

UNITED STATES PATENT OFFICE

2,524,218

WASHING COMPOSITION

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Serial No. 657,893

3 Claims. (Cl. 252-117)

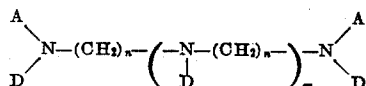
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This invention relates to derivatives of alkylene polyamines, and more particularly to such compounds which combine the properties of soap compatibility, detergent and wetting action, and ability to sequester metal ions. The synthetic detergents and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

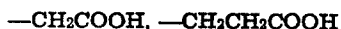
It is, therefore, an object of this invention to prepare alkylene polyamine derivatives which are detergents and wetting agents, are capable of sequestering metal ions, and are compatible with soap. Other objects will appear in the following disclosure.

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 my copending application, Serial Number 491,669, filed June 21, 1943, now 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 n is either 2 or 3 and m is either zero or a positive integer and wherein D is a member of the group consisting of



and their alkali metal salts, and wherein A is a hydrocarbon group containing at least two carbon atoms and having not more than two hydrogen atoms replaced by a member of the group consisting of $-(\text{CH}_2)_2\text{COOR}$, $-(\text{CH}_2)_2\text{COOM}$, $-\text{SO}_3\text{H}$, $-\text{SO}_3\text{M}$, $-\text{OR}$ and $-\text{OR}'\text{OR}$ wherein R is alkyl or hydrogen, M is an alkali metal, and R' is alkylene, said groups being spaced at least two carbon atoms from the nitrogen atoms.

The compounds of this invention may be prepared in several ways. One of these methods consists in reacting one mol of a suitable polyamine, such as ethylene diamine, trimethylene diamine, diethylene triamine, etc., with two mols of a chloro derivative of the substituent desired in the 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 copending application Serial No. 491,669 filed June 21, 1943, now U. S. Patent 2,407,645.

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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 positions. This compound is then reacted in either of the two general ways described above to provide the proper substituents in the D positions.

It is essential that either two or three ($-\text{CH}_2$) groups be present separating the nitrogen atoms and it is further necessary for the purposes of this invention that the groups in the D positions 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 less than the specified number of ($-\text{CH}_2$) groups seriously reduces or eliminates this sequestering action.

It has been discovered that in general the longer the hydrocarbon chain in the A positions the more soap-like the entire compound becomes. It has been further found that when this chain is four carbon units in length or longer it is water dispersible, and when it is more than seven carbon units in length the calcium complex is soluble in water, foams strongly, cleans well and is compatible with soap.

Another requirement of these compounds is that any hydrophylic groups attached to the hydrocarbon chain must be at least two carbon atoms removed from the nitrogen atoms. The substitution of a relatively long alkyl chain in the primary nitrogen position also destroys any electrolyte effect of the compound. It becomes possible, therefore, with proper substitutions in the A positions to prepare compounds which are miscible with materials such as soap without causing any deleterious effects to the soap, and form emulsions with liquid hydrocarbons, and other water insoluble organic compounds.

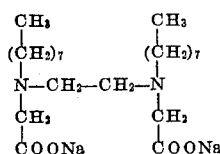
In order to understand this invention more clearly the following examples are given:

Example 1

One mol of ethylene diamine added to two mols of octyl chloride is heated under atmospheric pressure until the reaction is substantially complete. The resulting compound is reacted with chloroacetic acid in methyl alcohol keeping the reaction solution at a pH of 8 to 8.5. The mixture is heated and held to a gentle refluxing of the methyl alcohol for a period of six to eight hours. The material is filtered from the formed sodium chloride and the methyl alcohol is distilled off. The product is a semi-solid paste with an appearance somewhat like stearic acid and is soluble

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in alkalies and acids, compatible with soap and has the power of sequestering metal ions. It is believed that this compound has the following formula:



