

UNITED STATES PATENT OFFICE

2,308,021

DYE BATH FOR THE DYEING OF TEXTILE GOODS

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4 Claims. (Cl. 8-87)

This application is a continuation in part of my co-pending application Serial No. 107,020, filed October 22, 1936 and patented May 6, 1941, No. 2,240,957.

The present invention relates to dye-baths for the dyeing of textile goods. More particularly it relates to dye-baths which contain alkali metal salts of aminocarboxylic acids containing only basic nitrogen atoms and in relation to one basic nitrogen atom more than one carboxylic acid group standing in α -position thereto. Such dye-baths characterized by the fact that they are free from the disturbing effects on textile goods which are caused by the use of water containing salts of di- and trivalent metals, particularly hard water, and of metallic vessels and apparatus for preparing the dyebaths and while working therewith.

As it is well known, the use of hard water for preparing dye-baths can have a very disturbing effect, since a considerable number of dyestuffs is sensitive towards the metal salts contained in hard water and tends to form insoluble precipitates therewith. However, even when using dyestuffs which are not sensitive towards chalk, precipitates of calcium carbonate may occur, particularly at higher temperatures.

In many cases other metal salts which tend to form together with dyestuffs difficultly soluble or insoluble precipitates may also have a disturbing effect. Thus, for instance, water which contains iron salts effects a strong turning to yellow of the textile goods treated therewith and injures badly the shade of some dyestuffs. Further difficulties may occur when textile goods are dyed in vessels or apparatus which have been made from or are lined with metals such as iron and especially copper; in these cases the shades of the dyeings obtained by means of some dyestuffs may be considerably injured, even when employing soft water for the dyebaths.

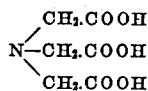
According to the present invention the disturbing effect of the aforesaid metal salts contained in the water which is employed for preparing the dyebaths as well as the difficulties caused by the metals from which the vessels or apparatus employed for the dyeing processes have been made, can easily be avoided by adding to the water employed for the dye-baths alkali metal salts of aminocarboxylic acids containing only basic nitrogen atoms and in relation to one basic nitrogen atom more than one carboxylic acid group standing in α -position thereto.

By adding these substances to water containing salts of di- and trivalent metals which tend

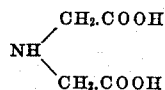
to form or have already formed difficultly soluble or insoluble precipitates, particularly to hard water, such precipitates are avoided or made harmless respectively. Hard water acts after the addition of the said substances like soft water towards agents which precipitate chalk. It may be that the above described aminocarboxylic acids are binding calcium-ions in a complex form. When precipitates of insoluble calcium or other metal salts have already been formed, they can be easily redissolved without the use of strong acids which may be detrimental to the textile materials or to the apparatus.

Instead of preparing dye-baths by dissolving first the sodium salts of the aforesaid aminocarboxylic acids in water and employing then the thus obtained aqueous solutions for dissolving the dyestuffs, one may also proceed in such a way that the dyestuff powders or pastes are mixed together with the necessary amounts of the above sodium salts and the mixtures thus obtained are employed for preparing the dye-baths by dissolving them in water. The use of such dyestuff preparations is of great advantage for practical purposes, since any kind of hard water just being at hand acts like soft water when such a dyestuff preparation is dissolved therein.

There exists a great number of aminocarboxylic acids of the aforesaid type which are useful for the present invention and of which only some examples can be named. Among the simplest compounds which are obtainable by acting with ammonia on monochloroacetic acid or by saponifying the corresponding nitrils, the trimethylamine- α -, α' -, α'' -tricarboxylic acid or nitrilotriacetic acid of the formula:



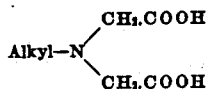
(Beilstein, fourth edition, volume IV, page 369) is particularly suitable. The iminodiacetic acid of the formula:



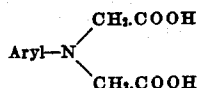
(l. c. page 365) has a somewhat reduced effect.

From the latter a large number of substituted iminocarboxylic acids are derived by substituting the hydrogen atom of the iminogroup by an alkyl-, aryl-, aralkyl-, oxalkyl-group and the like. In all of these groups various substituents may be present. The degree of efficacy of such

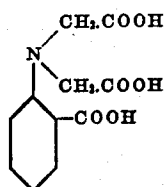
substances is individually different; for instance alkyliminodiacetic acids of the formula:



are essentially more effective than the less useful aryliminodiacetic acids of the formula:

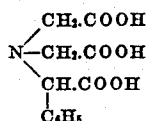


But if the latter contain in the benzene nucleus an acid group standing in ortho position to the carbon atom to which the imino-group is attached the efficacy is essentially increased. Thus, for instance, the anthranilic -N,N-diacetic acid of the formula:

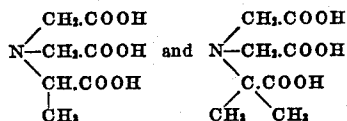


(Bellstein, fourth edition, vol. 44, page 354) is very effective.

