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ALKYLOLAMINE DERIVATIVES OF ALIPHATIC ACIDS

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8 Claims. (Cl. 260—112)

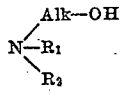
This case is a division of our copending application Serial No. 210,714, filed August 4, 1927, now Patent No. 1,799,821, dated April 7, 1931.

This invention relates to alkylolamine salts of aliphatic acids both saturated and unsaturated and to the sulfonic acid derivatives of these acids and more particularly to the ethanolamine salts of the higher fatty acids.

This invention has as objects the preparation of soluble oils, solvents and detergents as well as of antiseptic soaps.

These objects are accomplished by making the salts of the bases known as alkylolamines or hydroxy-alkylamines, more particularly of the ethanolamines, by combination with the fatty acids mentioned above by any of the well known methods for the production of salts.

The bases used for our purpose may be represented by the following general formula:



where *Alk* represents an aliphatic or hydroxy aliphatic radical, R_1 and R_2 represent hydrogen or an aliphatic radical or a hydroxy aliphatic radical or a poly hydroxy aliphatic radical. In making these new soluble oils we may proceed as follows:

The free fatty acids are combined directly with an organic base or a mixture of such bases. If the fatty acid is a solid the preparation is aided by the application of heat. It is also possible to start from the glycerides of the fatty acids, i. e., olive oil, cottonseed oil, castor oil, linseed oil and the like by saponifying the glycerides by heating with the base to a high temperature. In this case we find that the reaction is complete when a sample of the mixture dissolves entirely in water. If water is present at the start this may be driven off, the base not being volatile, until a concentrated product is left behind. When making these products by this method it is found that an excess of base is necessary to give the most satisfactory results.

When preparing the products obtained from the sulfonated fatty acids we may proceed as follows:

The acid product of the mixture of the sulfonated unsaturated acid as obtained by the action of sulfuric acid on an unsaturated oil such as castor oil in the well known manner is freed of mineral acid by washing. It is then freed of water either by settling or by any other suitable means and then enough of the alkylolamine base is added at ordinary temperature to neutralize the acidity of the sulfonic acid group or of both sulfonic acid and the carboxylic acid groups. The following examples will serve to illustrate our method of procedure, but it is to be understood that the invention is not to be limited thereby:

Example 1

2823.7 parts of free oleic acid are mixed with
1490 parts of tri-ethanolamine.

Example 2

1960 parts of oleic acid are mixed with
950 parts of a mixture containing 75% tri-ethanolamine and 20% of di-ethanolamine.

The products resulting from this procedure are semi-solids, particularly water soluble and ready for use without further treatment. It is possible that the resultant material may be a compound of the base with the oleic acid but this has not been definitely established and is, in fact, immaterial to the success of the invention.

Example 3

298.37 parts of ricinoleic acid $C_{17}H_{32}(OH)COOH$ are mixed with
105 parts di-ethanolamine.

The resultant product is a clear yellow oil, very soluble in water.

Example 4

372 parts castor oil are mixed with
260 parts tri-ethanolamine
200 parts water.

The above mixture is heated on the water bath for several hours. The saponification proceeds slowly and in order to make it complete within reasonable time it is of advantage to add an excess, for example 30% tri-ethanolamine, above the quantity mentioned.

Example 5

284.39 parts of stearic acid are melted. Into the melt are stirred

149 parts tri-ethanolamine,—stirring is continued at a temperature of about 80° C. until the mixture is uniform.

The resultant product on cooling is a solid, not very soluble in water but very soluble in alcohol. It acts as an excellent assistant in promoting solution.

Example 6

282 parts oleic acid
91 parts of amino-propane diol

$$NH_2—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—OH$$

are heated together until completely mixed. The product is very soluble in alcohol. In water the solution is cloudy but becomes clear on the addition of some excess base, e. g. 15 to 20%.

Example 7

282 parts oleic acid are caused to react as given in the above example with
119 parts of methyl di-ethanolamine

$$CH_3—N=(CH_2—CH_2OH)_2$$

The soap obtained in this way has the property, when in alcoholic solution, of dissolving mercuric oxide and giving a relatively stable product soluble in water. This is altogether a surprising result and illustrates the use of these new soaps for pharmaceutical purposes.

