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ALKYLENE OXIDE CONDENSATION PRODUCTS OF DIMERIZED FATTY ACID ALKYLOL AMIDES

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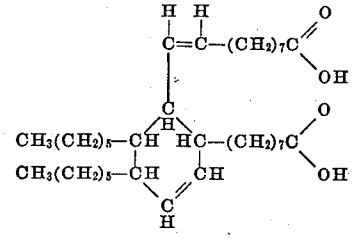
12 Claims. (Cl. 260—404.5)

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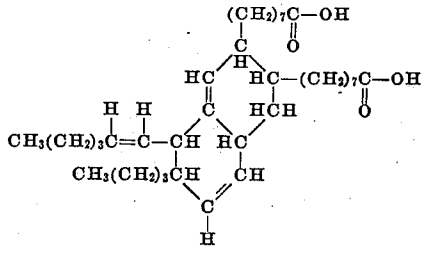
This invention relates to water-soluble alkylene oxide condensation products of bis-alkylol amides of heat-polymerized or dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, and to their methods of preparation. Objects of the invention are to obtain non-ionic surface-active agents having good dispersing and emulsifying properties, which are particularly valuable as assistants in dyeing processes employing preformed metallized dyes in an acid dye bath.

It is well known that the polyunsaturated fatty acids of 18–20 carbon atoms, and particularly the dienic and trienic fatty acid mixtures obtained by the saponification of semi-drying oils such as cottonseed oil, soya bean oil, dehydrated castor oil, linseed oil, tung oil, fish oils and the like, are converted by heating to dimers which are essentially organic dicarboxylic acids of the cycloaliphatic series. The most probable structural formulas for these dimerized fatty acids are given in volume 32 of Industrial Engineering Chemistry, page 808, as follows:

Dimerization of octadecadienic acids and their esters by 1,4-diene addition leads to compounds of the following structure, or isomers thereof:



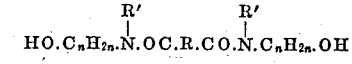
Conjugated and unconjugated octadecatrienic acids and their esters polymerize by a bimolecular addition involving and additional intramolecular ring closure, forming a compound of the following structure, or isomers thereof:



In our copending application Serial No. 677,525 filed concurrently herewith we have shown that by heating these compounds or their lower alkyl esters such as the methyl or ethyl esters with

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mono- or dialkylolamines containing alkylene radicals of 2–4 carbon atoms they are converted into diamides of the formula



in which R is the residue of the dimerized polyunsaturated fatty acid, n is 2, 3 or 4, and R′ is either hydrogen or the radical—$C_nH_{2n}.OH$ depending on whether the mono- or dialkylolamine was used. These diamides, which vary in appearance from dark, viscous liquids to non-crystalline solids, are soluble in alcohols and in aromatic hydrocarbon solvents but are insoluble in water and are not surface-active.

Our present invention is based on the discovery that these bis-alkylol amides can be converted into water-soluble non-ionic surface-active agents by condensing them with sufficient quantities of alkylene oxides of 2–4 carbon atoms to render the product water-soluble. The invention therefore consists in the production of water-soluble derivaties of bis-alkylol amides of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, in which the alkylol radicals contain 2–4 carbon atoms, by condensing them with ethylene, propylene or butylene oxide or similar compounds such as epichlorhydrin which contain a water-solubilizing lower alkylene oxide ring.

Any polyunsaturated fatty acid of approximately 18 carbon atoms may be used as a starting material in preparing the compositions of the present invention. Fatty acid mixtures containing polyunsaturated fatty acids of approximately 18 carbon atoms are employed in preparing the dimerized fatty acids because they are readily obtainable by the hydrolysis of natural oils of vegetable and animal origin, and it will be understood that the expression "dimerized polyunsaturated fatty acids of approximately 18 carbon atoms" refers to the monomeric fatty acids from which the dimerized acids are prepared by heat treatment rather than to the resulting dimers, which contain approximately 36 carbon atoms. The dimer acids may be used either in the form of the free acids or as the lower alkyl esters thereof, such as the methyl, ethyl or propyl esters, in preparing the alkylol amides employed in the process of our invention.

