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[54] POLYAMIDE DYEING WITH A REACTION PRODUCT OF A REACTIVE DYE-N-ALKYLAMINE ALKYL CARBOXYLIC OR SULFONIC ACID OR SALT THEREOF

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** .... **8/41 R,** 8/41 B, 8/1 A
[51] **Int. Cl.** **D06p 3/22,** D06p 3/28
[58] **Field of Search** 8/1.212

[56] **References Cited**

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[57] **ABSTRACT**

Process for the dyeing of nitrogen-containing fibers, preferably wool, with reactive dyestuffs by treating the goods with aqueous baths of such reactive dyestuffs with which the nitrogen-containing fibers react according to an addition mechanism and which have been converted into a more soluble and more reactive form by the action of N-alkyl-amino-alkyl carboxylic acids and/or N-alkyl-amino-alkyl-sulfonic acids or their salts.

7 Claims, No Drawings

POLYAMIDE DYEING WITH A REACTION PRODUCT OF A REACTIVE DYE-N-ALKYLAMINE ALKYL CARBOXYLIC OR SULFONIC ACID OR SALT THEREOF

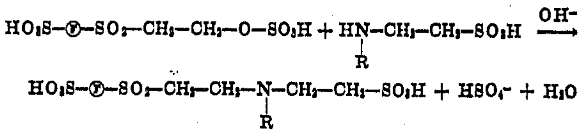
It is known that wool can be dyed according to the exhaust process brilliant shades which have a very good fastness to wet processing, with reactive dyestuffs of the sulfatoethylsulfone type containing sulfonic acid groups. A precondition therefor is that the pH-value of the boiling dyebath can be kept for at least half an hour at pH 6. Under these conditions, the sulfato-ethyl-sulfone dyestuff is converted into the reactive vinyl-sulfone form which is decisive for the dyestuff undergoing a covalent linkage with the protein fiber (cf. Melliand Textil-berichte 12/1968, pages 1,444 – 1,448). This linkage is the reason for the excellent properties of fastness to wet processing of the wool dyeings so produced. If, however, the dyeing is carried out at a lower pH-value, an unsufficient quantity of vinyl-sulfone dyestuff is formed which results in an essential reduction of the fastness to wet processing of the dyeings. If, on the other hand, the dyestuff is applied at a higher pH-value the wool is more or less damaged. In addition, it is often not easy to maintain a pH-value of 6 in a boiling dyebath. In most cases, these baths are prepared with water decalcified with ion exchangers, thus their pH-value rises considerably during the dyeing.

Therefore, with regard to the use of sulfato-ethyl sulfone dyestuffs for the dyeing of woollen materials, it has already been proposed to submit such reactive dyestuffs, before the dyeing process, to an alkaline pre-treatment by exposing the aqueous dyestuff solution in the reaction vessel for 5 minutes at 80°C to the action of, for example, tri-sodium phosphate. Thereby, the dyestuff is converted into the reactive vinyl-sulfone form required for the dyeing. This alkaline dyestuff solution is added to the dyebath which has been adjusted to a pH-value of 5 by means of acetic acid and the wool can then be dyed at the isoelectric point, i.e. under the mildest conditions for wool fibers, shades that are fast to wet processing. During the mentioned alkaline pre-treatment of the sulfatoethyl-sulfone dyestuffs, the vinyl-sulfone dyestuff formed loses a solubilizing group:

$$HO_3S—Ⓕ—SO_2—CH_2—CH_2—O—SO_3H \xrightarrow{OH^-} HO_3S—Ⓕ—SO_2—CH{=}CH_2 + HSO_4^- + H_2O$$

(F = dyestuff molecule)
With the mostly concentrated dyestuff solutions this loss provokes precipitation of the dyestuff in the preparing vessels, because in alkaline baths these dyestuffs are normally soluble in a quantity of 5 – 40 g/l only.

