5 mole) of 4,7-dimethyl-5-decyne-4,7-diol and 10 g. of N,N-dimethylaniline. After flushing out the autoclave lines with nitrogen, 315 g. of liquid ethylene oxide was weighed into the autoclave and the reaction mixture heated for five hours from 48° to 160° C., during which time the pressure varied from 56 to 530 p.s.i.g. Upon cooling to room temperature and venting unreacted ethylene

oxide, the adduct was warmed to remove the last traces of ethylene oxide. The resultant product, on decolorization, was a light amber oil containing a ratio of 1:9.0 of glycol to oxyethylene moieties. The adduct was soluble in water, yielding a cloudy to turbid solution.

EXAMPLE VIII

Adducts of 3-methyl-1-nonyn-3-ol

To a one-liter autoclave were added 100 g. (0.65 mole) of 3-methyl-1-nonyn-3-ol and 5 g. of triethylamine as a catalyst. After purging all lines in the autoclave system with nitrogen at 25 p.s.i.g., the nitrogen pressure was adjusting to zero gauge pressure, and 198 g. (4.5 moles) of liquid ethylene oxide slowly added to the surface of the molten carbinol at temperatures between 30° and 100° C. After the addition of about 75% of the total amount of ethylene oxide, the absorption rate diminished and the pressure began to rise. The reaction temperature was then gradually lowered to about 25° to 40° C. to control the autoclave pressure and to allow the remainder of ethylene oxide to be added at a pressure of about 50 p.s.i.g.

Following the addition of all of the ethylene oxide, the system was again purged with nitrogen, the autoclave sealed and the reaction mixture heated to 151° C., or until a maximum pressure of 205 p.s.i.g. was generated. Upon cooling, the resultant product was a mobile, light orange-brown oil which was cleansed of any unreacted ethylene oxide and triethylamine by vacuum topping at 120°–130° C./25 mm. The amine catalyst was removed from the product which altered its color to a light amber shade. If further purification is required or desired, the product may be treated with several drops of concentrated hydrochloric acid, and decolorized with charcoal. The reaction product contained a molar ratio of 1:10.0 of carbinol to ethylene oxide units.

The adduct was freely soluble in water, and was used without the further purification step in blending a detergent mixture. The yield of the desired adduct was in excess of 95% of theory, based on the ethylene oxide consumed. The use of triethylamine as a catalyst in the reaction effectively prevented alkali cleavage of the starting carbinol to methyl n-hexyl ketone, via the reverse-Favorski reaction.

EXAMPLE IX

Adducts of 3,5-dimethyl-1-hexyn-3-ol

To a one-liter autoclave were added 125 g. (1.0 mole) of 3,5-dimethyl-1-hexyn-3-ol and 2 g. of dry triethylamine. The autoclave was sealed, purged with nitrogen, and pressurized to 40 p.s.i.g. with nitrogen. A total of 176 g. (4.0 moles) of ethylene oxide was gradually added. During the addition of the first half of the ethylene oxide, the temperature was maintained in the range of 50° to 90° C. with occasional cooling as required. The remainder of the ethylene oxide was added at a reactor temperature of 50° to 55° C. The autoclave was then sealed and heated at a temperature of 100° to 115° C. for three hours. The reaction mixture was allowed to cool overnight. The crude ethylene oxide adduct weighed 313 g. The adduct was freed of unreacted ethylene oxide, triethylamine, and by-product methyl isobutyl ketone by vacuum topping. A pure ethylene oxide adduct of 3,5-dimethyl-1-hexyn-3-ol weighing 264 g. was obtained. Based on weight increase and the amount of recovered methyl isobutyl ketone, the molar ratio of 3,5-dimethyl-1-hexyn-3-ol to ethylene oxide was 1:3.8. The adduct was a pale, clear yellow, mobile liquid.

The other ethylene oxide adducts of acetylenic tertiary glycols and carbinols coming within the scope of this invention can be prepared in a similar manner to that described in detail in the above specific working examples.

