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2,530,147

ALKYLENE POLYAMINE DERIVATIVES

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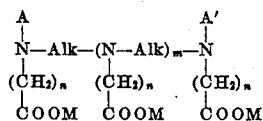
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This invention relates to derivatives of alkylene polyamines, and more particularly to such compounds which combine the properties of soap compatibility, detergent and wetting action, and ability to sequester metal ions. Still more particularly it relates to carboxylic and hydrocarbon derivatives of such alkylene polyamines. The synthetic detergents and wetting agents hitherto known fail to combine these properties in the effective manner of the compounds of the present invention.

It is, therefore, an object of this invention to prepare alkylene polyamine carboxylic and hydrocarbon derivatives which are detergents and wetting agents, are capable of sequestering metal ions, and are compatible with soap. Other objects will appear in the following disclosure.

It has been shown by Munz, in U. S. Patent 2,240,957, that acetic acid derivatives of amines and diamines are useful for treating hard water. The compounds shown by Munz are not, however, compatible with soap in more than very small amounts. In my U. S. Patent 2,407,645, a method of preparing these acetic acid derivatives is shown. Various other methods are known.

The alkylene polyamine derivatives of the present invention are represented by the following formula:



wherein Alk is an alkylene radical of the group consisting of ethylene and propylene, n is a positive integer not greater than 2, m is zero or a positive integer, M is selected from the group consisting of hydrogen and alkali metal, and A and A' are hydrocarbon groups containing together a total of at least ten carbon atoms and having not more than two of their hydrogen atoms replaced by a carboxyl radical of the group consisting of $-\text{COOH}$, $-\text{COOR}$ and $-\text{COOM}'$, M' being an alkali metal and R being the radical of an alcohol ROH . The term alkali metal as used above, and in the claims, is intended to include particularly sodium, potassium, and ammonium. The term hydrocarbon group includes carbocyclic groups, both alicyclic and aromatic.

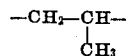
The compounds of this invention may be prepared in several ways. One of these methods consists in reacting one mol of a suitable alkylene or polyalkylene polyamine, such as ethylene diamine, trimethylene diamine, propylene 1,2 di-

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amine, diethylene triamine, triethylene tetramine, etc., with two mols of a chloro derivative of the substituent desired in the A and A' positions. The secondary (imino) hydrogens are then substituted either by the chloroacetic acid method shown below, or by my process as set forth in my U. S. Patent 2,407,645. Other methods may be used if desired.

A second method for preparing these compounds consists of reacting one mol of the alpha beta dichloro derivative of ethylene with two mols of an alpha amine of the substituent desired in the A and A' positions. This compound is then reacted in either of the two general ways described above to provide the proper substituents in the secondary (imino) positions.

It is essential that either two or three $(-\text{CH}_2)$ groups be present separating the nitrogen atoms. Consequently, the alkylene radicals separating the nitrogen atoms must be either ethylene or propylene radicals, and if propylene, they may be either $-(\text{CH}_2)_3-$ groups or



groups.

It is further necessary for the purposes of this invention that the groups replacing the secondary hydrogen atoms be either acetic acid or propionic acid radicals or their alkali metal salts. These conditions insure sequestering action of the compound and tend to make the compound water miscible. The presence of more or fewer carbon atoms than those specified in these alkylene and $(\text{CH}_2)_n$ groups of the foregoing formula seriously reduces or eliminates this sequestering action.

The following is believed to be an explanation of the physical characteristics of the compounds briefly described above. The groups in the secondary (imino) positions give the various compounds water solubility (or colloidal dispersal properties) as well as the property of sequestering polyvalent metal ions such as calcium without radically altering the solubility of the compound. Groups in the A and A' positions ending in the radical $-\text{COOM}$, where M is an alkali metal such as ammonium, sodium or potassium, also influence the characteristics of the product. More than three per cent of compounds such as described by Munz in U. S. Patent 2,240,957 "salt" out soap, making them undesirable for some purposes. The reason for this effect is believed to be due to the fact that the group $-\text{CH}_2\text{COOM}$ is an electrolyte. When the total number of "hydro-