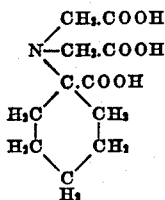
Analogous products are obtained by acting with an excess of chloroacetic acid on hydrazine and hydroxylamine. Aminocarboxylic acids which are derived from ethylenediamine and the corresponding polyamines are particularly valuable. By replacing the hydrogen atoms of the methylene groups of the above nitrilotriacetic acid by alkyl- or arylgroups suitable compounds are obtained, for instance C-phenyl-nitrilotriacetic acid of the formula:



furthermore C-monomethyl-nitrilotriacetic acid and C-dimethyl-nitrilotriacetic acid of the formula:



N-(1-carboxycyclohexyl)-iminodiacetic acid of the formula:



The alkali salts of all these aminocarboxylic acids exert, according to their chemical constitution, more or less the above described softening effect when dissolved in hard water.

The term "textile goods" as used throughout the present application is not limited to any special example named herein, but it comprises all kinds of textile materials such as wool, cotton, silk, artificial silk, linen, hemp, jute, hair, feathers, leather and the like. Furthermore it comprises these materials in any state of manufac-

ture, the raw materials as well as the threads, yarns, fabrics, ribbons, lines, pelts or their products produced therefrom.

The term "dye-bath" as used throughout this application is not limited to aqueous solutions containing dyestuffs, but it comprises also aqueous solutions of naphthol compounds which are employed as impregnating baths for the so-called "Naphthol-AS dyeing method." Furthermore it comprises dyestuff pastes which are used for the printing of textile goods as well as the several baths and solutions of dyeing expedients which are necessary during the usual dyeing and printing processes for treating the dyeings until they are ready to be dried.

In order to further illustrate my invention the following examples are given. I wish it, however, to be understood that my invention is not limited to the examples given nor to the exact conditions stated therein.

Example 1

Cotton yarn is dyed with 3% of its weight of Sirius light green BL (Schultz, Farbstofftabellen, (1934) first supplementary volume, page 131) in a dyebath containing per liter 10 grs. of sodium sulfate and 5 grs. of the sodium salt of methyliminodiacetic acid (Bellstein, fourth edition, vol. IV, page 367) for about an hour at 90 to 95° C. while using a hard water containing 0.12 gr. of calcium oxide per liter.

The goods are dyed in an unobjectionable manner whereas without the addition of the methyliminodiacetic acid the goods are dyed unequally and with stains owing to the sensitivity of the dyestuff towards chalk.

A similar good effect is obtained by adding to the dye-bath the sodium salt of nitrilotriacetic acid instead of the sodium salt of methyliminodiacetic acid.

One may also prepare mixtures of these substances with the corresponding amounts of the above dyestuff which mixtures are very suitable for preparing the dye-baths in the usual manner in spite of the use of hard water.

Example 2

Cotton goods in the form of cops or cross bobbins are dyed on a usual dyeing apparatus with 15% of their weight of a paste of Indanthrene scarlet B (Schultz, Farbstofftabellen, vol. II (1932), page 132) according to a process usual for such a vat dyestuff while using hard water containing 0.15 gr. of calcium oxide per liter, the dyeing liquor containing per liter 3 grs. of the sodium salt of anthranilic-N,N-diacetic acid. The goods are dyed in an unobjectionable manner whereas without such an addition white dusty precipitates of calcium salt are formed.

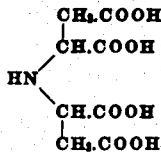
The same good result is obtained when replacing the sodium salt of anthranilic-N,N-diacetic acid by the sodium salt of C-phenyl-nitrilotriacetic acid.

Instead of adding these substances to the dye-bath, they can also be mixed with the corresponding amounts of the dyestuff and these dyestuff mixtures can be employed for preparing the dye-baths in the usual manner.

Example 3

According to one of the usual methods 2 grs. of 2.3-hydroxy-naphthoic acid-β-naphthalide are dissolved in a caustic soda solution with the addition of hot water while using hard water containing 0.12 gr. of calcium oxide per liter and

subsequently adding per liter 3 grs. of the sodium salt of imino-bissuccinic acid of the formula:

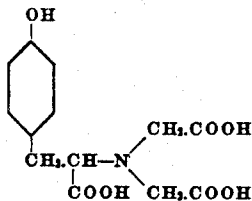


(which salt is obtainable by saponifying the ethyl ester by means of an alcoholic caustic soda solution, cf. Bellstein, vol. IV, page 486). The solution remains clear, and the dyeings obtained on cotton in the usual manner by impregnating it with this solution and treating it hereafter with a diazonium salt solution are fast to rubbing. Without the addition of the aforesaid salt precipitates are formed and in consequence thereof the analogous dyeings obtained on cotton are not fast to rubbing.

Similar good results are obtained by employing the sodium salt of C-dimethyl-nitrilotriacetic acid instead of the sodium salt of iminobissuccinic acid.

