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3,672,815

**PROCESS FOR DYEING MIXTURES OF POLYESTER AND POLYACRYLONITRILE FIBERS IN ONE BATH**

Hans-Ulrich von der Eltz, Frankfurt am Main, Johannes Jeths, Weiskirchen, and Alfons Bernhard Boecker, Kelkheim, Taunus, Germany, assignors to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brönig, Frankfurt am Main, Germany  
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6 Claims

**ABSTRACT OF THE DISCLOSURE**

Process for the single-bath dyeing of mixtures made of polyester and polyacrylonitrile fibers simultaneously with disperse dyestuffs and cationic dyestuffs according to the thermosol method wherein non-ionic dispersing agents are added to the acidic padding baths which contain the cationic dyestuff in dissolved form.

It is known that mixed materials from linear polyester fibers and polyacrylonitrile fibers can be dyed simultaneously with disperse and cationic dyestuffs according to the thermosol process.

In this method, the cationic dyestuffs may form addition compounds with the anionic dispersing agents used for disperse dyestuffs which may cause precipitation of the disperse dyestuff in the padding liquor, resulting in a distinct loss of colour yield and in uneven and specky dyeings.

In order to avoid such effects, it has been proposed to precipitate the cationic dyestuffs in the dyebath by means of anionic products and then to apply them onto the polyacrylonitrile fibers in analogous manner as the disperse dyestuff. For preventing the precipitation being coarse-grained it is necessary to add thickening agents to the padding liquor. This process has the disadvantage that the fine distribution of the precipitated cationic dyestuffs can be controlled and reproduced with difficulty only and that the precipitation requires an additional process step. Furthermore, the simultaneous use of thickening agents causes considerable soiling of the drying apparatus usually employed in the thermosol process and essentially reduces the properties of fastness, especially the fastness to rubbing and to washing, of the dyeings.

In mixtures which contain, besides polyester and polyacrylonitrile fibers, also cellulose fibers, the application of thickening agents results in a strong staining of the cellulose fiber portion by the disperse dyestuff, which has a negative influence on the fastness to rubbing and to washing of the dyeing.

Finally, thickening agents which cannot be removed by washing after the thermosol process impart onto the goods, in addition, a hard handle. Thus, it is almost impossible to obtain an even and speck-free dyeing with this process.

Now, we have found that the above-described disadvantages in the dyeing of mixtures of polyester and polyacrylonitrile fibers in one bath with disperse and cationic dyestuffs according to the thermosol process can be overcome by adding non-ionic dispersing agents to the acid padding liquors which contain the cationic dyestuff in dissolved form.

As non-ionic dispersing agents, there may be used according to the invention either polyglycols, oxyethylated

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oxazoline derivatives or oxalkylated fatty acid derivatives or mixtures of these products.

Among the suitable polyglycols, there may be used in particular polyethylene glycols having an average molecular weight in the range of from 1500 to 8000, especially those having a molecular weight of about 6000.

As oxalkylated fatty acid derivatives, there may be used according to the invention products which are derived from fatty amines, fatty acid amides or fat alcohols, preferably the oxethylation products of fat alcohols and fatty amines having polyether chains that correspond to 12 to 25 mols of ethylene oxide or mixtures of these compounds having a different degree of oxethylation, the reaction products of 1 mol of stearyl alcohol and 25 mols of ethylene oxide or of 1 mol of oleyl alcohol and 22.5 mols of ethylene oxide or of 1 mol of stearyl alcohol and 12 mols of ethylene oxide showing the most favourable behaviour.

As oxethylated oxazoline derivative, the reaction product of 1 mol of 2-heptadecyl-4-ethyl-4-hydroxymethyl-oxazoline and 70 mols of ethylene oxide is preferably used.

The mixture obtained from the reaction product of 1 mol of stearyl alcohol and 25 mols of ethylene oxide, polyethylene glycol having a molecular weight of about 6000, and the reaction product of 1 mol of 2-heptadecyl-4-ethyl-4-hydroxymethyl-oxazoline and 70 mols of ethylene oxide in a mixing proportion of 1:1:1 to 8:1:2, preferably 4:1:1, has proved especially favourable for the process of the invention. In general, 20 to 40 g., preferably 25 to 35 g., of non-ionic dispersing agent are added per liter to the padding liquor.

