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UNITED STATES PATENT OFFICE

2,147,401

WATER-SOLUBLE SALTS OF AMIDINES AND DERIVATIVES THEREOF

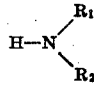
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7 Claims. (Cl. 260—564)

The present invention relates to water-soluble salts of amidines and derivatives thereof and to fibrous materials treated with these products.

We have found that fibrous materials, such as textiles, paper or pasteboard may be advantageously treated with the hitherto unknown water-soluble salts of amidines or derivatives thereof which are obtainable by treating mixtures of at least 2 imidoether salts or imidothioether salts, at least one of which contains more than 6 carbon atoms, with compounds of the following general formula:



wherein R_1 and R_2 may stand for hydrogen or an aliphatic, aromatic or hydroaromatic radical.

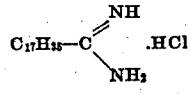
As mixtures of imidoether salts there may be mentioned, for instance, the imidomethylether hydrochloride of technical stearic acid, the imidoethylether hydrochloride of entirely brominated technical stearic acid, the imidoethylether hydrochloride of montanic acid, the imidobutylether hydrochloride of coco-nut oil fatty acid, the imidomethylether hydrochloride prepared from mixtures containing oxystearic acid and oxypalmitic acid, the imidoethylether hydrochloride of technical resin acid, the imidophenylether hydrochloride of coco-nut oil fatty acid, the imidoethylthioether hydrochloride of technical stearic acid, the imidoethylether hydrochloride of technical naphthenic acid.

As products of the general formula

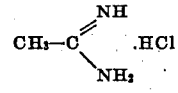


there may be used: ammonia, amines such as methylamine, ethylamine, diethylamine, butylamine, dibutylamine, ethylenediamine, monoethanolamine, diethanolamine, phenylene diamine, furthermore, urea, urethanes, amides, or the like.

As water-soluble salts of amidines there may be mentioned, for instance: mixtures of salts of amidines prepared from pure acid nitriles, for instance, by mixing pure stearamidine hydrochloride of the following constitution:



with acetamidine hydrochloride of the following constitution:



furthermore, the amidine hydrochloride of technical stearic acid, the diethylamidine hydrochloride from coco-nut oil fatty acid, the amidine hydrochloride obtained from the nitrile of a paraffin carboxylic acid which has been prepared by oxidation of paraffin with air, the amidine hydrochloride prepared from imidoethylether hydrochloride of technical stearic acid by reaction with ethylene diamine, the amidine formate of palm nut oil fatty acid, the amidine oxalate of coco-nut oil fatty acid, the product prepared by entirely methylating the amidine obtained from palm nut oil fatty acid nitrile.

All these substances have besides a good dispersive and emulsifying power an excellent action as softening agent. By treating fibrous material such as colored or uncolored textiles, paper or paste board, with solutions of these substances there are obtained very good dressing and impregnation effects since the substances improve the soft feel of the fibers. According to their construction, the products are suitable for being used, for instance, as washing, wetting, levelling, emulsifying or dispersing agents, as resists for rendering viscose artificial tissues fast to creasing, for delustring artificial silk and for after-treating colored materials.

The solubility and stability of the solutions of certain of the salts of these amidines may be enhanced by using simultaneously during the preparation or application of the solutions emulsifying or dispersing agents or protective colloids. As such assistants there may be mentioned, for instance, the salts of urethanes carrying sulfo or carboxyl groups, fatty alcohol sulfonates, water-soluble oxethylated fatty alcohols, oxethylated fatty amines, oxethylated esters or amides of higher fatty acids, carbohydrates, oxethylated or other water-soluble albuminous products and similar water-soluble highly-molecular substances or mixtures of the said products.

In some cases, for instance, in the preparation of dressings which are fast to washing and impregnations which are fast to creasing it is advantageous to add buffering substances such as, hexamethylenetetramine in order to protect the fiber from being deteriorated. In other cases the stability to washing of dressings or impregnations

may be improved by working in the presence of inorganic or organic ammonium salts.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight unless otherwise stated:

1. 100 parts of imidoethylether hydrochloride, obtainable from coco-nut oil fatty acid nitrile, are dissolved in absolute alcohol. Thereupon, an amount of ammonia gas is added which exceeds the calculated quantity by a little, and the whole is slowly warmed to 50° C., whereupon the ammonium chloride which has first precipitated, disappears for the most part. After filtration, the alcohol is removed by distilling it off in vacuo, and the amidine hydrochloride is washed out with ether. The yield amounts to 87 parts; the product obtained is easily soluble in water.

This product is suitable for being used as wetting agent in the textile industry.

2. 32 parts of anhydrous methyl alcohol are added to 195 parts of nitrile mixture prepared from palm nut oil fatty acid (boiling at 100° C. to 125° C. under a pressure of mercury of 2 mm., corresponding with about 68% of laurylnitrile and about 32% of myristilnitrile) and, at about 10° C., 38 parts of hydrogenchloride are introduced into the mixture. After a prolonged standing in the cold the reaction mass solidifies. By treating it with ethylene diamine in a methylalcoholic solution, it is converted into the corresponding amidine.

By treating mixed fabrics consisting of viscose artificial silk and natural silk with a formaldehyde solution of 20% strength which contains per liter 20 grs. of the above described product, the goods obtained, after squeezing and drying at 80° C., to 90° C., are fast to creasing and have an agreeable soft feel.