Example 4

Cotton goods are dyed as described in Example 2, but while adding to the dyebath per liter 2 grs. of the sodium salt of an acid of the formula:

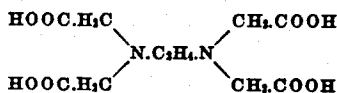


which is obtainable by acting with an excess of monochloroacetic acid on para-hydroxyphenylalanine (tyrosin).

The goods are dyed in an unobjectionable manner even when using hard water containing 0.15 gr. of calcium oxide per liter.

Example 5

In the same manner as described in the foregoing examples the theylene-bis-iminodiacetic acid of the formula:



may be added to the dye-bath. It can be prepared either by saponifying the corresponding nitrile or by acting with monochloroacetic acid on theylene diamine.

Example 6

Bleached calico is dyed with 1% of its weight of the disazodyestuff which is obtained by coupling one mole of tetrazotized benzidine with one mole of salicylic acid and one mole the 3-methyl-5-pyrazolone derivative of 2-naphthylamine-5,7-disulfonic acid. The dyeing process is performed in a copper vessel in a dyebath containing per liter 1 gr. of the sodium salt of nitrilotriacetic acid. Thereby a clear yellow dyeing is obtained, whereas merely dirty orange shades are obtained when using a copper vessel without adding the aforesaid sodium salt of nitrilotriacetic acid to the dyebath.

When calico is dyed under the same conditions as above described by means of the trisazodyestuff which is obtained by coupling one mole of

tetrazotized m-phenylenediamine with one mole of 1,3-dioxybenzene and one mole of 2-amino-5-naphthol-7-sulfonic acid, further diazotizing the disazodyestuff obtained and coupling it with one mole of 1,3-dioxybenzene, clear reddish-violet dyeings are obtained. Without the addition of the sodium salt of nitrilotriacetic acid to the dyebath merely valueless red-brown shades are obtained when employing a copper vessel for the dyeing process.

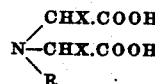
Such valueless dyeings obtained by working in a copper vessel without the aforesaid addition to the dyebath can be improved in a surprising manner by aftertreating them for about half an hour at about 90° C. in a bath containing per liter 3 grs. of the sodium salt of nitrilotriacetic acid or also of the sodium salt of one of the other acids described in the foregoing examples.

Example 7

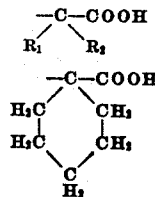
Merino wool is dyed in a copper vessel with 2% of its weight of the dyestuff obtained by coupling diazotized o-toluidine-m-sulfonic acid with β -naphthol while adding to the usual dyebath 0.5% (of the weight of the wool) of the triethanolamine salt of nitrilotriacetic acid. Clear yellow dyeings are obtained whereas merely turbid shades are obtained when working in a copper vessel without the addition of the aforesaid salt to the dyebath.

I claim:

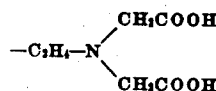
1. As a composition of matter a dyebath for the dyeing of textile goods containing an alkali metal salt of an aminocarboxylic acid of the formula:



wherein X stands for a member selected from the group consisting of hydrogen and $-\text{CH}_2\text{COOH}$ and R stands for a member of the group consisting of hydrogen, alkyl, aryl, and the radicals

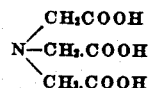


and



R₁ standing for a member of the group consisting of hydrogen, alkyl, phenyl and benzyl and R₂ standing for a member of the group consisting of hydrogen and alkyl.

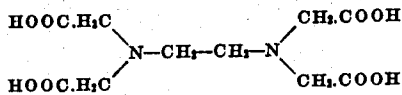
2. As a composition of matter a dyebath for the dyeing of textile goods characterized by containing an alkali metal salt of nitrilotriacetic acid of the formula:



which dyebath is free from the disturbing effects on textile goods caused by the use of water containing salts of di- and trivalent metals and by the use of metallic vessels and apparatus for preparing the dyebaths and while working therewith.

3. As a composition of matter a dye-bath for

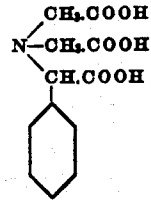
the dyeing of textile goods characterized by containing an alkali metal salt of ethylene-bis-imino-diacetic acid of the formula:



which dyebath is free from the disturbing effects on textile goods caused by the use of water containing salts of di- and trivalent metals and by the use of metallic vessels and apparatus for preparing the dyebaths and while working there-with.

4. As a composition of matter a dyebath for the dyeing of textile goods characterized by contain-

ing an alkali metal salt of C-phenyl-nitrilotri-acetic acid of the formula:



which dyebath is free from the disturbing effects on textile goods caused by the use of water containing salts of di- and trivalent metals and by the use of metallic vessels and apparatus for preparing the dyebaths and while working there-with.

FERDINAND MÜNZ.