In the course of investigations in this field, it has now been found that the solubility of such reactive dyestuffs in alkaline baths, at a temperature of 40°C or higher, can be increased, without dyestuff precipitations occurring to 60 – 110 g/l by the addition of secondary aliphatic amines which contain sulfonic acid groups or carboxylic acid groups. It can be proved by paper chromatography that during the alkaline pre-treatment of the sulfatoethyl-sulfone dyestuffs the mentioned amino compounds react at temperatures of over 40°C with the reactive system of these products:



$$HO_3S—Ⓕ—SO_2—CH_2—CH_2—O—SO_3H + \underset{\substack{|\\R}}{HN}—CH_2—CH_2—SO_3H \xrightarrow{OH^-} HO_3S—Ⓕ—SO_2—CH_2—CH_2—\underset{\substack{|\\R}}{N}—CH_2—CH_2—SO_3H + HSO_4^- + H_2O$$

(F = dyestuff molecule; R = lower alkyl group).

Accordingly, the present invention provides a process for the dyeing of nitrogen-containing fibers, preferably wool, with reactive dyestuffs, wherein the goods are treated with aqueous baths of such reactive dyestuffs with which the nitrogen-containing fibers react according to an addition mechanism and which have been converted into a more soluble and more reactive form by the action of N-alkyl-amino-alkyl-carboxylic acids and/or N-alkyl-amino-alkyl-sulfonic acid or the salts thereof.

When the reaction products, formed by the action of the afore-mentioned amino-compounds from the reactive dyestuffs, are applied according to the process of the invention onto nitrogen-containing fibers at pH-values in the range of about 5, dyeings are obtained which are more intense and have a better fastness to wet processing than those obtained, for example, with the conventional sulfato-ethyl-sulfone dyestuffs. The latter enter, with regard to their colour build up at this pH-value, a covalent linkage with the nitrogen-containing fibers in a rate of about 70–80 percent only, whereas the remaining proportion is bound in the form of a salt. In contradistinction thereto, the above-mentioned reaction products are almost completely fixed. Furthermore, these dyestuffs can be applied on wool at pH-values of between 2 and 3, contrary to the sulfato-ethyl products, without chemical reaction with the fiber, and then permanently fixed by an increase of the pH to 5. This also yields a remarkable improvement of the levelness of such dyeings. Thus, these are reactive dyestuffs which have a considerably higher reactivity towards nitrogen-containing fibers than the starting sulfato-ethyl-sulfone products themselves.

The dyestuffs used according to the invention for producing the dyeings are obtained by boiling for 1 – 2 minutes the above-mentioned amino-compounds in an alkaline bath with reactive dyestuffs which react with nitrogen-containing fibers according to an addition mechanism. Suitable starting dyestuffs of this category belong, for example, to the series of the oxazine, triphenylmethane, xanthone, nitro, acridone or phthalocyanine dyestuffs, especially however to the type of metal-free or metallized mono- or polyazo dyestuffs and to anthraquinone dyestuffs, which contain at least one water-solubilizing group such as the sulfonic acid group or the carboxylic acid group, and contain preferably the group $—SO_2—CH_2—CH_2—OSO_3H$ once or several times. In contast thereto, reactive dyestuffs of the type reacting according to a substitution mechanism are inactivated by the above-mentioned amino-compounds.

Of the amino-compounds to be used according to the invention, there may be mentioned, for example,
N-alkyl-aminoacetic acid,
N-alkyl-aminoethyl-sulfonic acid, and
N-alkyl-amino-propionic acid,
the alkyl radicals in these substances being such containing one to four carbon atoms. The amino compounds may also be used in the form of their water-soluble salts, for example as alkali salts.

With the aid of these amino compounds, for example, the sulfato-ethyl-sulfone dyestuffs may be dissolved, in the vessels usually employed in the dyeing industry, with water and alkalis by short boiling in a concentrated form, without precipitations occurring which are unbearable in the dyeing industry. The conversion of the dyestuffs into its more reactive form may also be effected in the dye-bath by addition of the amino compounds to the dye-bath. It is suitable to add the amino compounds in a 1.5 to 4-fold molar quantity, referred to the starting dyestuff.

