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RICINOLEIC ACID ESTER OF TRIETHANOL-AMINE

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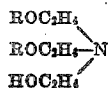
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This invention relates to new products adapted for use as wetting, dispersing or emulsifying agents. It relates more particularly to new products obtained by the partial esterification of triethanolamine by ricinoleic acid, that is, to the mono- and di-ricinoleic acid esters of triethanolamine, and to mixtures thereof; and it includes not only the new products, but also a new process for their production. The new products of the invention are very stable, and highly effective, in acid solution.

It has heretofore been proposed to prepare condensation products of higher fatty acids, such as stearic acid, etc., with alkylolamines, including primary, secondary and tertiary amines, by heating mixtures of the fatty acids and the alkylolamines to temperatures in the neighborhood of 160° C. Such proposed processes in fact result in the production of complex mixtures containing both the simple salt or soap of the fatty acid with the amine and esters of the alkylolamine with the fatty acid, and, where primary or secondary amines are used, the mixtures also contain amides or esters amides of these higher fatty acids and the amines. Apparently in such processes, the fatty acid initially reacts with the amine, particularly when tertiary amines are used, by simple addition, with the formation of the soap or salt, which product is subsequently converted in part into the ester upon heating at the relatively high temperatures, by rearrangement with elimination of water. Nevertheless, in the product finally produced, there has always been present, so far as we have been able to determine, a substantial amount of the soap or salt of the amine and the fatty acid, the condensation to form the ester always being incomplete. While such proposed processes may be used with some degree of success with such fatty acids as stearic acid, and result in the production of mixtures of esters and salts of the alkylolamines, the mono- and di-ricinoleic acid esters of triethanolamine cannot be produced by such a process because the ricinoleic acid, when heated to such high temperatures, polymerizes with more or less rapidity, so that the product obtained is a polymerized ricinoleic acid, rather than the desired ester or esters.

The new products produced in accordance with the present invention may be represented by the graphic formula:



in which one of the R's may represent the chain $\text{C}_{17}\text{H}_{33}\text{OHCO}$ characteristic of ricinoleic acid, and the other hydrogen, or both may represent the chain $\text{C}_{17}\text{H}_{33}\text{OHCO}$.

In accordance with the present invention, these new products are produced by alcoholysis by heating together, in proper proportions, castor oil or other ester of ricinoleic acid and triethanolamine. If it is desired to produce a product which contains predominantly the mono-ester, 3 moles of triethanolamine should be used for each mole of castor oil; while if it is desired to produce a product containing predominantly the di-ester, about 3 moles of triethanolamine should be used for each 2 moles of castor oil. It will be understood that, as in all organic reactions, the yields of the desired products are not quantitative and the products obtained, while containing a major and predominating proportion of the desired ester, will necessarily contain smaller proportions of other esters of triethanolamine and ricinoleic acid as well as unreacted starting material, etc. For example, if triethanolamine and castor oil are reacted in the proportions of about 3 moles of triethanolamine to 1 mole of castor oil, for the production of the mono-ricinoleic acid ester of triethanolamine, the product obtained will contain a major and predominating proportion of this compound, but it will also contain relatively small amounts of the di-ricinoleic acid ester, the tri-ricinoleic acid ester, as well as unreacted castor oil, triethanolamine, etc. If esters of ricinoleic acid other than castor oil, for example, ricinoleic ethyl ester, be used, the molar ratios of the triethanolamine and the ester will, of course, be different than for castor oil, but will be such that for each mole of triethanolamine there is used an amount of ester equivalent to from about 1 to about 2 moles of ricinoleic acid.

The new products of the present invention are advantageously produced in neutralized form, by neutralizing the reaction product with suitable acids, such as acetic acid, which form salts with the esterified amine. Tertiary amines form salts with acids by a simple additive reaction, and such salts may be formed directly by the addition of the proper amount of the acid to the anhydrous reaction mixture, or, if desired, the reaction product obtained may be dissolved in an acidulated aqueous solution, in which it dissolves or disperses to form clear solutions of dispersions.

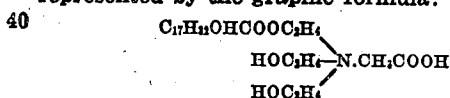
The new products are insoluble in hydrocarbon solvents. They differ from ordinary wetting, dispersing or emulsifying agents in that the surface-active ion is the cation, and not the anion. Such

materials as soaps, Turkey red oils, sulfonic acids, sulfonated alcohols, etc., which are wetting, dispersing or emulsifying agents, have, as their surface-active ion, the anion. The new products are, accordingly, highly stable and effective in acid solutions.

In forming the new products, as pointed out above, castor oil and triethanolamine, in selected proportions, are heated together to temperatures in excess of 100° C., but below the temperature at which decomposition might take place. Advantageously, the mixture is heated to a temperature between about 150° C. and about 180° C. for a sufficient length of time to permit the reaction to go to substantial completion, for example, for about two hours, the reaction proceeding smoothly and readily, and yielding a reaction product in the form of a yellow oil. In this product, there is present not only the desired esters, but also the glycerin set free in the reaction. For many purposes, the presence of glycerin in the final product is unobjectionable as there is no necessity for its removal if the product is intended for such purposes. On the other hand, if desired, the glycerin is readily removed as by washing with a suitable salt solution.

The invention will be further illustrated by the following specific example, but it is not limited thereto.

Example.—930 parts of castor oil and 420 parts of triethanolamine are heated to a temperature between about 150° C. and 180° C. for about two hours. The product obtained, when cooled, is a yellow oil. 216 parts of acetic acid are added to the product to neutralize it. The product so obtained consists predominantly of the acetate of mono-ricinoleic acid ester of triethanolamine, represented by the graphic formula:



If, in the process of the above example, the proportion of castor oil be increased, the final product obtained will contain more of the di-ricinoleic acid ester, and less of the mono-ester, but in any case the product obtained will contain certain proportions of the mono-ester, the di-

ester, and the tri-ester. Furthermore, it will be understood that the triethanolamine used is a commercial product, and as such is not pure triethanolamine, but contains relatively small amounts of mono- and di-ethanolamine, ethanol-ethylamines, and other alkylol or alkylol alkylamines, all of which to some extent enter the reaction and result in the production of corresponding esters in the final product, even though these esters are present but to a minor extent.

The products obtained may be used in the form of the free base, that is, the free amine, but are advantageously neutralized by the addition of an acid, or dissolved in aqueous acid to form a dispersion or solution therein. In the example, the acetate has been specifically described, but it will be understood that instead of acetic acid, the product may be neutralized with other organic acids, such as propionic acid, butyric acid, lactic acid, by inorganic acids, such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, or other inorganic acid, or by higher fatty acids, such as ricinoleic acid, or other higher fatty acids with the formation of the corresponding salts. In this specification and the appended claims, the term "ester of triethanolamine" is used to designate not only esters in the form of the free bases, but also their salts or neutralized derivatives.

We claim:

1. Products of the class consisting of the mono-ricinoleic acid ester of triethanolamine and the di-ricinoleic acid ester of triethanolamine.
2. The mono-ricinoleic acid ester of triethanolamine.
3. The di-ricinoleic acid ester of triethanolamine.
4. The process of preparing the mono-ricinoleic acid ester of triethanolamine which comprises heating castor oil and triethanolamine in the molecular proportions of about 3 moles of triethanolamine to 1 mole of castor oil to a temperature in excess of 100° C. for a sufficient period of time to permit substantial esterification of the triethanolamine.

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