Any mono- or diahyloloamine in which the alkylene radical or radicals contain 2–4 carbon atoms may be condensed with the dimerized higher fatty acids described above, or with their methyl, ethyl or propyl esters, to form diakylol

amides. Typical dialkyloloamines which may be used are monoethanolamine, diethanolamine, monopropanolamine, dipropanolamine, monobutanolamine, dibutanolamine or mixed dialkylolamines containing one ethanol and one propanol substituent, or one ethanol and one butanol substituent, etc. These and other similar amines may be condensed with the dimerized higher fatty acids by refluxing a solution containing about one mol of the dimerized acid and two mols of the amine in an organic solvent such as toluene, xylene and the like while distilling off the water produced by the amide formation. When esters of the dimerized fatty acid are employed the organic solvent may be omitted, the two reagents being simply mixed and heated at about 150°–200° C. in an inert atmosphere for several hours. The liberated alcohol may then be removed, together with any excess amine, by distillation at reduced pressures.

The alkylene oxide condensation can be carried out in the absence of solvents by heating the dimer acid diamides with ethylene, propylene or butylene oxide in an autoclave under pressures up to 4–5 atmospheres, preferably in the presence of a small quantity of a catalyst such as sodium alcoholate at temperatures of 100°–160° C. We have found, however, as another important feature of the invention that the condensation reaction can be carried out at considerably lower pressures and temperatures, and in most cases at atmospheric pressures, by the use of polar solvents such as isopropyl alcohol, tertiary butyl alcohol and the like, preferably with the addition of a lower alkyl amine such as diethylamine or triethylamine as catalyst. Under these conditions, solubilizing amounts of lower alkylene oxides can be condensed with the dimer acid diamides simply by passing the alkylene oxide compound into the solution under a reflux condenser, and at approximately the boiling point of the solvent used.

The quantity of alkylene oxide to be condensed with the dimer acid diamides to obtain the proper degree of water-solubility for optimum dispersing, emulsifying or dye-assistant properties may vary throughout a wide range. With diamides of relatively low molecular weight, such as the bis-monoethanolamides, as little as 8 mols of ethylene oxide or 10–15 mols of propylene oxide or 15–25 mols of butylene oxide for each mol of the dimer acid diamide will produce adequate water-solubility. As shown in Example 4, as much as 175 mols of alkylene oxide for each mol of the dimer acid can easily be combined if desired.

The invention will be further illustrated by the following specific examples. It should be understood, however, that although these examples may describe in detail certain specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

The diamides of dimerized polyunsaturated fatty acids with mono- or dialkylolamines are prepared by refluxing a xylene solution containing one mol of the acid and two mols of the amine while distilling off the water produced by the amide formation. Sometimes an additional 10% molecular excess of the amine is added near the end of the reaction, since some of the amines may tend to distill off with the water.

For example, 56 parts by weight of dimerized cottonseed fatty acid were dissolved in 31 parts of xylene and 125 parts of monoethanolamine were added. The mixture was heated under a reflux condenser with a water trap until the distillation of water was almost complete, after which an additional 12 parts of monoethanolamine were added. Reflux was continued until no more water was evolved, after which the xylene was distilled off at 140°–150° C. under a pressure of 20–30 mm. of mercury. This bis-ethanolamide of the dimerized acid was obtained as a dark, viscous liquid.