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carbon" carbon atoms in the A and A' groups together (i. e. exclusive of those in any carboxyl groups) is increased to ten or greater, the product loses its electrolyte character and assumes a soap-like character which becomes more pronounced as the number of "hydrocarbon" carbon atoms increases. Such compounds, e. g. those having a total of from 10 to 20 "hydrocarbon" carbon atoms in the A and A' positions, appear to have little electrolyte effect and may be mixed with soap freely. When a total of 12 or more "hydrocarbon" carbon atoms are present in the A and A' positions, it is found that the compound is completely miscible with soap and is itself a good detergent. Those compounds having 14 or more such carbon atoms are oil soluble and such solubility is particularly marked in the case of the ammonium salts or the complex metal salt. In all cases the compounds, because of the groups in the secondary (imino) positions, appear to have the power of sequestering calcium or other metal ions without precipitation from solution. As these compounds become quite soap-like in character, i. e. where the total number of "hydrocarbon" carbon atoms in the A and A' positions exceeds 12, the compound is soluble in water in much the same manner as is soap.

Ordinarily the groups A and A' will be identical, merely because it is usually easier to manufacture such products than to make those wherein A and A' are different. When A and A' are the same, each will, of course, contain at least five "hydrocarbon" carbon atoms. However, A and A' may not only have different numbers of "hydrocarbon" carbon atoms, but neither, or both, or only one, may be provided with one or two carboxyl substituents of the group hereinbefore defined—see for instance Examples 6 and 7, below.

The group —COOH gives to the compounds of this invention fatty acid characteristics, while the group —COOM (M being alkali metal) provides soap-like properties in these compounds.

The esters of these compounds are not generally soluble in water, but are oil soluble.

In order to understand this invention more clearly, the following examples are given:

Example 1

A preferred type of compound of this invention is the derivative of ethylene diamine in which an undecylenic acid derivative is substituted in the A and A' positions. Two compounds using undecylenic acid are of particular interest and the method of making them is described below.

The methyl ester of the acid is first produced by any conventional esterification procedure. The ester is in turn reacted with hydrobromic acid. This halogenation is carried out in "wet" ligroin, i. e. containing a small amount of water, in the presence of air and at a temperature of 0° C. The hydrobromic acid is forced into a saturated solution of the acid in ligroin in the form of hydrogen bromide gas. Under the conditions as carried out, the gas causes sufficient agitation. The resulting brominated methyl ester is soluble in ligroin and does not crystallize out, but is recovered by evaporation. 558 grams of the brominated ester (two mols) are dissolved in methyl alcohol to form a substantially saturated solution. 100 grams of ethylene diamine (70%) is added slowly with agitation to the ester solution while a pH of about 8.0 is maintained by the addition of dry caustic soda. In the course of the reaction there is some foaming because of the water present. To separate all the sodium bro-

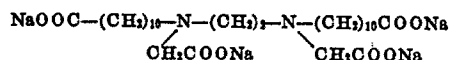
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mide, the mixture is dehydrated with benzene, thus precipitating the sodium bromide and making vacuum distillation trouble free. There is no appreciable hydrolysis of the methyl ester during the reaction. After removing the alcohol by distillation a yield of 452 grams (95% yield) is obtained, in the form of a yellowish, semi-crystalline mass which is soluble in organic solvents and miscible with water to form a milky solution. The compound is not very soluble in acids, but forms a slurry similar to semi-precipitated calcium soap.

The product of the above reaction is re-dissolved in methyl alcohol and the alcoholic solution added to a slurry of chloracetic acid sodium salt in methyl alcohol. Two mols of such salt is added for each mol equivalent of the reaction product with good agitation. Considerable heat of reaction is developed and is allowed to run its course for two hours. Using 2000 cc. of methyl alcohol and five molar equivalents of the diamine-ester reaction product and ten molar equivalents of the sodium salt of chloracetic acid, the temperature of the reaction is 60° C. At the end of two hours, heat is applied and the temperature maintained at the reflux temperature of methyl alcohol for about 6 to 8 hours. Sodium carbonate is added from time to time to maintain the pH between 7.5 to 8.5. The formed sodium chloride is removed by filtration.

The product thus produced by the above reaction is highly effective as a cleaner and foams and cleans in any type of water. It is not precipitated by any amount of electrolyte, and is a powerful wetting agent in water of 400 P. P. M. hardness and in salt water. Soap added to a solution of the compound is not precipitated in hard water nor is the soap salted out.

