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TREATMENT OF FIBROUS MATERIALS AND COMPOSITIONS THEREFOR

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16 Claims. (Cl. 252—8.8)

The present invention is concerned with the chemical treatment of fibrous materials, especially cellulosic materials, whereby useful properties are imparted thereto. More particularly, the invention is directed to a method of softening the hand of textiles such as cotton.

It is an object of the invention to provide a method of chemically treating fibrous materials such as paper and textiles with new and improved chemical compositions whereby they are rendered soft to the touch as well as possessing properties of lubricity and, if desired, water repellency.

Another object is to furnish aqueous treating baths or rinses for textiles which contain relatively minor amounts of new and improved softening chemicals. Other objects will appear hereinafter.

In accordance with the invention, it has been found that properties of softness, lubricity and water repellency can be imparted to fibrous materials such as textiles, by treating such materials with an aqueous bath containing minor amounts of a colloidally dispersible 1,2-substituted imidazoline salt. The imidazoline salts that are particularly effective are those containing at least two aliphatic groups each of at least 11 carbon atoms in chain length. Treatments can be used in aqueous textile treating baths at dosages ranging from .001% to 1% by weight of said baths. Excellent softening treatments are afforded at dosages of from .005% to .01% by weight.

The expression "colloidally dispersible" refers to the character and physical appearance of aqueous suspensions containing at least 3% by weight of the 1,2-substituted imidazoline salts. They range from milk white to light amber in color and vary in their viscosities from that of about light cream to thick, rich viscous liquids. They may or may not be suspensions at the concentrations of use suggested herein.

The starting imidazolines from which the compounds of the invention are prepared are readily synthesized from organic acids, particularly fatty acids, and polyamino compounds in accordance with the teachings of Wilson U.S. Patents 2,267,965 and 2,355,837. The preferred starting acids are the saturated fatty acids containing from 12 to 24 carbon atoms. Of all the saturated fatty acids in this group, stearic acid is the most preferable. While saturated fatty acids are preferred, the unsaturated fatty acids such as oleic, palmitoleic, linoleic, myristoleic and lauroleic may also be used. In addition to the fatty acids per se, the natural oils and fats or crude mixtures of the acids may also be effectively employed.

The polyamino compounds useful in preparing the starting imidazolines are the diamines, e.g., ethylene diamine, the polyalkylene polyamines, e.g., diethylene triamine, tetraethylenepentamine and the hydroxyalkyl alkylenediamines and polyamines, e.g., aminoethylethanolamine.

In all the cases above, the imidazolines produced are substituted in the 1-position of the imidazoline ring by a monofunctional or polyfunctional radical, save when ethylene diamine is used, in which instance a hydrogen

atom is the only substituent on the 1-position. In any event, however, the substituents on the 1-position or a hydrogen atom are capable of reacting with such functional organic compounds as acyclic organic acids or alkyl halides to add one or more groups to the imidazoline or substituted imidazoline molecule.

Illustrative of the substituents that may be added to the imidazoline molecule are the acylation or esterification products formed by reacting an organic acid, such as for instance, a fatty acid with several typical imidazolines. If, for instance, 2-heptadecyl imidazoline is reacted with stearic acid the compound, 2-heptadecyl-1-stearoyl imidazoline, is produced. The reaction of stearic acid with 1-(2-aminoethyl)-2-heptadecyl imidazoline would form 1-(2-stearoylaminoethyl)-2-heptadecyl imidazoline. Where a 2-hydroxyethyl group is a substituent at the 1-position, a suitable ester could readily be prepared. Where a primary amino group as well as one or more secondary amino groups are positioned as substituents on the 1-position, a number of acylated groups can be attached to the molecule.

When several 1,2-substituted imidazolines were tested as textile softeners, it was soon found that only the colloidally dispersible materials gave outstanding results. The water soluble derivatives, for instance, 1-(2-hydroxyethyl)-2-heptadecyl imidazoline hydrochloride, were relatively ineffective as textile treating agents. The water immiscible imidazolines were also ineffective.

The 1,2-substituted imidazolines containing at least two aliphatic groups each of at least 11 carbon atoms in chain length can be rendered colloidally dispersible in aqueous media by preparing the inorganic mineral acid salts or the low molecular weight, organic carboxylic acid salts thereof. Such compounds were admirably suited for the treatment of fibrous materials.

The salts of the imidazolines may be prepared by melting the imidazoline and slurrying it in a suitable liquid media such as a low molecular weight water immiscible aliphatic alcohol and adding the necessary amount of acid to form the salt.