Example 2

t-Butanol, 300 cc., 190 grams of the N,N'-di-2-hydroxyethylamide of the dimer acid of Example 1 and 20 cc. of triethylamine were heated together in a flask provided with stirrer, inlet tube, thermometer, and spiral coil reflux condenser. Ethylene oxide was bubbled through the resulting solution, maintained under atmospheric pressure, at 70°–80° C. until 244 grams were absorbed. This required about 12 hours. During the reaction ice water was circulated through the reflux condenser to prevent escape of the unreacted ethylene oxide. When the addition was complete the reaction mixture was allowed to reflux for 2 or 3 hours or until the temperature reached 90°–95° C. after which the solvent and volatile material were stripped at reduced pressure (20–30 mm.). The product was 418 grams of dark, viscous liquid.

Example 3

The ethanolamide of the dimer acid of Example 1, 192 grams, 225 cc. of t-butanol, and 15 cc. of triethylamine were heated at atmospheric pressure with agitation to 70°–80° C., and ethylene oxide was bubbled through the solution as in Example 2. After 477 grams of gas had been absorbed (about 24 hours), the solution was refluxed for 3 hours. The t-butanol and triethylamine were then removed by distillation at reduced pressure. The product was 655 grams of thick, dark brown liquid which was soluble in water to form clear foaming solutions.

Example 4

A mixture of 21 grams of the dimer acid ethanolamine of Example 1, 100 cc. of t-butanol and 15 cc. of triethylamine were heated with agitation to 70°–80° C. as in Example 3 and 266 grams of ethylene oxide were absorbed. The yield was 271 grams of a product containing 175 ethenoxy units per molecule.

Example 5

A solution of 840 grams (1.5 mols) of dimerized cottonseed fatty acids and 321 grams of diethanolamine in 550 cc. of xylene was heated under reflux at 135°–145° C. for about 12 hours while stripping out water from the distillate. After 66 cc. of water were collected the xylene was stripped off under reduced pressure at temperatures up to 160° C. 1107 grams of bis-diethanolamide of dimerized cottonseed fatty acids were obtained as a dark brown, very viscous oil.

Example 6

A 250-gram portion of the product of Example 5 was mixed with 200 cc. of t-butanol and 10 cc. of triethylamine in a flask fitted with stirrer, thermometer, gas inlet tube, and a coil condenser open to the atmosphere through which ice

water was circulated. Ethylene oxide was passed into the solution at 70°–85° C. for 7 hours at the end of which time 243 grams were absorbed. Refluxing was continued for 2 hours, and the volatile material was then distilled off at reduced pressure. The product was 485 grams of a dark brown, oily liquid, which was soluble in water to a clear yellow, foaming solution. 16 mols of ethylene oxide were condensed in each mol of product

Example 7

A mixture of 200 grams (.342 mol) of the dimethyl ester of dimerized linseed acid (prepared according to Bradley, Industrial & Engineering Chemistry 32, 802 (1940)), and 57 grams (.684 mol plus 20% excess of 95% ethanolamine) was heated with stirring at 170°–180° C. for two hours in a nitrogen atmosphere. At the end of this time the excess ethanolamine and the methyl alcohol were distilled off under water-pump pressure up to a temperature of 160° C. The product was a dark red oil. Yield 200 grams, 100% of theory.

Example 8

A mixture of 200 grams (0.36 mol) of dimerized soya bean fatty acid and 60 grams (0.72 mol plus 10% excess of normal propanolamine) and 130 ml. of xylene was refluxed with stirring, stripping off the water in a trap as it formed. The reaction required 12½ hours at 135°–148° C. When the reaction was complete, as shown by the fact that no more water formed, the xylene and excess normal propanolamine were stripped off by distillation under water-pump pressure up to a temperature of 150° C. The product was a viscous greenish-black oil. Yield 243 grams, 100% of theory.

Example 9

A mixture of 200 grams (0.36 mol) of dimerized soya beam fatty acid, 80 grams (0.72 mol plus 10% excess of 2-amino-1-butanol) and 150 ml. of xylene was refluxed at a temperature of 145°–155° C. for 20 hours. The water was stripped out in a trap as it formed. When the reaction was complete the xylene and excess butanolamine were stripped off under water-pump pressure up to a temperature of 160° C. The product was a dark green viscous oil. Yield 250 grams, 99% of theory.