It is believed that the formula of the hydrolysis product of the above compound may be written as follows:



Unsaturated acids of the acrylic acid series having five or more carbon atoms in the "hydrocarbon" chain when halogenated may be reacted similarly to undecylenic acid to give the compounds of this invention. Of such acids, hexenic and teracrylic in the lower range of chain lengths, and oleic in the higher range serve to complete the understanding as described above of the effect of chain length in the A and A' positions on the characteristics of the final compound.

A product similar to that shown above may be formed by employing HCl as the halogenating agent. In such case it is believed that the chlorine adds to the double bond according to Markownikoff's rule in contrast to the addition of HBr. Consequently the carbon chain separating the the carboxyl group from the amino group is one less when HCl is employed (although the total number of carbon atoms in the compound is of course the same).

Example 2

141 grams of oleic acid is dissolved in 500 cc. of methyl alcohol, and placed in an apparatus equipped with a reflux condenser. Carrying out the reaction at 50° C., dry HCl is introduced into the alcohol solution of acid until a saturated solution of hydrochloric acid is formed. In ¾ of an hour the chlor ester has formed, and separates from the alcohol solution. The ester is then washed with dilute caustic soda, dried, and puri-

$\frac{1}{4}$ mol (83 grams) of the ester and $\frac{1}{2}$ mol + 2 grams excess of a hydrous ethylene diamine (14 grams) are mixed together. The mixture is heated on a water bath for 6 hours with agitation. The product when refluxed with caustic soda yields the sodium salt.

$$\begin{array}{ccccccc} \text{NaOOC}(\text{CH}_2)_7 & & & & & & (\text{CH}_2)_7\text{COONa} \\ & \diagdown & & & \diagup & & \\ & \text{CH} & - \text{N} & - \text{CH}_2 - \text{CH}_2 - & \text{N} & - \text{CH} & \\ & \diagup & | & & | & \diagdown & \\ \text{CH}_3 - (\text{CH}_2)_8 & & \text{CH}_3 & & \text{CH}_2 & & (\text{CH}_2)_8 - \text{CH}_3 \\ & & | & & | & & \\ & & \text{COONa} & & \text{COONa} & & \end{array}$$

Example 3

$$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HOOC}-\text{CH} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{HOOC}-\text{CH} \quad \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$$
$$\begin{array}{c}
 \text{CH}_3 \\
 \diagup \quad \diagdown \\
 \text{CH}_2 \quad \text{CH}-\text{COOCH}_3 \\
 \diagdown \quad \diagup \\
 \text{Cl}-\text{CH} \quad \text{CH}-\text{COOCH}_3 \\
 \diagup \quad \diagdown \\
 \text{CH}_2
 \end{array}$$
$$\begin{array}{c}
 \text{NaOOC}-\text{CH} \begin{array}{l} \nearrow \text{CH}_2 \\ \searrow \text{CH}_2 \end{array} \\
 \text{NaOOC}-\text{CH} \begin{array}{l} \nearrow \text{CH}_2 \\ \searrow \text{CH}_2 \end{array}
 \end{array}
 \begin{array}{c}
 \text{CH}_2 \\
 | \\
 \text{CH}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH} \\
 | \qquad \qquad \qquad | \\
 \text{CH}_2\text{COONa} \qquad \qquad \text{CH}_2\text{COONa}
 \end{array}
 \begin{array}{c}
 \text{CH}_2 \\
 | \\
 \text{CH}-\text{COONa} \\
 | \\
 \text{CH}_2\text{COONa}
 \end{array}
 \begin{array}{c}
 \text{CH}_2 \\
 | \\
 \text{CH}-\text{COONa} \\
 | \\
 \text{CH}_2\text{COONa}
 \end{array}$$
$$\text{R}-\text{NH}_2 + \text{CH}_2=\text{CH}-\text{R}'\text{COOR} \rightarrow \text{R}-\text{NH}-\text{CH}_2-\text{CH}_2\text{R}'\text{COOR}$$

Example 4

$$\begin{array}{c} \text{CH}_3 \\ | \\ (\text{CH}_2)_7 \\ | \\ \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \\ | \qquad \qquad | \\ \text{CH}_2 \qquad \qquad \text{CH}_2 \\ | \qquad \qquad \qquad | \\ \text{COONa} \qquad \qquad \text{COONa} \end{array}$$

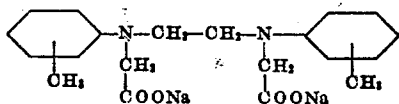
If the A and A' groups are oil soluble, the calcium complexes of the compound are oil soluble. 75 An example of such a compound is given below.