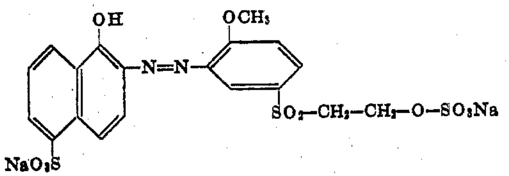
The dyeings according to the invention of nitrogen-containing fibrous material of natural or synthetic origin is preponderantly effected by exhausting the liquor at temperatures of 70 – 125°C of the aqueous dyestuff solution, from a weakly acidic preferably acetic medium. According to a variant of these dyeing conditions the levelness of such dyeings can be considerably increased, as has already been mentioned above, by entering the goods at first into a mineral acidic dye-bath and then completing the dyeing process at a weakly acidic pH value.

It is true that French Pat. No. 1,558,340 describes preparations for the dyeing and printing of wool, in which certain amino compounds, among others taurine or derivatives thereof, are added to alkaline padding baths or printing pastes for the stabilization of reactive dyestuffs of the sulfato-ethyl-sulfone or vinyl-sulfone type. However, the technical teaching involved in the present invention, that in the dyeing of nitrogen-containing fibers with reactive dyestuffs of this type — contrary to an improvement of the dyestuff stability according to the mentioned reference — the presence of, for example, methyl-taurine yields surprisingly an increase of the reactivity as well as of the solubility of these dyestuffs in neutral, acidic or alkaline baths, cannot be gleaned from the said prior art.

The following examples illustrate the invention.

EXAMPLE 1

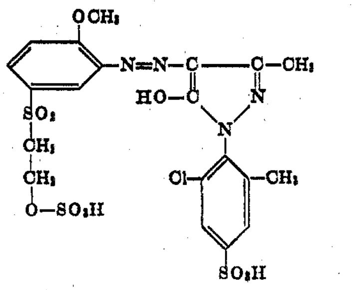
25 g of the reactive dyestuff of the formula



were dissolved together with 2.5 g of sodium carbonate and 3.8 g of the sodium salt of N-methyl-amino-ethyl-sulfonic acid in 500 ml of water by boiling for 1 to 2 minutes in the reaction vessel, without dyestuff precipitations occurring during that time. Then, 1 kg of woollen worsted yarn was dyed for 1 hour at a pH-value of 5 and a temperature of 100°C with 40 l of a solution containing, per liter of water, 40 ml of 60 percent acetic acid and 250 ml of the above dyestuff solution. The yarn so dyed was then rinsed hot and cold with water. After drying, a brilliant red dyeing was obtained which had an excellent fastness to washing.

EXAMPLE 2

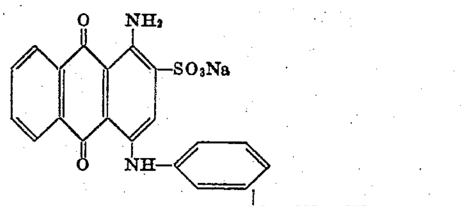
10 g of the reactive dyestuff of the formula



were dissolved together with 1 g of sodium carbonate and 1.5 g of the sodium salt of N-methyl-amino-acetic acid in 140 ml of water by boiling for 1 – 2 minutes in the reaction vessel whereupon no dyestuff precipitation occurred. Subsequently, 1 kg of woollen slubbing was dyed with 35 l of a solution, containing, per liter of water, 40 ml of 60 percent acetic acid and 140 l of the above-mentioned dyestuff solution, at a pH-value of 5 and a temperature of 100°C. The combed material so dyed was then rinsed hot and cold with water. After drying, a brilliant yellow dyeing having excellent fastness to washing was obtained.