Example 10

A mixture of 228 grams (0.39 mol) of the dimethyl ester of dimerized tung oil fatty acid (prepared according to Industrial & Engineering Chemistry 32, 802 (1940)) and 60 grams (0.78 mol plus 20% excess) of 95% ethanolamine was heated for two hours at 170°–180° C. in a nitrogen atmosphere. The excess ethanolamine and the methanol were distilled off under water-pump pressure up to a temperature of 190° C. The product was an amber colored viscous oil. Yield 253 grams, 100% of theory.

Example 11

A solution of 97 grams (0.151 mol) of the bis-monoethanolamide of dimerized linseed fatty acid prepared as described in Example 7, 100 ml. of tertiary butyl alcohol, and 10 ml. of triethylamine was placed in a flask fitted with a stirrer, gas inlet tube and thermometer, both reaching below the surface of the solution. The flask was attached to a reflux condenser through which ice water was circulated. Ethylene oxide was passed into the flask at a temperature of 70°–86° C., during 3½ hours. At the end of this time 125 grams (2.84 mols) had been absorbed. The reaction mixture was heated for another three hours during which time the reflux temperature rose to 96° C. The solvent and volatile material were distilled off under water-pump pressure up to a temperature of 130° C. The product was a dark red oil, yield 217 grams.

Example 12

A solution of 100 grams (0.156 mol) of the bis-monoethanolamide of dimerized linseed fatty acid, 100 ml. of tertiary butyl alcohol and 10 ml. of triethylamine was placed in the apparatus described in the preceding example. Ethylene oxide was passed into the solution during 5½ hours at a temperature of 68°–88° C. During this time 217 grams (4.93 mols) were absorbed. The reaction mixture was heated for an additional three hours and the reflux temperature rose to 95° C. The solvent and volatile materials were distilled off under water-pump pressure up to 130° C. The product was a dark red oil, yield 310 grams.

Example 13

A solution of 100 grams (0.156 mol) of the bis-monoethanolamide of dimerized tung fatty acid, 100 ml. of tertiary butyl alcohol and 10 ml. of triethylamine was placed in the apparatus described above. Ethylene oxide was passed into the solution during 4½ hours at a temperature of 75°–84° C. During this time 129 grams (2.93 mols) were absorbed. The mixture was heated for an additional four hours at 92°–95° C. to complete the reaction. The solvent and volatile materials were distilled off as in the preceding examples. The product was a brown viscous oil, yield 224 grams.

Example 14

A solution of 100 grams (0.156 mol) of the bis-monoethanolamide of dimerized tung fatty acid, 100 ml. of tertiary butyl alcohol, and 10 ml. of triethylamine was placed in the apparatus described above. Ethylene oxide was passed into the solution during 8½ hours at 77°–86° C. During this time 218 grams (4.95 mols) were absorbed. The mixture was heated for an additional three hours at 90°–100° C. to complete the reaction. The solvent and volatile materials were distilled off as in the preceding examples. The product was a dark reddish-brown oil, yield 311 grams.

Example 15

A solution of 100 grams (0.149 mol) of the bis-monopropanolamide of dimerized cottenseed fatty acid, 100 ml. of tertiary butyl alcohol and 10 ml. of triethylamine was placed in the apparatus described above. Ethylene oxide was passed into the flask during seven hours at 80°–86° C. During this time 170 grams (3.86 mols) were absorbed. The mixture was heated at 95°–105° C. for an additional three hours to complete the reaction. The solvent and volatile materials were distilled off as before. The product was a brown viscous oil, yield 263 grams.