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Example 5

Two mols of toluidine, $\text{MeC}_6\text{H}_4\text{NH}_2$, are reacted by known procedures with one mol of ethylene dichloride to form a symmetrical disubstituted product. The secondary hydrogen atoms are then reacted to substitute acetic acid groups or propionic acid groups as described in the previous examples.

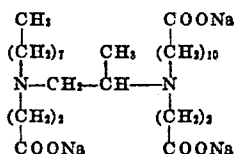
The formula for the compound resulting when acetic acid groups are substituted may be represented as follows:



Example 6

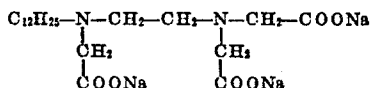
A compound having characteristics part way between those having hydrocarbon groups in both A and A' positions and acid groups in both A and A' positions may be prepared by reacting a mixture of one mol of the halogenated derivative of the alkyl compound and one mol of the halogenated acid with the alkylene polyamine. The product thus produced may then be reacted according to the chloracetic acid process, or otherwise, to add substituents for the secondary (imino) hydrogen atoms.

For example, one mol of octyl chloride and one mol of the hydro-chlorinated undecylenic acid described in Example 1 are heated with one mol of propylene 1,2-diamine until the reaction is complete. The secondary hydrogen atoms in the nitrogen atoms are then replaced by $-\text{CH}_2\text{COONa}$ groups or $-(\text{CH}_2)_x\text{COONa}$ groups as described above. The resulting product, when the latter group is the replacing group, has the following probable formula:



Example 7

One mol of lauryl chloride is heated to boiling with one mol of ethylene diamine until the reaction is complete. The resulting product is then reacted with three mols of chloracetic acid to yield a product which may be represented by the formula



The product has excellent detergent properties, is soluble in water, is compatible with soap, and is capable of sequestering metal ions.

A product having properties similar to those of this lauryl-trisodium-acetate-substituted ethylene diamine results when one mol of ethylene diamine is reacted with one mol of hydrochlorinated undecylenic acid ester and the resulting product reacted with three mols of chloracetic acid. Chlorpropionic acid may be used with satisfactory results, both as to operating procedure and characteristics of products, in either case—in place of chloracetic acid.

While most of the foregoing examples show the $-(\text{CH}_2)_x-\text{COOM}$ groups to be acetic acid groups or alkali metal salts thereof, these groups may be propionic acid groups instead, without any marked change in the properties of the com-

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pounds. To add the propionic acid groups, however, I find it best to use chlorpropionic acid, whereas to add the acetic acid groups I may use either chloroacetic acid, or the process of my U. S. Patent 2,407,645 above mentioned, to good advantage.

Most of the compound shown in the foregoing examples are ethylene diamine derivatives as ethylene diamine is the most readily available of, and is typical of, the alkylene or polyalkylene polyamines embraced by the present invention. However, other polyamines which fall within the definitions herein given may be used in the same manner, following the same procedures given in the foregoing examples—as has already been stated in Example 2, for instance, where diethylene triamine is referred to. Obviously, if these polyamines contain more than two nitrogen atoms, a correspondingly larger number of acetic or propionic acid radicals must be added to provide the final compound. Thus, whereas in making the products of this invention two mols of $-\text{CH}_2\text{COOH}$ or $-(\text{CH}_2)_x\text{COOH}$ (or their alkali metal salts) are required per mol of ethylene diamine (or propylene 1,2 diamine, or trimethylene diamine) radical, three mols are required per mol of diethylene triamine (or dipropylene triamine, etc.) radical, and four per mol of triethylene tetramine (or tripropylene tetramine, etc.) radical—and so on.

As has already been indicated in Example 2, an increase in the number of amino nitrogen atoms—and consequently in the number of $-(\text{CH}_2)_x-\text{COOM}$ groups mentioned in the basic formula given at the beginning of this specification—results in increased water-solubility of the corresponding alkali-metal salt compounds. For example, the diethylene triamine derivatives are more water-soluble than the ethylene diamine derivatives, and the triethylene tetramine derivatives are still more water-soluble.