As disperse dyestuffs, there may be used according to the invention the dyestuffs usually employed for the dyeing of fibrous materials of linear polyesters, for example those of the series of azo or anthraquinone dyestuffs. Disperse dyestuffs of said type are known, for example, from Colour Index, second edition (1956), vol. 1, pages 1659-1742 and Supplement (1963), pages S 179-S 224 as well as from the corresponding Additions and Amendments No. 1 (September 1963) to No. 26 (January 1970).

Among the cationic dyestuffs used according to the invention, there may be especially mentioned those of the series of azo, azomethine, methine, anthraquinone, nitro, di- and triphenylmethane, phenazine, oxazine, thiazine, xanthene and quinophthalone dyestuffs. Suitable cationic dyestuffs are described in Colour Index, second edition (1956), vol. 1, pages 1617-1653 and in Supplement (1963), pages S 149-S 177 as well as in the corresponding Additions and Amendments No. 1 (September 1963) to No. 26 (January 1970).

As free acid which, according to the invention, increases the solubility of the cationic dyestuffs in water, there may be used organic acids, for example acetic acid and formic acid, preferably acetic acid.

The process of the invention is carried out by applying onto the textile material of polyester and polyacrylonitrile fibers an aqueous preparation having a temperature of from 20° to 40° C., preferably 30° C. and containing, in addition to dispersed disperse dyestuffs and dissolved cationic dyestuffs, free acid and non-ionic dispersing agents.

In order to prepare the padding liquors, the cationic dyestuff is first pasted up with the acid and dissolved by the addition of boiling hot water. After cooling to 20° to 40° C., this solution is added to an aqueous dispersion of the disperse dyestuffs having a temperature in the range of from 20 to 40° C. and to which a mixture of non-ionic agents had previously been added.

Following the padding process, the wet mixed material is dried at a temperature in the range of from 80° to 130° C., preferably at 100° C., and then subjected to a heat

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treatment for 30 to 90 seconds, preferably 60 seconds, at 180 to 210° C., preferably at 200° C., by means of hot air, superheated steam, a mixture of heated air and superheated steam or on heated cylinders, during which time the disperse dyestuff is fixed onto the polyester fiber and the cationic dyestuff is fixed onto the polyacrylonitrile fiber. This heat treatment simultaneously fixes the polyester portion of the mixed material and imparts its optimal technological properties.

After this dyeing process, the goods are rinsed and soaped and further treated in the usual manner.

It is noteworthy that in the process of the invention the addition of the non-ionic dispersing agents provides a good stability of the padding liquors containing disperse and cationic dyestuffs and that, with interesting bicolor effects, even and speck-free dyeings are obtained with a very good colour yield and good general fastness properties. Finally, it was surprising that, in contradistinction to the opinion of experts, a negative influence on the textile-technological properties of the polyester fibers is not exerted by the auxiliary agents at the elevated temperatures used according to the invention.

The textile material to be dyed according to the present invention, which consists of mixtures of linear polyesters, preferably polyethylene terephthalate, and polyacrylonitrile fibers, alone or in admixture with native or regenerated cellulose fibers, may have the form of a yarn, fabric or knitted fabric.

In the case of mixed materials which contain, in addition to polyester and polyacrylonitrile fibers, also cellulose fibers and in which the individual components are present in the ratio of 1:1:1, the cellulose fiber portion of the goods is dyed with dyestuffs of the classes usually employed for cellulose fibers, especially reactive dyestuffs, according to the methods known for these purposes, after the heat treatment, without/or after previous intermediate cleaning.