Example 16

A dye bath was made up of 300 parts of water and 0.1 parts of chromium complex of the azo dyestuff from diazotized anthranilic acid and 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone. Two parts of 10% sulfuric acid were added and 5 parts of wool yarn thoroughly wet out were then introduced into the bath. 7.5 parts of a 1%

solution of the product of Example 2 were then added and the bath brought slowly to the boil and maintained there at the boil for sufficient time to complete dyeing. The yarn was then removed, well rinsed, and dried. The dyeing was bright, level, and of excellent color value.

A dye bath was made up having the same composition as before but without the surface-active agent. The resulting dyeing was definitely inferior in brightness, levelness and strength of shade.

Example 17

A dye bath was made up of 4000 parts of water heated to 100° F. and 100 parts of wool fabric gradually introduced and maintained for a sufficient time to assure thorough wetting. 5 parts of concentrated sulfuric acid was diluted, added to the dye bath, and allowed to penetrate the wool. Thereupon the solutions of the following dyes were introduced and allowed to disperse:

1 part of the chromium complex of the azo dyestuff obtained from diazotized anthranilic acid and 1-(4'-sulfophenyl)-3-methyl - 5 - pyrazolone.

1 part diazotized 1-amino-2-hydroxy-naphthalene-4-sulfonic acid coupled to 1-phenyl-3-methyl-5-pyrazolone

1 part diazotized 1-amino-2-hydroxy-naphthalene-4-sulfonic acid coupled to 1-hydroxynaphthalene-8-sulfonic acid

Two parts of the product of Example 2 dissolved in warm water were then added, the temperature of the dye bath raised to the boil gradually, and boiled for a sufficient time to complete dyeing. Thereupon the dye bath was run off, the wool fabric rinsed in cold water, and dried.

The goods dyed were level, free of skitteriness, and showed no oil blotches. The shade of the fabric was strong, approximately 20% stronger than the same dyeing effected under identical conditions and without surface-active agent. The latter, in addition to the weaker strength, was uneven, skittery, and showed the presence of oil blotches due to the oil present in the undyed material.

When the dyeing was effected without the surface-active agent but with double the amount of sulfuric acid, approximately the same strength and levelness was obtained as with the surface-active agent and half the amount of acid. However, the fabric was definitely harsher, mechanically weaker, and poorer in fabric texture due to felting.

Example 18

A dye bath was made up of 300 parts of water and 0.4 part of the chromium complex of the azo dyestuff obtained from diazotized 1-amino-2-hydroxy-6-nitro-naphthalene - 4 - sulfonic acid coupled to 2-naphthol. 0.5 part of calcined Glaubers salt and 0.1 part of 56% acetic acid were then added, whereupon 5 parts of thoroughly wet out wool yarn were introduced into the dyebath. 10 parts of a 1% solution of the product of Example 2 were introduced and the temperature raised to 180° F., whereupon 0.075 part of formic acid was added, the temperature raised to the boil, the bath boiled for a short time, 0.1 part sulfuric acid added and the boil continued for about twice the length of time until dyeing was complete.

Example 19

A dye bath was made up of 300 parts of water and 0.1 part of well dissolved chromium complex of the azo dyestuff obtained from diazotized 4-nitro-2-amino-phenol coupled to 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone. 3 parts of 10% ammonium sulfate solution were then added with 4 parts of calcined Glaubers salt. Thereupon 7.5 parts of a 1% solution of the product of Example 11 were added and 5 parts of thoroughly wet out wool yarn then introduced. The bath was slowly brought to the boil, boiled for a short time, 0.5 part of 56% acetic acid added, boiling continued for about the same length of time, followed by an addition of another 0.1 part of 56% acetic and the boiling then continued for the same time until the dyeing was complete. The yarn was removed, rinsed and dried, and presented a bright dyeing which was level and of excellent color value.

A similar dyeing procedure was followed with no surface-active agent added but all other factors kept the same. The resulting dye was quite inferior in brightness, levelness and strength of shade.