Surfactant properties of the adducts

Table 2 summarizes the results of a series of physical tests which were performed on various glycol adducts to illustrate their surfactant and foaming properties. Each compound was tested for its cloud point, and the surface and interfacial tensions of aqueous solutions of the compounds in dynes per centimeter determined with a du Nouy ring tensiometer at 25° C. using varying concentrations.

In addition, the wetting activity of each compound was measured by the Draves-Clarkson wetting test. In this test, a standard 5 gram skein of grey cotton yarn is held submerged in the test solution at 25° C. (0.1% and 0.5% aqueous solutions of the adducts) by means of a weight. As the solution wets, the air within the yarn is continuously displaced, and the buoyancy decreased until the skein sinks. The time in seconds that the skein remains afloat is considered to be the index of wetting. The wetting activity determined in this manner is an excellent indication of the ease and efficiency of fabric wetting of a surfactant.

Finally, the foaming characteristics of each adduct was measured by the Ross-Miles foam test. This procedure consists of allowing a stream of the adduct in aqueous solution to perpendicularly fall through a clean thermostated condenser maintained at 110° F. until the stream hits the bottom of the condenser and causes foaming. The height of the foam in centimeters is read when the last drop of the stream hits the bottom of the condenser and again after a period of five minutes has elapsed.

The following abbreviations of names of compounds are used in Table 2:

DMD=dimethyl decylenediol (4,7-dimethyl-5-decyne-4,7-diol).

TMD=tetramethyl decylenediol (2,4,7,9-tetramethyl-5-decyne-4,7-diol).

DMHD=dimethyl hexadecylenediol (7,10-dimethyl-8-hexadecyne-7,10-diol).

MN=methyl nonynol (3-methyl-1-nonyl-3-ol).

DMH=dimethyl hexynol (3,5-dimethyl-1-hexyn-3-ol).

TABLE 2.—SURFACTANT PROPERTIES OF THE ADDUCTS

Starting Material	Ratio	Cloud Point (° C.)	Surface Tension (dynes/cm.)			Draves Test (sec.)			Interfacial Tension (dynes/cm.)			Ross-Miles Foam (cm.) 1.0%
			0.1%	0.5%	1.0%	0.1%	0.5%	1.0%	0.1%	0.5%	1.0%	
DMD	1:9.0	-----	39.5	32.5	31.2	>300	34	6	-----	-----	-----	-----
DMD	1:19.8	-----	-----	35.5	-----	-----	>300	-----	-----	9.2	-----	-----
DMD	1:51.4	>100	-----	42.4	-----	-----	>300	-----	-----	16.1	-----	-----
TMD	1:4.0	<25	-----	29.68	-----	172	Inst.	Inst.	7.0	3.4	-----	-----
TMD	1:4.1	25	-----	27.2	-----	-----	Inst.	-----	4.1	4.1	-----	1.5
TMD	1:6.5	46-48	-----	28.5	-----	-----	Inst.	-----	6.0	6.0	-----	3.2
TMD	1:6.8	25	34.0	27.3	-----	145	Inst.	-----	11.0	4.2	-----	1.9
TMD	1:7.0	<25	-----	29.3	-----	140	5-6	Inst.	6.9	3.7	3.4	0.8
TMD	1:7.5	42-44	-----	28.7	-----	-----	1	-----	4.9	4.9	-----	8.0
TMD	1:7.8	-----	-----	27.2	-----	-----	Inst.	-----	5.3	5.3	-----	-----
TMD	1:9.0	-----	-----	28.8	-----	172	Inst.	Inst.	13.8	6.7	-----	5.4
TMD	1:15	-----	31.9	-----	-----	>300	>300	-----	17.9	9.3	-----	-----
TMD	1:16	<25	33.4	29.9	28.5	>300	6-7	Inst.	9.4	5.2	3.7	0.8
TMD	1:16	-----	-----	31.0	-----	-----	19	-----	-----	8.9	-----	-----
TMD	1:17	-----	-----	29.0	-----	-----	Inst.	-----	7.1	7.1	-----	-----
TMD	1:30	>100	-----	36.3	-----	-----	>300	-----	-----	10.8	-----	14.6
DMHD	1:7.3	<25	-----	27.0	-----	21	4	3-4	3.2	2.4	-----	1.4
						(0.05%)			(0.05%)			
						11			2.6			
									(0.1%)			
DMHD	1:15	54-58	28.4	29.0	-----	9	1	-----	-----	3.2	-----	8.0
DMHD-MN	1:10.4	44-46	27.5	28.4	-----	-----	Inst.	-----	3.4	2.9	-----	10.4
MN	1:1	-----	33.7	33.4	-----	88	-----	-----	-----	-----	-----	-----
			(0.05%)	(0.06%)	-----	(0.06%)	-----	-----	-----	-----	-----	-----
			Insol	-----	-----	-----	-----	-----	-----	-----	-----	-----
			(0.1%)	-----	-----	-----	-----	-----	-----	-----	-----	-----
MN	1:3.5	-----	-----	28.9	-----	>300	Inst.	-----	-----	-----	-----	-----
			(0.05%)	-----	-----	(0.05%)	-----	-----	-----	-----	-----	-----
MN	1:10.0	<25	-----	29.9	-----	-----	5.5	-----	-----	6.0	-----	0.4
DMH	1:3.8	-----	-----	33.4	30.0	-----	26	Inst.	-----	-----	-----	-----