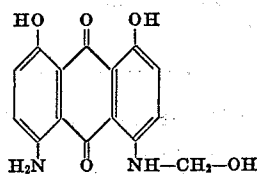
The dyestuffs used in this further embodiment of the process of the invention are, preferably, such organic compounds which contain at least one group capable of reacting with the cellulose fiber, a precursor for such a group or a substituent capable of reacting with the cellulose fiber. The parent components of these dyestuffs may belong to different classes of compounds; particularly suitable are those of the series of the anthraquinone, azo and phthalocyanine dyestuffs; the azo and phthalocyanine dyestuffs may be metal-free or metalliferous. Within the group of these dyestuffs, the reactive groups and precursors, which form such reactive groups in an alkaline medium, are, for example epoxy-groups, the ethylene-imide group, the vinyl group within the vinyl-sulfone- or acrylic acid radical, furthermore the  $\beta$ -sulfato-ethyl-sulfonyl group, the  $\beta$ -chloroethyl-sulfonyl group, the  $\beta$ -thio-sulfato-ethyl-sulfonyl group, the  $\beta$ -phosphatoethyl-sulfonyl group. It is in this connection without importance whether the aforementioned radicals are connected directly or over an intermediate member, especially —NH— or —NR— (R=lower alkyl) to the dyestuff molecule, as, for example in the case of the ethionyl-amino radical. Reactive substituents in reactive dyestuffs may also be such substituents which are easy to split off and which leave behind an electrophilic residue. As examples of such substituents, there may be mentioned halogen atoms at the following ring systems: quinoxaline, triazine, pyrimidine, phthalazine and pyridazone. Examples of reactive dyestuffs of the kind cited above are described in U.S. Pats. Nos. 2,670,265 (vinylsulfone, sulfatoethylsulfone and phosphatoethylsulfone); 2,657,205 (vinylsulfone); 3,197,456, 3,349,097, 3,324,151 and 3,261,823

(ethionylamino and N-alkyl-ethionylamino); 3,417,074 (vinylsulfonylamino and N-alkyl-vinylsulfonylamino); 3,278,549 (N-alkyl-ethionylamino); and 3,360,524, 3,278,516, 3,360,509, 3,360,505 and French Pat. 1,448,660 (tetrafluorocyclobutyl-carbonylamino and tetrafluorocyclobutyl-acryloylamino).

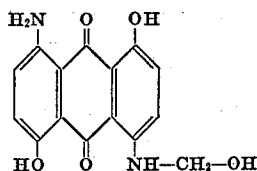
The following examples illustrate the invention:

## EXAMPLE 1

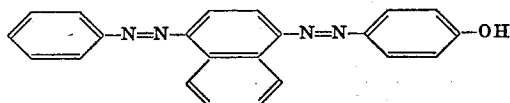
A mixed fabric consisting of polyethylene terephthalate fibers and polyacrylonitrile fibers in a mixing ratio of 50:50 was padded on the fouldard with a squeezing effect of 50% by weight, with a bath having a temperature of 30° C. and containing, per liter of water, 24 g. of a mixture of about equal parts of disperse dyestuffs (U.S. Pat. No. 3,195,973) of the formulae



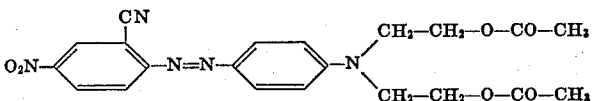
and



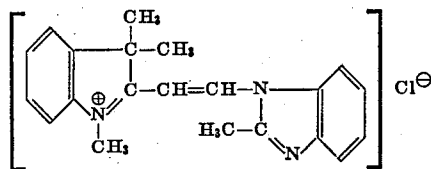
11 g. of the disperse dyestuff (Color Index No. 26080) of the formula



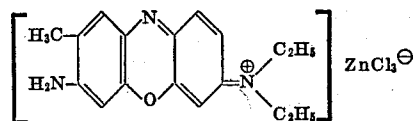
3 g. of the disperse dyestuff (C.I. 26080) (U.S. Pat. No. 3,125,402) of the formula



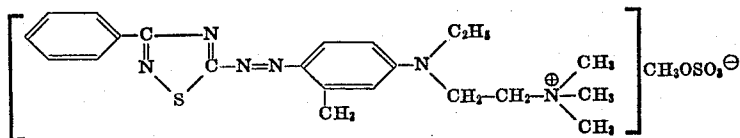
8 g. of the cationic dyestuff (U.S. Pat. No. 2,906,588) of the formula



16 g. of the cationic dyestuff (French Pat. No. 1,597,864) of the formula



and 12 g. of the cationic dyestuff (German Pat. No. 1,011,396) of the formula



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(British Pat. 855,153) in commercial form and composition, and

24 g. of the reaction product of 1 mol of stearyl alcohol and 25 mols of ethylene oxide,

6 g. of a polyethylene glycol having a molecular weight of about 6000,

5 g. of the reaction product of 1 mol of 2-heptadecyl-4-ethyl-4-hydroxymethyl-oxazoline and 70 mols of ethylene oxide, and

20 cc. of acetic acid (60% strength).

The padded fabric was then dried for 40 seconds at 100° C. and subjected to a heat treatment with heated air for 60 seconds at 200° C.

