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IMIDAZOLINE DERIVATIVES AND PROCESS
OF MAKING THE SAMERobert Radcliffe Ackley, Jersey City, N. J., as-
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This invention relates to certain new and useful imidazoline derivatives, and to a new and useful process for the preparation thereof.

More particularly, the invention relates to a process of preparing compounds of the class: μ -alkyl N-amidoalkyl imidazolines, and to the products so produced.

Preparation of the novel compounds may be accomplished, according to my invention, by acylating a primary or secondary amino group of a μ -alkyl N-amino alkyl imidazoline. Such acylation may take place either prior to or during neutralization, with an organic or inorganic acid, of the tertiary amino group of the μ -alkyl N-amino alkyl imidazoline. Preferably, the acylation and neutralization are performed simultaneously, although, under proper conditions, the steps of acylation and neutralization may be carried out separately and in succession, as hereafter explained.

By acylation I mean, essentially, replacing a hydrogen atom attached to a nitrogen atom by the group:



where Y is an alkyl, aryl or aralkyl group.

Examples of acylating agents which may be employed, according to my invention, to produce simultaneous acylation and neutralization, are the aliphatic acid anhydrides (e. g., acetic anhydride), the aromatic acid anhydrides (e. g., phthalic anhydride), and the acid halides (e. g., acetyl chloride).

Objects of the invention include the provision of such a novel process as has been indicated, and the novel products thereof. I have found that these products, and certain organic and inorganic salts thereof, have many novel, useful and valuable properties. They have been found, for example, to be particularly advantageous as textile treating or finishing agents, as softening and plasticizing agents for cellulosic materials, for improving the dyeing qualities of cellulosic fabrics, and for other applications in the textile arts. The products have also been found to overcome certain difficulties heretofore frequently encountered in the use of other textile treating or finishing materials, and, more particularly, a tendency, in certain products heretofore proposed for the purpose, to instability in the presence of anions and negatively-charged colloidal particles.

It has heretofore been proposed, for example, in processing or treating textile fibers, to employ certain materials which have been rendered solu-

ble in water by the addition of groups which characteristically carry a positive electrical charge, or which exist in aqueous solution in the form of large cations and small anions. Such cation-active materials are substantive when applied to cotton and rayon and may therefore be applied in extremely minute quantities to produce the desired result. A variety of materials have been suggested for this purpose, as for example the salts and quaternary ammonium compounds of N-oleyl N' diethyl ethylene diamine, stearyl diethylene triamine, hexadecyl diethylamine, cetyl pyridinium bromide and pentadecyl imidazoline.

I have found, however, that in order to produce satisfactory softening and sizing effects, it is ordinarily preferable to use, as finishing agents, compounds which contain a fatty residue of more than sixteen carbon atoms in an open chain, although for other purposes compounds containing ten or more carbon atoms in an open chain may be employed, as hereafter illustrated. Some of the materials previously proposed are not suitable for their intended purposes, due to the fact that the hydrophilic portion of the molecule is not sufficiently strong in its action to carry the hydrophobic residue into solution. When attempts are made to obtain greater solubility by introducing more than one positively charged solubilizing group into the molecule, compounds are obtained which are extremely sensitive to negatively charged ions and colloidal particles. For example, stearyl diethylene triamine acetate is readily precipitated from dilute aqueous solution by traces of sulphates, phosphates, soaps, sulphonated oils or alkali metal alkyl sulphates.

As distinguished from such products heretofore proposed or suggested, compounds according to the present invention are characterized by the fact that they contain, in addition to the positively charged solubilizing group, an amido group. This serves as a solubilizing group, without carrying a strong positive charge. Thus the sensitivity of the resulting molecule to anions and negatively charged colloidal particles is greatly reduced. Such compounds dissolve readily in water and are not easily precipitated by anions and negatively charged colloidal particles, therefore possessing marked practical and commercial advantages.