Example 2

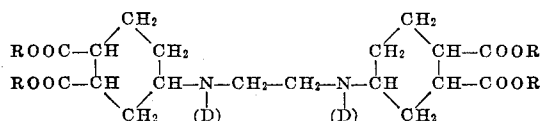
Two mols of hexyl amine are heated with symmetrically substituted trimethylene dichloride in methyl alcohol. The resulting product is treated according to my application Serial Number 491,669 filed June 21, 1943, now U. S. Patent 2,407,645. This method, briefly, consists of adding two mols of formaldehyde and two mols of sodium cyanide slowly and in small balanced quantities under strongly alkaline conditions to the diamine and heating the mixture with rapid agitation. The compound is compatible with soap and is capable of sequestering metal ions such as calcium ions.

Acrylic type unsaturated acids may be used advantageously in the preparation of compounds included within the scope of this invention. Several methods of employing those unsaturated acids are possible. In general they are first esterified to form a stable ester. Two mols of the ester may then be reacted directly with a diamine, such as ethylene diamine, according to the following equation:



It is noted that the ester group is sufficiently stable so that the hydrogen of the primary amino group acts as a hydrogen donor saturating the double bond. The remaining hydrogen of the amino groups is then reacted according to either of the methods described above. R in the case just described may be $-(\text{CH}_2)_n-(\text{NH}(\text{CH}_2)_m)-$ where n is 2 or 3 and m is 0, 1 or 2. A second general method of utilizing an unsaturated ester is hydro-halogenation in the presence of methyl alcohol using dry HCl to form the chloride ester. The halogen ester is then reacted with a polyamine in methyl alcohol in the ratio of two mols of ester to one of the polyamine as in the previous cases. It will be noted that only the primary hydrogens are treated as being in the A positions.

In addition to the compounds described above derivatives using the condensation products from the Diels-Alder reaction may be used. A preferred compound of this series is produced from maleic anhydride and butadiene and is represented by the following formula:

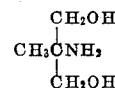


The dicarboxylic acid resulting from the condensation of the butadiene and maleic anhydride is condensed with ethylene diamine in the same manner that the unsaturated acids described above are condensed, that is, the di-acid is esterified and is reacted with hydrochloric acid and the hydrochloride is in turn reacted with ethylene diamine or other suitable diamines, triamines or tetramines. As in the other compounds de-

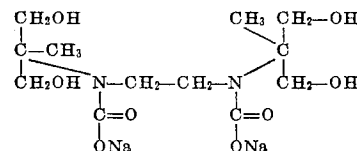
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scribed, the secondary hydrogens attached to the nitrogen groups are reacted to substitute acetic acid or propionic acid radicals. The product is compatible with soap and is an excellent cleaning agent. If desired, the ester may be saponified to yield the alkali metal salt, and if the acid is preferred, the salt is treated with an acid in the conventional manner.

Still other types of compounds may be produced by reacting 2 amino, 2 methyl, 1-3 propane diol, the formula of which is



with ethylene dichloride. The compound 2 amino, 2 methyl, 1-3 propane diol is dispersed in methyl alcohol. To this well dispersed, well agitated suspension two mols of ethylene dichloride are added to each ten mols of the amine. The mixture is refluxed for about 1 hour. Sodium carbonate is added from time to time to maintain the pH between 8.0 and 8.5. The reaction is over in approximately 5 hours and requires about two mols of sodium carbonate and 1500 cc. of methyl alcohol. Sodium chloride formed is removed by filtration and the alcohol is removed by distillation. Secondary hydrogen atoms on each of the nitrogen atoms are reacted according to my application Serial Number 491,669 filed June 21, 1943, now U. S. Patent 2,407,645 and are substituted by the radical CH_2COONa . The formula of the resulting product is believed to be as follows:



The product as produced is a yellow-white solid. It has been discovered that if the amine diol is reacted according to the chloracetic acid method some of the hydroxyl groups are involved to form ether acids. The compound forms a clear calcium complex and is an excellent detergent. While it increases the foam of soap solutions it, by itself, is not a foaming agent as are the other compounds described above.