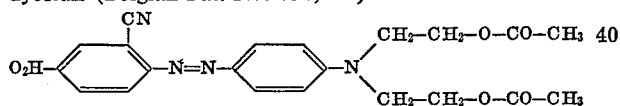
The dyeing was then rinsed hot and cold in the usual

manner, soaped with a solution containing, per liter of water, 2 g. of a non-ionic surface-active agent, rinsed again and worked up.

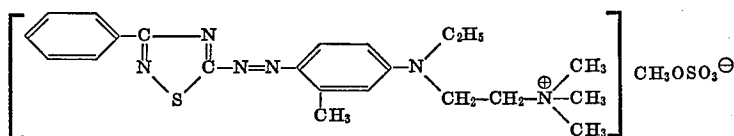
A fabric was obtained in which the polyester and polyacrylonitrile portions were dyed black tone-in-tone. If the dyeing is carried out according to the above-described method, but without the non-ionic dispersing agents of the invention, a dyeing is obtained which is uneven and in which the colour yield is markedly lower.

## EXAMPLE 2

A mixed fabric consisting of polyethylene terephthalate fibers and polyacrylonitrile fibers in a ratio of 50:50 was padded on the foulard with a squeezing effect of 50% by weight, with a bath having a temperature of 20° C. and containing, per liter of water, 30 g. of the disperse dyestuff (Belgian Pat. No. 636,010) of the formula



and 20 g. of the cationic dyestuff (German Pat. No. 1,011,396) of the formula



in commercial form and composition, and

16 g. of the reaction product of 1 mol of stearyl alcohol and 25 mols of ethylene oxide,

4 g. of a polyethylene glycol having a molecular weight of about 6000,

5 g. of the reaction product of 1 mol of 2-heptadecyl-4-ethyl-4-hydroxymethyl-oxazoline and 70 mols of ethylene oxide, and

20 cc. of acetic acid (60% strength).

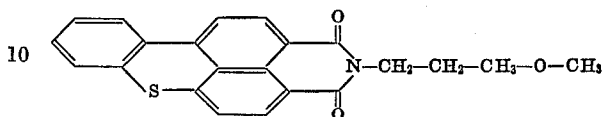
The padded fabric was then subjected, without intermediate drying, to a treatment for 2 minutes with saturated steam at 125° C. The dyeing was then completed in the usual manner.

A dyeing was obtained in which the portions of polyester and polyacrylonitrile fibers were dyed red tone-in-tone.

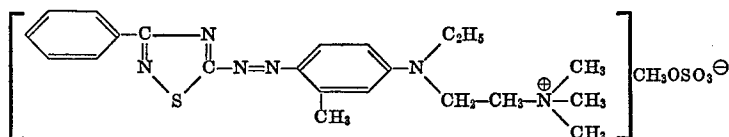
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## EXAMPLE 3

A mixed fabric of polyethylene terephthalate fibers and polyacrylonitrile fibers in a mixing ratio of 50:50 was padded on the foulard with a squeezing effect of 50% weight increase, with a bath having a temperature of 20° C. and containing, per liter of water, 60 g. of the disperse dyestuff (U.S. Pat. No. 3,367,937) of the formula



and 20 g. of the cationic dyestuff (German Pat. No. 1,011,396) of the formula



in commercial form and composition, and

24 g. of the reaction product of 1 mol of stearyl alcohol and 25 mols of ethylene oxide,

6 g. of a polyethylene glycol having a molecular weight of about 6000,

5 g. of the reaction product of 1 mol of 2-heptadecyl-4-ethyl-4-hydroxymethyl-oxazoline and 70 mols of ethylene oxide, and

20 cc. of acetic acid (60% strength).

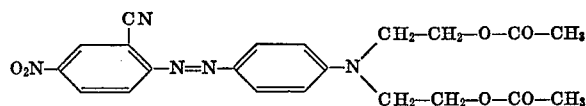
The padded fabric was dried for 40 seconds at 100° C. and then subjected for 60 seconds to a treatment with hot air at 200° C. The dyeing was then completed in the usual manner.

A fabric was obtained in which the polyester fiber portion was dyed yellow and the polyacrylonitrile fiber portion was dyed red.