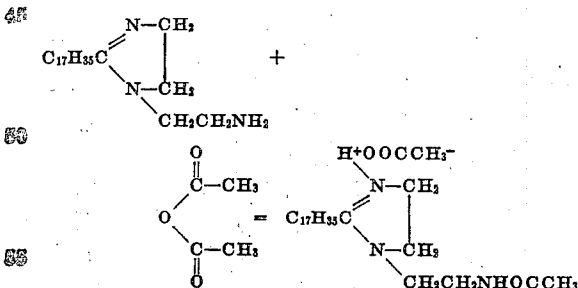
For example, when μ -heptadecyl N-amino ethyl imidazoline is neutralized with an aqueous solution of acetic acid to form μ -heptadecyl N-amino ethyl imidazoline diacetate, a product is obtained which, while it may possess adequate

solubility in water, is nevertheless highly sensitive to the salts and soaps encountered in textile finishing operations, and is, for that reason, unsatisfactory for many commercial uses. I have discovered, however, that when μ -heptadecyl N-amino ethyl imidazoline is treated with acetic anhydride, according to my invention, to produce acylation of the primary amino group, the resulting μ -heptadecyl N-acetamidoethyl imidazoline acetate is soluble in water to give a clear solution and, in addition, has the advantage of being remarkably stable toward negatively charged ions and colloidal particles.

A number of products according to my invention may be obtained, as illustrated in the foregoing example, by preparing N-amino alkyl imidazolines by causing various fatty acids to react with polyalkylene polyamines under condition which produce ring closure. These imidazolines may then be treated with acylating agents which simultaneously produce acylation and neutralization, as already described. Examples of such agents are maleic anhydride, acetic anhydride and propionic anhydride, or the aromatic acid anhydrides such as phthalic anhydride, or the acid halides, such as acetyl chloride and benzoyl chloride.

In addition, compounds according to my invention may be made, under proper conditions, as already stated, by first acylating the primary amino group and subsequently neutralizing the tertiary amino group. Such acylation may be produced by heating the free base with carboxylic acids in such a manner as to remove water and form the corresponding amides; and the subsequent neutralization of the residual tertiary amino group may be performed by the addition of an organic or inorganic acid, or quaternary ammonium compounds may be formed by treatment with an alkylating agent, such as diethyl sulfate or benzy chloride.

When μ -heptadecyl N-amino ethyl imidazoline is neutralized with acetic anhydride, the reactions involved are believed to be as follows:



The resulting product exemplifies the class of products forming the subject-matter of the present invention, and has many new and useful properties.

I have also obtained satisfactory results by forming imidazolines by the action of the fatty acids of Montan wax with diethylene triamine, with subsequent reaction with acetic anhydride. I have also prepared new and useful products by using a commercial mixture of polyalkylene polyamines containing diethylene triamine, triethylene tetramine, and tetraethylene pentamine. I have also found that the products obtained by the reaction of the fatty acids of coconut oil with diethylene triamine possess useful properties, primarily as detergents and wetting agents, as well as for their ability to prevent dyestuffs from crocking and bleeding.

Other specific examples of the novel process and product, according to the present invention, are as follows:

Example 1

To the mixed imidazolines resulting from the treatment of 275 kilograms of commercial stearic acid [generally comprising a mixture of stearic and palmitic acids, with other minor constituents] with 175 kilograms of diethylene triamine at 240° C. for fifteen hours, acetic anhydride is added with stirring below 60° C. until the product is neutral. The resulting product, comprising primarily a mixture of μ -heptadecyl-N-acetamidoethyl imidazoline acetate and μ -pentadecyl-N-acetamidoethyl imidazoline acetate, with some μ -heptadecyl-N-stearamidoethyl imidazoline acetate, is a light yellow waxy substance, readily dissolving in hot water to give a strongly foaming solution which imparts a permanent soft hand to cellulosic textile fabrics.

Example 2

To the condensation product obtained from the reaction of 275 kilograms of commercial stearic acid with 175 kilograms of diethylene triamine at 250° C. for seventeen hours, with the subsequent removal by vacuum distillation of excess amine, is added benzoyl chloride until a neutral reaction is obtained. The resulting solid, consisting primarily of μ -heptadecyl-N-benzamidoethyl imidazoline hydrochloride and μ -pentadecyl N-benzamidoethyl imidazoline hydrochloride, dissolves readily in water to give a strongly foaming solution which may be used in low concentration (for example, about 0.1%) for imparting a pleasant soft "hand" to textile fabrics, thus rendering them pleasing to the touch.