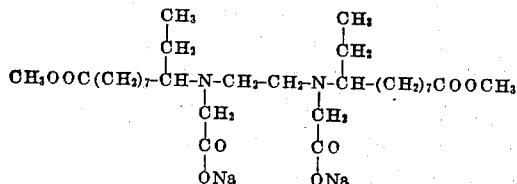
A preferred type of compound of this invention is the derivative of ethylene diamine in which a long chain acid such as undecylenic acid is substituted in the A positions. Two compounds using undecylenic acid are of particular interest and the method of making them is described below.

The methyl ester of the acid is first produced. This is in turn reacted with hydrobromic acid. This halogenation is carried out in ligroin in the presence of air and at a temperature of 0° C. Two mols of the bromide ester react readily with ethylene diamine in the presence of methyl alcohol as a solvent. The reaction is carried out at a pH of 8.0 which is regulated by the addition of dry caustic soda. Sodium bromide is precipitated and may be filtered off. When 70% ethylene diamine is used some foaming will be experienced due to the water present. It has been found that the best procedure is to dehydrate the entire reaction mixture, after the reaction is completed, with benzene. There is no appreciable hydrolysis of the methyl ester during this reaction. After removing the alcohol by distillation, a compound is obtained of a yellowish

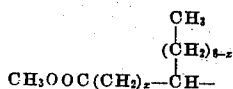
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semi-crystalline mass, soluble in organic solvents and miscible with water to form a milky solution. To react the secondary hydrogen atoms on the nitrogen atoms, the product produced above is redissolved in methyl alcohol and the alcohol solution added to a slurry of chloracetic acid sodium salt in methyl alcohol. Two mols of such salts are used per mol equivalent of the reaction product. There is considerable heat of reaction but if this is permitted to run its course using 200 cc. of methyl alcohol for each mol of chloracetic acid sodium salt, the heat of reaction is 60° C. After two hours sodium bromide begins to precipitate and heat is applied to maintain the reflux temperature of methyl alcohol for about six to eight hours. Sodium carbonate is added from time to time to regulate the pH between 7.5 and 8.5. Provision must be made to allow liberated carbon dioxide to escape. When the reaction is completed the water that is present due to the hydrous diamine is removed before filtering.

When the undecylenic acid used in the preparation of the foregoing product is of the usual type, $\text{CH}_3\text{—CH}_2\text{=CH}_2\text{—(CH}_2)_7\text{—COOH}$ (9-hendecenoic acid), the formula of that product is as follows:



It is obvious that the lengths of the two alkyl chains on either side of the carbon atom of the undecylenic acid ester radical attached to the nitrogen atoms will depend upon the location of the double bond in the undecylenic acid, as well as upon which carbon atom the halogen atom is attached. Hence a more general formula for these compounds, using the methyl ester of any undecylenic acid, will be represented by the following radical in the A positions:



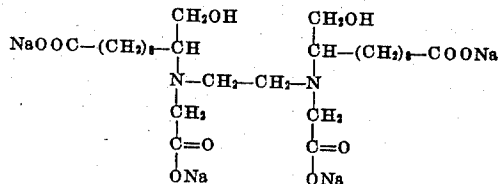
wherein, conformably with the requirements of the compounds of this invention, x is not less than 3—and is, of course, not greater than 8.

The above product is illustrative of these highly effective compounds. They act as cleaners and foam in any type of water. They are not precipitated or salted out by any amount of electrolyte and are powerful wetting agents even in water of 400 parts per million hardness and in sea water. They are compatible with soap and are not precipitated in the form of lime soap nor is the soap salted out. They have a unique dual action in that they will form highly soluble fillable calcium complexes. They also have the property of dispersing lime salts in an amount far greater than that calculated to form the clear complex. The calcium complex itself is soluble in alcohol. It may be noted that the compounds of this invention are both anionic and cationic in nature. For these reasons, and because these compounds are extremely stable in both alkaline and acid solutions, they have wide usefulness.