From an analysis of the results summarized in Table 2, it is apparent that an increase in the polyoxyethylene chain length results in a higher cloud point and solubility. Table 2 also shows that wetting time, as shown by the Draves test, is considerably shortened as concen-

tration is increased, and that instantaneous wetting is achieved with certain adducts, such as those of 2,4,7,9-tetramethyl-5-decyne-4,7-diol, in concentrations in excess of about 0.5 to 1.0%.

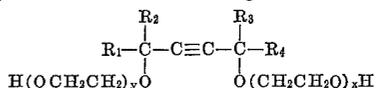
The adducts of this invention can be employed in various processes or incorporated in various compositions where it is desired to take advantage of their surfactant properties. For example, the adducts can be effectively used in various wet processing textile operations, such as dyeing of fibers, fiber scouring, and kier boiling, where their low foaming properties would be particularly advantageous. The adducts may be incorporated in dentifrices, toilet soaps, water base perfumes, shampoos, and various detergents where their marked ability to lower surface tension and at the same time produce substantially no foam would be highly desirable. These adducts may also be used in water base paints, adhesives, and latex compounds.

When compounding detergent compositions which include one or more of these adducts, the usual builders, detergents, and sequestering agents can be employed. The alkali-metal phosphates, silicates and carbonates, such as sodium phosphate, sodium dihydrogen phosphate, sodium tripolyphosphate, sodium hexametaphosphate, sodium carbonate, sodium silicate, sodium metasilicate, and mixtures of these materials have been found particularly useful in this regard. Sequestering agents such as sodium hexametaphosphate and trisodium phosphate may also be incorporated in such detergent formulations.

In preparing the compositions an amount of the adduct should be used sufficient to increase the wetting power of the system to which it will be added. It will be understood that the proportion of the adduct necessary to accomplish this result in each case cannot be exactly fixed since it is dependent upon the specific properties of the adduct employed, and the use to which the compositions are to be put. However, it has been found that generally the adduct can be employed in proportions from about 0.05 to about 10% by weight of the aqueous composition.

We claim:

1. Ethylene oxide adducts having the structural formula



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in which R_1 and R_4 are alkyl radicals containing from 3 to 6 carbon atoms, R_2 and R_3 are selected from the group consisting of methyl and ethyl, x and y have a sum in the range of 3 to 20, inclusive.

2. Ethylene oxide adducts of 4,7-dimethyl-5-decyne-4,7-diol containing 3 to 20 oxyethylene moieties per mole. 5

3. Ethylene oxide adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol containing 3 to 20 oxyethylene moieties per mole.

4. Ethylene oxide adducts of 7,10-dimethyl-8-hexadecyne-7,10-diol containing 3 to 20 oxyethylene moieties per mole. 10

5. Ethylene oxide adducts of a mixture of 7,10-dimethyl-8-hexadecyne-7,10-diol and 3-methyl-1-nonyl-3-ol containing a total of 3 to 20 oxyethylene moieties per mole. 15

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