Example 3

To 284 kilograms of oleic acid is added 170 kilograms of diethylene triamine and 225 kilograms of xylene. The mixture is refluxed rapidly for 18 hours at a temperature of 150–180° C., with continuous removal of water from the distillate. The xylene and excess amine are then removed by vacuum distillation, and the residue is neutralized with acetic anhydride at 30–60° C., yielding a product comprising primarily μ -heptadecenyl-N-acetamidoethyl imidazoline acetate and μ -pentadecyl N-acetamidoethyl imidazoline acetate, with some μ -heptadecenyl-N-stearamidoethyl imidazoline acetate. This product is in the form of a viscous oil, light yellow in color, and which dissolves readily in water to give a strongly foaming solution of great stability to lime salts. Cotton and rayon fabrics, after treatment with a dilute solution of this compound, acquire a soft, dry "hand," which is pleasing to the touch.

Example 4

To 275 kilograms of commercial stearic acid is added 160 kilograms of diethylene triamine and 225 kilograms of xylene. The mixture is refluxed rapidly for 18 hours, at a temperature of about 150–180° C., with continuous removal of water from the condensate. Thirty-four kilograms of water are removed. The xylene and excess amine are then removed by vacuum distillation, and to the residue in the still is added 100 kilograms of 2-ethyl butyric acid. The mixture is refluxed with strong agitation and continuous water removal until the reaction is completed, as shown by the cessation of evolution of water vapor. After cooling, the reaction mixture is neutralized with acetic acid. The resulting

product, consisting primarily of μ -heptadecyl N-(2-ethyl butyramido ethyl) imidazoline acetate, disperses in water to give a slightly turbid solution, which imparts a smooth waxy touch to textile fabrics, without materially detracting from their natural fullness and resilience.

Soft effects are also produced upon textile fabrics, when the acylated amino alkyl imidazolines are applied to silk and wool in very small amounts, but the effect is less permanent. In like manner, other acid halides and anhydrides, such as those mentioned above, may be used. The foregoing and other products made according to my invention are useful not only as softening compounds of plasticizers for cellulosic fabrics, but also as detergents for silk and wool, as additions to silk-boil-off liquors, and for improving the fastness to water of dyeings on cellulosic fabrics.

In the foregoing specification, and in the claims, I have used what I believe to be a standard and generally accepted system of nomenclature in organic chemistry, and one which is accurately descriptive of the compounds in question. Thus the term "N-amidoalkyl" is employed in the specification and claims to designate compounds according to my invention, and to prevent confusion with the term "N-aminoalkyl," applied to compounds which form starting materials for the process. While other systems of nomenclature might be used to designate the same materials, it is believed that the terminology which I have employed to designate my novel compounds is the clearest and most definite of the presently accepted systems of organic chemical nomenclature.

It is to be understood that the present invention is not necessarily or specifically limited to the compositions and processes herein specifically illustrated and described, but, under proper circumstances, may be carried out in other ways, without departure from its spirit, and within the scope of the following claims.

I claim:

1. Process of making compounds of the class μ -alkyl N-amidoalkyl imidazolines which com-

prises acylating and neutralizing compounds of the class μ -alkyl N-amino alkyl imidazolines, which are unsubstituted by salt-forming groups other than amino groups.

2. In a process of acylating imidazolines, the steps which comprise treating a μ -alkyl N-amino alkyl imidazoline, which is unsubstituted by any salt-forming group other than amino groups, with an acylating agent which is also a neutralizing agent, to acylate an amino group of lower order than tertiary of the imidazoline, and simultaneously neutralize a tertiary amino group to form a μ -alkyl N-amidoalkyl imidazoline.

3. The process of making μ -alkyl N-amidoalkyl imidazolines which comprises acylating μ -alkyl N-amino-alkyl imidazolines, which are unsubstituted by salt-forming groups other than amino groups, with an acylating agent under conditions producing simultaneous acylation and neutralization.

4. As a new composition of matter, an organic compound of the class μ -alkyl N-amidoalkyl imidazolines, which are unsubstituted by salt-forming groups other than amino groups.

5. As new compositions of matter, the water-soluble salts of organic compounds of the class: μ -alkyl N-amidoalkyl imidazolines which are unsubstituted by salt-forming groups other than amino groups.

6. μ -heptadecyl N-acetamidoethyl imidazoline acetate.

7. μ -pentadecyl N-acetamidoethyl imidazoline acetate.

8. μ -heptadecenyl N-acetamidoethyl imidazoline acetate.

9. A water-soluble textile treating or finishing preparation, suitable for use in rendering textile fabrics more pleasing to the touch, containing as its essential ingredient a water-soluble salt of an organic compound of the class: μ -alkyl N-amidoalkyl imidazoline, which is unsubstituted by salt-forming groups other than amino groups.

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