A second, and slightly different type of compound from that described above may be prepared from omega undecylenic acid by reacting the acid ester with hypochlorous acid, HOCl. This acid acts much the same way as does hy-

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drochloric acid in its addition to the double bond of undecylenic acid. The addition product is reacted with ethylene diamine and the secondary hydrogen atoms are reacted as described above; upon hydrolysis of the ester groups with alkali a compound of the following formula results:

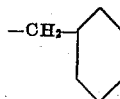


This compound is very similar in nature to the compound described above except that it is more soluble in water. Likewise, the lengths of the two alkyl chains of the undecylenic acid radical will depend upon conditions as set forth above.

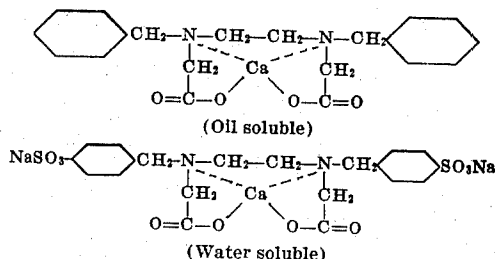
When the hydrochloric acid derivative of undecylenic acid ester is reacted with diethylene triamine, and the secondary hydrogen atoms on the three nitrogen atoms are reacted with chloropropionic acid sodium salt, there is produced a compound similar to the ethylene diamine derivative wherein the chloracetic acid sodium salt is used. The product is, however, more soluble in water.

The resulting esters formed by the reactions above may be hydrolyzed (as shown in the compound above) or may be retained. Ester groups tend to decrease the solubility of the compound in water.

If the A groups are insoluble or immiscible in water, the calcium complex of the compound is not soluble in water and precipitates. For instance if A is



the calcium complex precipitates in water. However, if this benzene nucleus is sulfonated the sodium sulfonate calcium complex is soluble and is useful for the purpose of this invention. If not sulfonated the compound is quite oil soluble, while the sulfonated compound (sodium salt) is quite water soluble. The compounds described above may be illustrated by the following formula:

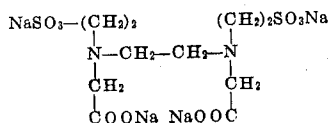


This compound illustrates the fact that materials particularly suitable for cleaning action and sequestering ability in oil may be secured, by substituting suitable oil soluble groups in the A positions.

The introduction of a ($\text{—SO}_3\text{Na}$) group into the compounds of this invention may be readily accomplished by reacting two mols of a compound such as taurine, $\text{NH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$, with each one mol of dichloro ethylene, $\text{Cl}(\text{CH}_2)_2\text{Cl}$. The reaction follows the general procedure outlined for that described of reacting 2 amino, 2 methyl, 1-3 propane diol with ethylene dichloride de-

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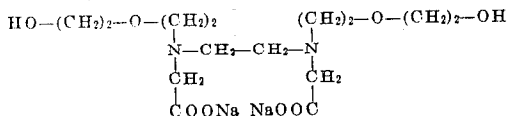
scribed above. The resulting product is then reacted according to my application Serial Number 491,669, now U. S. Patent 2,407,645, to substitute the secondary hydrogen atoms on the nitrogen atoms with $(-\text{CH}_2\text{COONa})$ groups. The completed compound is represented by the following formula:



The product may be crystallized from methyl alcohol solutions.

It is excellent as a detergent and for sequestering metal ions, and is completely miscible with soap.

Other types of radicals in the A positions are also advantageous for some cleaning purposes; for example, compounds prepared by reacting an hydroxylated ether with a diamine. The reaction between diethylene glycol and anhydrous ethylene diamine may be carried out merely by boiling the two together. Xylene or a dehydration catalyst may be added but such precaution is not essential. As in the previous examples, the secondary hydrogen atoms on the nitrogen atoms are substituted with $-\text{CH}_2\text{COONa}$ or $-\text{CH}_2\text{CH}_2\text{COONa}$ groups, and by the same method. The final compound may be represented by the formula:



This compound is an excellent detergent and sequestering agent and is completely miscible with soap.