EXAMPLE 3

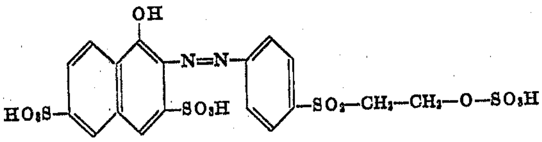
15 g of the reactive dyestuff of the formula



were dissolved together with 1.5 g of sodium carbonate and 2.3 g of the sodium salt of N-methyl-amino-ethyl-sulfonic acid in 210 ml of water by boiling for 1–2 minutes in the reaction vessel, without precipitation of dyestuff occurring. Then, 1 kg of a nylon fabric was dyed with 35 l of a solution containing, per liter of water, 40 ml of 60 percent acetic acid and 140 ml of the above-mentioned dyestuff solution, for 1 hour at 100°C. The dyed fabric was then rinsed hot and cold. After drying, a brilliant blue dyeing having excellent fastness to washing was obtained.

EXAMPLE 4

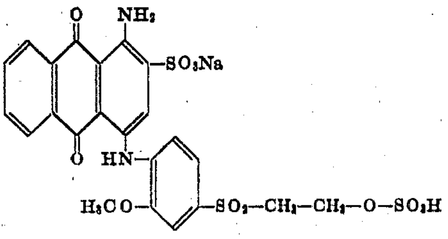
20 g of the reactive dyestuff of the formula



were dissolved together with 2 g of sodium carbonate and 3 g of N-ethyl-amino-propionic acid in 300 ml of water by boiling for 1–2 minutes, without a precipitation of the dyestuff occurring. Then, 1 kg of chlorinated woollen yarn was dyed, for 1 hour at a pH-value of 5 and a temperature of 100°C, with 40 l of a solution containing, per liter of water, 40 ml of a 60 percent acetic acid and 175 ml of the above dyestuff solution. The dyed woollen yarn was then rinsed hot and cold with water. After drying, a brilliant orange dyeing was obtained which showed an excellent fastness to washing.

EXAMPLE 5

15 g of the reactive dyestuff of the formula



were dissolved together with 1.5 g of sodium carbonate and 2.3 g of the sodium salt of N-methyl-amino-ethyl-sulfonic acid in 210 ml of water by boiling for 1–2 minutes in the reaction vessel, without dyestuff precipitation occurring. Then, 1 kg of woollen yarn was treated with 40 l of a solution containing, per liter of water, 40 ml of concentrated sulfuric acid and 170 ml of the above-mentioned dyestuff solution, for 45 minutes at 100°C. The pH-value of the bath was then increased to 5 by addition of 50 g of sodium acetate and 30 ml of sodium hydroxide solution of 38°Be, and the dyeing was then continued for 45 minutes at boiling temperature. The dyed fabric was then rinsed hot and cold with water. After drying, a brilliant blue dyeing having excellent fastness to washing was obtained which, with regard to its appearance, was considerably more level than the same dyeing produced from an acetic medium.

We claim:

1. An improved process for the exhaust dyeing of wool fibers with a sulfato ethyl sulfone dyestuff which reacts with said fibers according to an addition mechanism

consisting essentially of converting said dyestuff in an aqueous medium to a more soluble and more reactive form by reacting it with a compound selected from the group consisting of N-alkyl-amino-acetic acid, N-alkyl-amino-ethyl-sulfonic acid, N-alkyl-amino-propionic acid or an alkali metal salt thereof, the alkyl radicals in these compounds containing one to four carbon atoms; and

thereafter forming an aqueous solution of said converted dyestuff dyeing said fibers under acid condition at a pH below 5.0.

2. A process according to claim **1**, wherein the conversion of the starting reactive dyestuff is effected under alkaline conditions in the dye-bath or in the preparing vessel of the dye liquor.

3. A process according to claim **1**, wherein as nitrogen-containing fibers woollen fibers are used.

4. A process according to claim **1**, wherein the dyeings are effected in a weakly acidic medium.

5. A process according to claim **1**, wherein the dyeings are started under mineral acidic conditions and completed at weakly acidic pH-values.

6. A process according to claim **1**, wherein the dyeings are started at a pH-value of between 2 and 3 and completed at a pH-value of about 5.

7. A process according to claim **1**, wherein the dyeings are effected by exhausting the liquor at temperatures in the range of from 70° to 125°C.

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