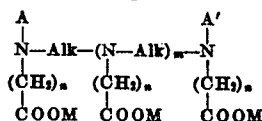
The compounds shown in the above examples as the sodium salts may be as readily prepared as the free acid or the potassium or ammonium salts. The free acid is obtained by adding hydrochloric acid, or other strong mineral acid, to a solution of the sodium salt until a pH of 2.0 to 2.5 is obtained. The precipitated acid may then be separated from the liquid present by filtration. Ammonium salts are readily prepared by dissolving the acid in aqueous ammonia. Potassium salts may be formed either by following the procedure of the examples using potassium compounds in place of the sodium compounds described, or by dissolving the acid in aqueous potassium hydroxide.

For the sake of clarity a definition of terms "radical" and "group" used in the claims will be given. A "radical" is attached to the rest of the molecule and has at least one valence which is satisfied by a "group." Thus the radical may be an acetic acid radical $-\text{CH}_2\text{COO}-$ attached through the bond on the $-\text{CH}_2$ carbon to the main part of the molecule, and through the bond on the $\text{COO}-$ portion to a "group." This group as pointed out hereinabove, may be hydrogen or an alkali metal such as sodium or potassium, and hence a member of group I of the periodic table of atomic weight less than 40.

The usefulness of the compounds produced in accordance with the present invention is apparent from their properties. Used alone they are excellent detergent agents and/or metal ion sequestering agents. They may be incorporated with soap in sufficient quantity to prevent the

The usefulness of such compounds is also enhanced by the fact that they may be made soluble in oils, organic solvents, or water by selecting an ester, metal salt, or acid of a compound having appropriate groups in the A and A' positions. Qualities such as the foaming power may be regulated since the more "hydrocarbon" carbon atoms in the A and A' positions, the greater the foaming power.

1. A compound having the formula



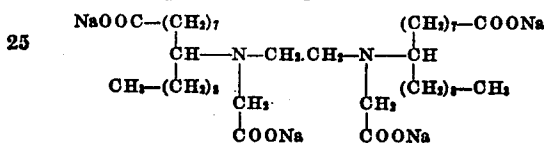
2. A compound according to claim 1 wherein n is 1.

3. A compound according to claim 1 wherein m is zero.

5. A compound according to claim 1 wherein A and A' are cyclic hydrocarbon radicals containing together at least 10 carbon atoms and having not more than two of their hydrogen atoms replaced by a carboxylic radical of the group consisting of $-\text{COOH}$, $-\text{COOM}'$, and $-\text{COOR}$, M' being an alkali metal and R being the radical of an esterifiable alcohol ROH.

$$\begin{array}{c}
 \text{CH}_3 \\
 \diagup \quad \diagdown \\
 \text{R}'\text{OOC}-\text{CH}-\text{CH}_2 \\
 \diagdown \quad \diagup \\
 \text{CH}_3 \\
 \text{R}'\text{OOC}-\text{CH}-\text{CH}_2 \\
 \diagup \quad \diagdown \\
 \text{CH}_3
 \end{array}
 \begin{array}{c}
 \text{CH}_2 \\
 | \\
 \text{CH}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH} \\
 | \qquad \qquad \qquad | \\
 \text{CH}_2 \qquad \qquad \qquad \text{CH}_2 \\
 | \qquad \qquad \qquad | \\
 \text{COOM} \qquad \qquad \text{COOM}
 \end{array}
 \begin{array}{c}
 \text{CH}_3 \\
 \diagup \quad \diagdown \\
 \text{CH}-\text{COOR}' \\
 \diagdown \quad \diagup \\
 \text{CH}_2 \\
 \text{CH}-\text{COOR}' \\
 \diagup \quad \diagdown \\
 \text{CH}_3
 \end{array}$$

7. A compound having the formula:


$$\text{NaOOC} \cdot (\text{CH}_2)_{11} \text{N} \begin{array}{c} \text{CH}_3 \\ | \\ \text{COONa} \end{array} \text{CH}_2 \text{CH}_2 \text{N} \begin{array}{c} \text{CH}_3 \\ | \\ \text{COONa} \end{array} (\text{CH}_2)_{11} \text{COONa}$$

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