Example 8

6 parts of a crude sulfonated oil made by the action of sulfuric acid on castor oil are mixed with
1 part of mono-ethanolamine.

Example 9

2.7 parts of a crude sulfonated oil mixture in the form of free acids are mixed with
1 part of a mixture of di- and tri-ethanolamine.

The products of Examples 8 and 9 are entirely soluble in water. They are thick yellow oils presumably containing salts of the bases of the sulfonic acids but this point has not been definitely established and is immaterial to the success of the invention. The products formed in this way are quite satisfactory for ordinary purposes.

In dyeing Ponsol Blue GD double paste, Schultz No. 842, on cotton yarn in the package machine, using
5% of color
2½% sodium hydroxide
3% hydrosulfite,
the addition of 1% of the product formed by combining 1 mole of sulfo-ricinoleic acid and 1 mole tri-ethanolamine, containing di-ethanolamine, results in a brighter, more level dyeing.

Example 10

If a pure product is needed the operation may be carried out as follows:

378 parts of pure sulfo-ricinoleic acid prepared by the action of chloro-sulfonic acid on pure ricinoleic acid are mixed with
149 parts of tri-ethanolamine.

In the above case the addition of a further molecular equivalent of base produces a more soluble oil. The reason may be that the extra quantity of base combines with the carboxyl group but again this point has not been determined.

In the above examples any one of the bases as defined by the general formula given above may be used either alone or in mixture. The fatty acids may also be varied through a wide range.

By the term "alkylol", as used herein, we mean to include an alkyl radical in which one or more hydrogens are replaced by a hydroxyl group, and may be represented by the following:

$$—C_nH_{2n}.OH$$

or

$$—C_nH_{2n-1}(OH)_2.$$

We have found that these products, which are essentially organic soaps possess a greater dissolving power or dispersing power for organic substances than do ordinary soaps. They possess the detergent property of soaps without the high alkalinity characteristic of sodium or potassium salts of the fatty acids. These products for these reasons have a distinct advantage for many purposes and particularly as assistants in dyeing, and those compounds which are derived from sulfonated castor oil by the process mentioned are in many ways superior to ordinary sulfonated oils. Their superiority is evidenced by the greater evenness of the shades developed, the better utilization of the color, and the greater brilliance of the dyeing.

When added to water they bring about solution or dispersion in so fine a form as to appear a solution of insoluble organic bases such as amino-azo-benzene, para-nitro-benzene, azo-diphenyl-amine, benzene- azo-naphthalene-azo-phenol, rosanthrene base, di-ethyl-para-amido-phenol-1:4 naphtho-quinone-mono-imide, 2.4 di-nitro-benzene-1-azo-di-ethyl-aniline, etc. It takes about 2 to 5 parts of the solvent for 1 part of the insoluble base. These solutions may be used very successfully for the purpose of dyeing fibers of esterified cellulose.

It has also been found that these soaps dissolve metallic hydroxides and oxides, for example, mercuric oxide, and this property indicates their probable value in pharmacology, for example, in the production of antiseptic soaps and the like.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not intend to limit ourselves to the specific embodiments thereof except as indicated in the appended claims.

We claim:

1. A product resulting from the chemical combination of oleic acid and an alkylolamine containing a plurality of alkyl groups.

2. A product resulting from the chemical combination of oleic acid and an ethanolamine containing a plurality of ethyl groups.

3. A product resulting from the chemical combination of oleic acid and at least one of the substances consisting of di-ethanolamine and tri-ethanolamine.

4. A product resulting from the chemical combination of oleic acid and one of the amines from the group consisting of di-ethanolamine, tri-ethanolamine and amino-propane diol.

5. A product resulting from the chemical combination of oleic acid and di-ethanolamine.

6. A product resulting from the chemical combination of oleic acid and a mixture of di- and tri-ethanolamines.

7. A product resulting from the chemical combination of oleic acid and tri-ethanolamine.

8. A product resulting from the chemical combination of oleic acid and amino-propane diol.

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