What we claim is:

1. Water-soluble condensation products of lower alkylene oxides of 2–4 carbon atoms with dialkylolamides of dimerized polyunsaturated fatty acids of the formula

$$HO.C_nH_{2n}.\underset{\displaystyle R'}{N}.OC.R.CO.\underset{\displaystyle R'}{N}.C_nH_{2n}.OH$$

wherein R is the residue of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, n is a whole number from 2 to 4 inclusive and R' is a member of the group consisting of hydrogen and $-C_nH_{2n}.OH$ said condensation products having from 8 to 175 mols of said lower alkylene oxide condensed therein.

2. Water-soluble condensation products of ethylene oxide with dialkylolamides of dimerized polyunsaturated fatty acids of the formula

$$HO.C_nH_{2n}.\underset{\displaystyle R'}{N}.OC.R.CO.\underset{\displaystyle R'}{N}.C_nH_{2n}.OH$$

wherein R is the residue of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, n is a whole number from 2 to 4 inclusive and R' is a member of the group consisting of hydrogen and $-C_nH_{2n}.OH$, said condensation products having from 8 to 175 mols of ethylene oxide condensed therein.

3. Water-soluble condensation products of lower alkylene oxides of 2–4 carbon atoms with bis-monoethanolamides of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, said condensation products having from 8 to 175 mols of said lower alkylene oxide condensed therein.

4. Water-soluble condensation products of lower alkylene oxides of 2–4 carbon atoms with bis-diethanolamides of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, said condensation products having from 8 to 175 mols of said alkylene oxide condensed therein.

5. Water-soluble condensation products of ethylene oxide with bis-monoethanolamides of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, said condensation products having from 8 to 175 mols of ethylene oxide condenser therein.

6. Water-soluble condensation products of ethylene oxide with bis-diethanolamides of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, said condensation products having from 8 to 175 mols of ethylene oxide condensed therein.

7. A method of producing water-soluble derivatives of dialkylolamides of dimerized polyunsaturated fatty acids of the formula

$$HO.C_nH_{2n}.N(R').OC.R.CO.N(R').C_nH_{2n}.OH$$

wherein R is the residue of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, n is a whole number from 2 to 4 inclusive and R' is a member of the group consisting of hydrogen and $-C_nH_{2n}.OH$ which comprises condensing therewith a sufficient quantity of an alkylene oxide of 2–4 carbon atoms to render the product water-soluble, said quantity being from 8 to 175 mols of the alkylene oxide for each mol of the dimer acid diamide.

8. A method according to claim 7 in which the alkylene oxide is ethylene oxide.

9. A method of producing water-soluble derivatives of bis-monoethanolamides of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms which comprises condensing therewith a sufficient quantity of an alkylene oxide of 2–4 carbon atoms to render the product water-soluble, said quantity being from 8 to 175 mols of the alkylene oxide for each mol of the dimer acid diamide.

10. A method according to claim 9 in which the alkylene oxide is ethylene oxide.

11. A method of producing water-soluble derivatives of bis-diethanolamides of dimerized

polyunsaturated fatty acids of approximately 18 carbon atoms which comprises condensing therewith a sufficient quantity of an alkylene oxide of 2–4 carbon atoms to render the product water-soluble, said quantity being from 8 to 175 mols of the alkylene oxide for each mol of the dimer acid diamide.

12. A method according to claim 11 in which the alkylene oxide is ethylene oxide.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,243,329	De Groote et al.	May 27, 1941
2,344,977	De Groote et al.	Mar. 28, 1944
2,379,413	Bradley	July 3, 1945

FOREIGN PATENTS

Number	Country	Date
337,368	Great Britain	Oct. 27, 1940
364,104	Great Britain	Dec. 28, 1931
380,431	Great Britain	1932

OTHER REFERENCES

Industrial & Eng. Chem., v. 32 (1940), pages 802 to 809 by Bradley et al.