3. 245 parts of nitrile of a carboxylic acid which is obtainable by oxidation of paraffin by means of air, are mixed with 64 parts of methyl alcohol. 76 parts of hydrogen chloride are introduced into this mixture at 0° C. to 5° C., while stirring. Stirring is continued and the product then is allowed to stand for several hours. Thereupon, the whole is mixed with 200 parts of methyl alcohol and 210 parts of methylalcoholic ammonia solution; the whole is then heated to 50° C. Thereupon, the methanol is distilled off under a feebly reduced pressure and the residue is taken up in ether. The solution obtained is cooled to about 0° C., filtered with suction and the solid matter is washed with ether. The pure amidine hydrochloride is thus obtained. By using this product for dyeing cotton tissue in a weight of 2% of that of the tissue to be dyed, there is obtained a very good levelling effect.

4. 175 parts of imidoethylether hydrochloride, obtainable from the nitrile of technical stearic acid, are introduced into 200 parts of an alcoholic monoethylamine solution of 30% strength. The whole is stirred for some time and heated for 8 hours at 70° C. to 75° C. The alcohol is distilled off and the diethylamidine hydrochloride is obtained. By treating cotton with a solution of amidine hydrochloride which contains 4% of the weight of the goods to be dyed, the material shows, when dyed with basic dyestuffs, a good resist effect, i. e. the cotton does not absorb the dyestuff.

5. 665 parts of imidomethylether hydrochloride, obtainable from the nitrile of technical stearic acid, are introduced into 1000 parts of methyl alcohol and, simultaneously, 162 parts of ethylene diamine of 74% strength are dropped in. The whole is boiled for 3 hours in a reflux apparatus. The whole is filtered by suction, the alcohol is distilled off and the amidino hydrochloride is washed out with ether. By treating cotton which has been dyed with a substantive dyestuff, with a solution of 0.1% of this product the dyeing becomes very fast to the action of water, perspiration and acids. Also the fastness to washing is considerably enhanced by such an after-treatment.

6. 150 parts of imidoethylether hydrochloride, obtainable from palm nut oil fatty acid nitrile, are dissolved in absolute alcohol. While stirring, about the calculated amount of ammonia gas is introduced and the whole is then warmed at about 40° C. to 50° C. After filtration, the alcohol is removed by distillation and the amidine hydrochloride is washed out with ether.

By treating crude viscose artificial silk which still contains sulfur for 1 hour at 90° C. with solution of 2% of this product, there is obtained a very desulfurized artificial silk which possesses an excellently soft feel.

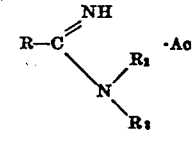
We claim:

1. Water-soluble mixtures of acid addition salts of amidines, said mixtures being obtainable by causing a mixture of acid addition salts of imido-ethers obtained by converting technical stearic acid into the corresponding acid addition salts of imido-ethers, to react with ethylenediamine.

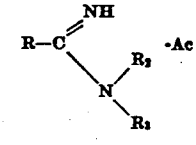
2. Water-soluble mixtures of acid addition salts of amidines, said mixtures being obtainable by causing a mixture of acid addition salts of imido-ethers obtained by converting technical stearic acid into the corresponding acid addition salts of imido-ethers, to react with diethylamine.

3. Water-soluble mixtures of acid addition salts of amidines, said mixtures being obtainable by causing a mixture of acid addition salts of imido-ethers obtained by converting paraffin carboxylic acid into the corresponding acid addition salts of its imido-ether, to react with ammonia.

4. Mixtures of acid addition salts of amidines containing at least one addition salt of the formula

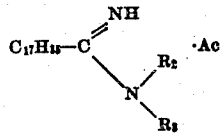


wherein R means an aliphatic hydrocarbon radical of at least 11 carbon atoms, R_2 and R_3 stand for a member of the group consisting of H and aliphatic hydrocarbon radicals, Ac means an acid, and at least one addition salt of the formula

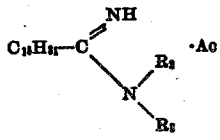


wherein R means an aliphatic hydrocarbon radical, R_2 and R_3 stand for a member of the group consisting of H and aliphatic hydrocarbon radicals, Ac means an acid.

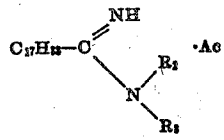
5. Mixtures of acid addition salts of amidines containing an addition acid salt of the formula



an addition salt of the formula

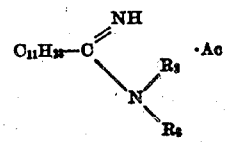


and an acid addition salt of the formula

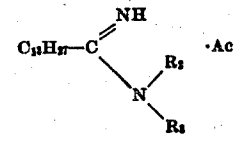


in which formulae R_2 and R_3 stand for a member of the group consisting of H and aliphatic hydrocarbon radicals, Ac stands for an acid.

6. Mixtures of acid addition salts of amidines containing an addition acid salt of the formula

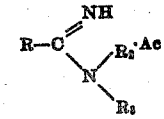


and an acid addition salt of the formula

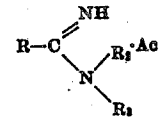


in which formulae R_2 and R_3 stand for a member of the group consisting of H and aliphatic hydrocarbon radicals, Ac stands for an acid.

7. Mixtures of acid addition salts of amidines containing at least one addition salt of the formula



wherein R means a member of the group consisting of aliphatic hydrocarbon radicals of at least 11 carbon atoms and cycloaliphatic hydrocarbon radicals, R_2 and R_3 stand for a member of the group consisting of H and aliphatic hydrocarbon radicals, Ac means an acid, and at least one addition salt of the formula



wherein R means a member of the group consisting of aliphatic hydrocarbon radicals, R_2 and R_3 stand for a member of the group consisting of H and aliphatic hydrocarbon radicals, Ac means an acid.

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