The inorganic mineral acids that may be used are such acids as hydrochloric, sulfuric, sulfurous, nitric and sulfamic. In the case of imidazolines prepared by reacting an alkyl halide with an imidazoline having only a hydrogen substituted in the 1-position, the alkylation reaction will form the hydrohalide salt of the imidazoline as a part of the reaction.

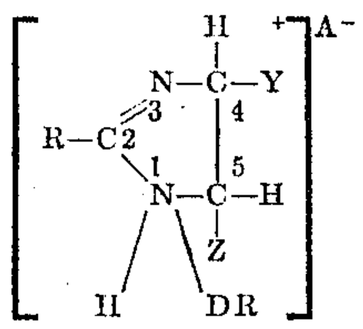
The low molecular weight organic carboxylic acids may be either aliphatic, cycloaliphatic or may contain an aromatic or substituted aromatic nucleus. The preferred acids will usually not contain more than 10 carbon atoms and preferably contain not more than 6. These acids may be monocarboxylic acids or polycarboxylic acids. Such simple acid as formic, acetic and propionic may be used as well as the substituted analogues, chloroacetic, vinyl acetic and the like. The carbocyclic acids, such as for instance those disclosed in Luvisi, U.S. Patent 2,659,731 may also be used but care should be exercised in the selection to insure the production of a colloidally dispersible 1,2-substituted imidazoline.

A preferred group of water miscible low molecular weight organic carboxylic acids are the hydroxy substituted carboxylic acids and the hydroxy substituted polycarboxylic acids. Examples of such acids are lactic, citric, gluconic and tartaric.

The preferred colloidally dispersible 1,2-substituted imidazoline salts which are extremely valuable for treat-

ing fibrous materials are exemplified by the following structural formulae:

I.



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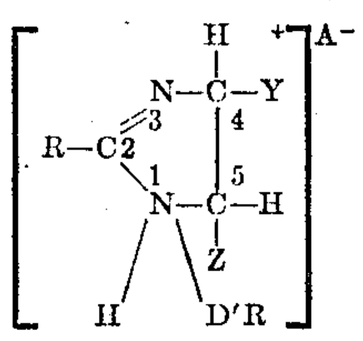

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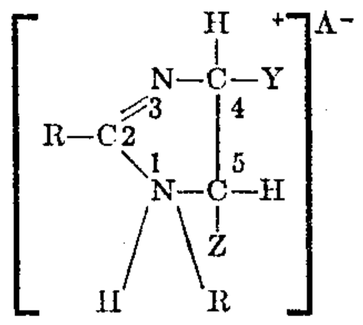
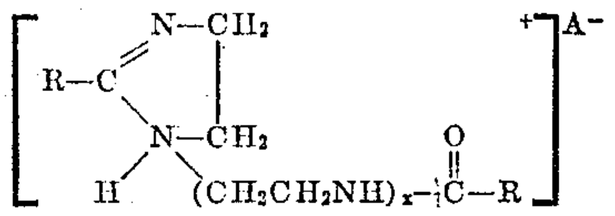


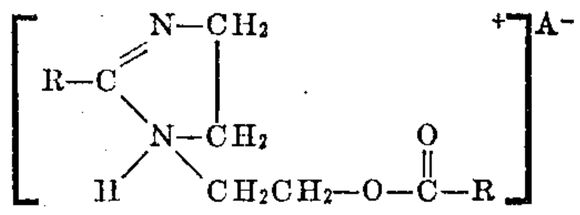
wherein D is a divalent, non-amino, organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N; D' represents a divalent, organic radical containing less than 25 carbon atoms composed of elements from the group consisting of C, H, O and N, and containing at least one amino group; R is an aliphatic group containing from 15 to 23 carbon atoms; Y and Z are from the group consisting of hydrogen and lower aliphatic groups containing not more than 6 carbon atoms, and A^- is an anion of an acid from the group consisting of inorganic mineral acids and low molecular weight organic carboxylic acids containing not more than 10 carbon atoms.

The most preferred colloidally dispersible 1,2-substituted imidazoline salts have the structural formulae:

IV.



V.



where R and A^- have the same significance shown above and x is a small whole number not greater than three. Very desirable results are produced when A^- is the anion of a hydroxy substituted carboxylic acid or a hydroxy substituted polycarboxylic acid.

Specific compounds that have proven themselves useful in the invention are the following:

(1) 1 - (2 - stearoylaminoethyl) - 2 - heptadecyl - imidazoline lactate.
(2) 1 - (2 - stearoylaminoethyl) - 2 - heptadecyl - imidazoline citrate.
(3) 1 - (2 - stearoylaminoethyl) - 2 - heptadecyl - imidazoline formate.
(4) 1-octadecyl-2-heptadecyl imidazoline chloride.
(5) 1-octadecyl-2-heptadecyl imidazoline sulfate.
(6) 1-(2-ethylstearate)-2-heptadecyl imidazoline tartarate.
(7) 1-(2-stearoylaminoethyl)-2-heptadecyl benzoate.
(8) 1-(2-stearoylaminoethyl)-2-pentadecyl chloride.