A summary of the properties of the compounds herein described will serve to point out obvious uses for them.

As prepared, the compounds have no deleterious electrolytic properties to soap. Accordingly as they are compatible with soap when incorporated with soap in which electrolytes are present, the electrolytes do not adversely affect the soap. They are of themselves good wetting agents and detergents but do not defat the skin. Being completely stable in both alkali and acid solutions, they may be incorporated in media of either type. The effectiveness of these compounds may be due, in part, to the fact that they are both cationic and anionic in action as well as the fact that they sequester metal ions, such as calcium ions, thus preventing the precipitation of calcium soaps. It can be seen from the above description that the compounds may be varied to make them soluble in oils, organic solvents, or water. The foaming power of the compound may be adjusted, as the longer the aliphatic chain in the A positions, the greater the foaming power, while the heterocyclic compound shown has very little foaming action (although it is a good detergent). More than six carbon atoms in the hydrocarbon chain insures the compound of having good wetting action, particularly if carboxyl groups or hydroxyl groups are present.

In the above discussion of this invention wherein alkali metal salts are disclosed, and in the claims, the term "alkali metal" is intended to include the group consisting of sodium, potassium, and ammonium $(-\text{NH}_4)$.

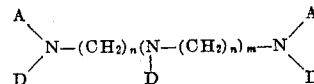
Although any desired amount of these com-

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pounds may be added to a water-soluble soap to form a washing compound, it has been found that from 1% to 5% by weight prevents the precipitation of calcium or magnesium soaps in any commonly used water, and yields a good detergent soap.

I claim:

1. A detergent composition consisting of a water soluble alkali metal-fatty acid soap and an alkylene polyamine derivative, the amount of said alkylene polyamine derivative in the said mixture being from 1% to 5% by weight of the mixture, said alkylene polyamine derivative being one conforming to the formula:

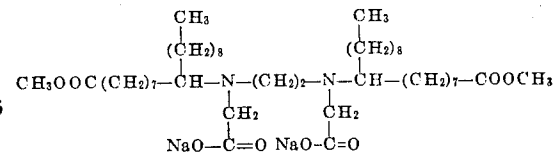


wherein n is an integer selected from the group consisting of 2 and 3; m has a value equal to one of the group consisting of zero, the numeral one (1), and any multiple of the numeral one (1); D is a member of the group consisting of $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, and their alkali metal salts; A is a hydrocarbon group containing at least two carbon atoms and having not more than two hydrogen atoms replaced by a member of the group consisting of

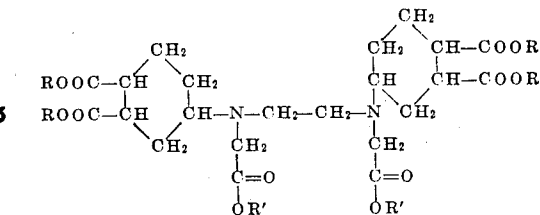
$-(\text{CH}_2)_2\text{COOR}$, $-(\text{CH}_2)_2\text{COOM}$, $-\text{SO}_3\text{H}$, $-\text{SO}_3\text{M}$, $-\text{OR}$

and $\text{OR}'\text{OR}$ wherein R is one of the group consisting of alkyl and hydrogen, M is an alkali metal, and R' is an alkylene group, said replacing groups being spaced from the N atoms of the compound by at least two carbon atoms of the hydrocarbon group containing the same.

2. The detergent composition of claim 1, wherein said alkylene polyamine derivative comprises the compound:



3. The detergent composition of claim 1, wherein said alkylene polyamine derivative comprises the compound:



wherein R is one of the group consisting of hydrogen and alkyl and R' is one of the group consisting of hydrogen and alkali metal.

FREDERICK C. BERSWORTH.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,240,957	Munz	May 6, 1941
2,387,976	Bersworth	Oct. 30, 1945
2,407,645	Bersworth	Sept. 17, 1946
2,412,945	Bersworth	Dec. 24, 1946