In order to evaluate the compositions of the invention as textile softeners, the following test method was employed.

The test specimens were cotton diapers and cotton wash cloths which were indelibly numbered in one corner for purposes of identification. A portable 4 gallon, 1½ lb. capacity washer and spin drier was used to treat from ¾ to 1 lb. of fabrics. The specimens were washed 3 minutes in 4 gallons of Chicago tap water containing 75 cc. of a commercial anionic detergent. The water was drained and the test cloths spun dry for 1 minute. The washer was refilled with water to which had been added the treating chemical from an aqueous suspension thereof. The dosage of the treating chemical in these tests was .001% by weight of the rinse water. The rinse cycle was conducted for 3 minutes. The washer was drained and the specimens again spun dried for 1 minute. Another rinse cycle was run on washed but non-treated specimens for purposes of comparison.

Both the treated and untreated specimens were felt by an average of twelve persons who rendered their opinions as to the softness of the specimens. In all cases the cloths and diapers treated with compositions 1 through 8 were readily distinguishable from the untreated. Composition 1, for example, imparted an excellent hand to the specimens.

The higher dosages have the effect of making the fabrics treated soft and fluffy even after several subsequent washings without treatment. When dosages of about .05% to 1% by weight are used in the rinse operation, water repellency is imparted to the fabrics. If the user does not desire such an effect, treatments can be temporarily suspended or the dosage diminished until such effects are mitigated. In any event, simple experimentations can determine optimum concentrations.

It is desirable to place the materials in a low molecular weight aliphatic alcohol such as isopropanol to prevent freezing during shipment. The compositions of the invention are relatively stable when prepared in an alcohol suspension but in the event separation occurs after a lapse of time, heating or agitation will restore the suspension to its original conditions. Laboratory tests have shown fabrics treated in accordance with the invention will not yellow with age or with repeated treatment. The compositions are relatively safe for home use when employed in the concentrations suggested herein. The treatment is especially advantageous where it is desired to overcome harshness of feel or to enhance softness to touch or to enhance water repellency of cloth or paper.

The compositions of the invention are especially useful in treating hydratable fibers and cloth or sheets in which such fibers predominate, especially cellulose fibers such as cotton or blends of fibers in which cellulose predominates. The invention is also applicable to the treatment of wood fibers and cloth, glass fibers and cloth, and synthetic fibers and cloth made therefrom or made from blends of synthetic fibers and natural fibers, e.g., blends of Dacron (polyethyleneterephthalate) and wool, blends containing Orlon (acrylic fiber) and the like.

The invention is hereby claimed as follows:

1. The method of treating hydratable fibrous materials in which the predominating fibers are cellulose fibers which comprises contacting said materials with an aqueous bath of a colloidally dispersed 1,2-substituted imidazoline salt of an acid selected from the group consisting of inorganic mineral acids and low molecular weight, organic carboxylic acids having not more than 10 carbons, said imidazoline being substituted in the 1 and 2 positions by aliphatic groups each having at least 11 carbon atoms.

2. The method of treating cellulose fibrous materials which comprises contacting said materials with an aqueous bath of a colloidally dispersed 1,2-substituted imidazoline inorganic mineral acid salt, said imidazoline being substituted in the 1 and 2 positions by aliphatic groups each having at least 11 carbon atoms.

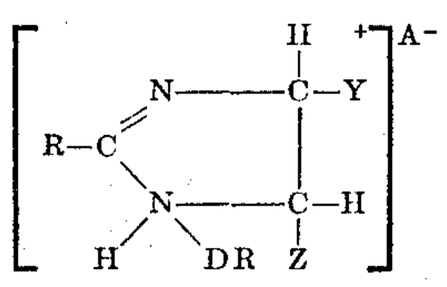
3. The method of treating cellulose fibrous materials which comprises contacting said materials in an aque-

ous bath of a colloidally dispersed 1,2-substituted imidazoline low molecular weight organic carboxylic acid salt, said carboxylic acid having not more than 10 carbons, said imidazoline being substituted in the 1 and 2 positions by aliphatic groups each having at least 11 carbon atoms.

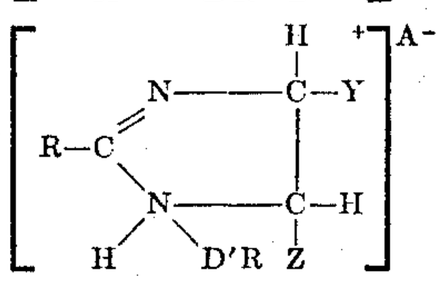
4. The method of claim 3 wherein the low molecular weight organic carboxylic salt forming acid is from the group consisting of hydroxy substituted monocarboxylic acids and hydroxy substituted polycarboxylic acids.

5. The method of softening textiles which comprises contacting said textiles with an aqueous bath of a colloidally dispersed 1,2-substituted imidazoline salt from the group consisting of

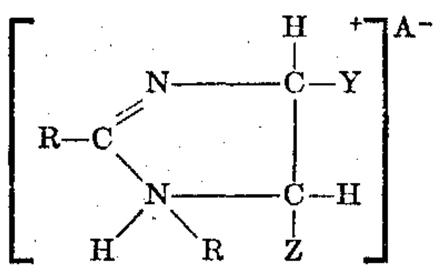
I.



II.



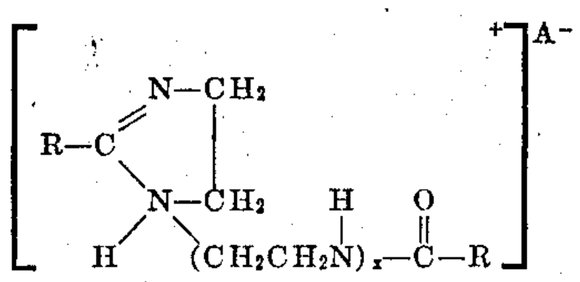
III.



wherein D represents a divalent, non-amino, organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N; D′ represents a divalent, organic radical containing less than 25 carbon atoms composed of elements from the group consisting of C, H, O and N, and containing at least one amino group; R is an aliphatic group containing from 15 to 23 carbon atoms; Y and Z are from the group consisting of hydrogen and lower aliphatic groups containing not more than 6 carbon atoms, and A^- is an anion of an acid from the group consisting of inorganic mineral acids and low molecular weight organic carboxylic acids.

6. The method of claim 5 wherein the low molecular weight organic carboxylic acid is a hydroxy substituted carboxylic acid.

7. The method of softening textiles which comprises contacting said textiles with an aqueous bath of a colloidally dispersed 1,2-substituted imidazoline salt having the formula:



wherein R is an aliphatic hydrocarbon group containing from 15 to 23 carbon atoms; x is a small whole number not greater than 3 and A^- is an anion of an acid from

the group consisting of inorganic mineral acids and low molecular weight organic carboxylic acids.

8. The method of claim 7 wherein said low molecular weight organic carboxylic acid is a hydroxy substituted carboxylic acid.

9. The method of claim 8 wherein said low molecular weight organic hydroxy substituted carboxylic acid is a lactic acid.

10. The method of softening textiles which comprises rinsing said textiles in an aqueous suspension of from .001% to 1% by weight of 1-(2-stearoylaminoethyl)-2-heptadecyl-2-imidazoline lactate.

11. The method of claim 10 wherein the textile is predominantly cotton.

12. An aqueous treating bath for treating fibrous materials which comprises a dispersion in water of a minor amount of a colloidally dispersed 1,2-substituted imidazoline salt of an acid selected from the group consisting of inorganic mineral acids and low molecular organic carboxylic acids having not more than 10 carbons, said imidazoline containing at least two aliphatic groups each having at least 11 carbon atoms.

13. A bath as claimed in claim 12 wherein the 1,2-substituted imidazoline salt is dispersed in the treating bath at a concentration of .001% to 1% by weight.

14. A paper sheet composed of cellulose fibers impregnated with a minor amount of a colloidally dispersible 1,2-substituted imidazoline salt of an acid selected from the group consisting of inorganic mineral acids and low molecular weight organic carboxylic acids having not more than 10 carbons, said imidazoline being substituted in the 1 and 2 positions by aliphatic groups each having at least 11 carbon atoms.

15. A textile in which the predominating fiber is a hydratable cellulose fiber, said textile being impregnated with a minor amount of a colloidally dispersible 1,2-substituted imidazoline salt of an acid selected from the group consisting of inorganic mineral acids and low molecular weight organic carboxylic acids having not more than 10 carbons, said imidazoline being substituted in the 1- and 2-positions by aliphatic groups each having at least 11 carbon atoms.

16. A textile in which the predominating fiber is cotton, said textile being impregnated with a minor amount of a colloidally dispersible 1,2-substituted imidazoline salt of an acid selected from the group consisting of inorganic mineral acids and low molecular weight organic carboxylic acids having not more than 10 carbons, said imidazoline being substituted in the 1 and 2 positions by aliphatic groups each having at least 11 carbon atoms.

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