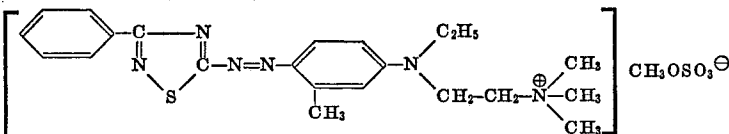
## EXAMPLE 4

A mixed fabric of polyethylene terephthalate fibers, polyacrylonitrile fibers and fibers of regenerated cellulose in a mixing ratio of 33:33:33 was padded on the foulard with a squeezing effect of 65% weight increase, with a bath having a temperature of 30° C. and containing, per

liter of water, 30 g. of the disperse dyestuff (Belgian Pat. No. 636,010) of the formula



and 20 g. of the cationic dyestuff (German Pat. No. 1,011,396) of the formula



in commercial form and composition, and

24 g. of the reaction product of 1 mol of stearyl alcohol and 25 mols of ethylene oxide,

6 g. of a polyethylene glycol having a molecular weight of about 6000,

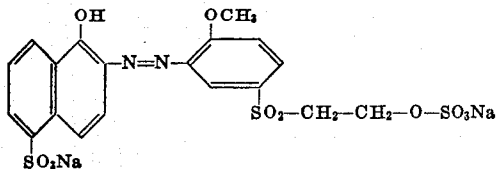
5 g. of the reaction product of 1 mol of 2-heptadecyl-4-ethyl-4-hydroxymethyl-oxazoline and 70 mols of ethylene oxide, and

75 20 cc. of acetic acid (60% strength).

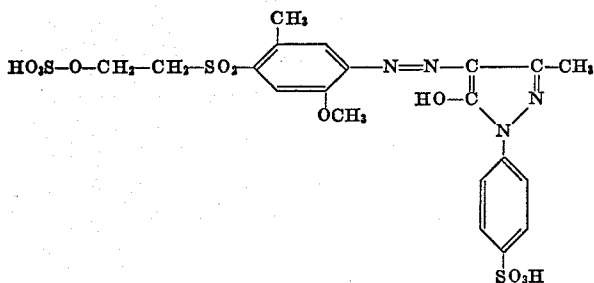
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The padded fabric was then dried for 40 seconds at 100° C. and subjected for 60 seconds to a heat treatment with hot air at 200° C.

Subsequently, the fabric was padded on the foulard, without intermediate cleaning, with a squeezing effect of 65% by weight, with a bath having a temperature of 20° C. and containing, per liter of water, 20 g. of the reactive dyestuff (U.S. Pat. No. 2,670,265) of the formula



and 2 g. of the reactive dyestuff (German Pat. No. 1,150,163) of the formula



in commercial form and composition, and

12 cc. of sodium hydroxide solution (32.5% strength),  
and  
30 g. of calcinated sodium sulfate.

The padded material in rolled up state was left to dwell for 6 to 8 hours at room temperature. The fabric was then rinsed in the usual manner, with a solution containing, per liter of water, 2 ml. of a 60% acetic acid, acidified, rinsed again, soaped with a bath containing, per liter of water, 2 g. of a non-ionic surface-active agent and completed.

A fabric was obtained in which the portions of polyester, polyacrylonitrile and regenerated cellulose fibers were dyed red.

We claim:

1. A process for the dyeing of a textile material made of a mixture of polyester fibers and polyacrylonitrile fibers simultaneously with a disperse dyestuff and a cationic dye-

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stuff according to the Thermosol method which comprises padding said textile material with a padding bath consisting essentially of said cationic dyestuff in dissolved form, said disperse dyestuff, a low molecular weight alkanolic acid and a dispersing agent that is a mixture of polyalkylene glycol, a long-chain alkyloxazoline reacted with alkylene oxide and a fatty amine, fatty acid amide or fatty alkanol reacted with alkylene oxide, and thermosoling the padded material to fix said cationic dyestuff on said polyacrylonitrile fibers and said disperse dyestuff on said polyester fibers.

2. A process according to claim 1 wherein said polyalkylene glycol is a polyethylene glycol having an average molecular weight in the range of 1500 to 8000.

3. A process according to claim 2 wherein said polyethylene glycol has an average molecular weight of about 6000.

4. A process according to claim 1 wherein said dispersing agent is a mixture consisting of the reaction product of 1 mol of stearyl alcohol and 25 mols of ethylene oxide, a polyethylene glycol having a molecular weight of about 6000 and the reaction product of 1 mol of 2-heptadecyl-4-ethyl-4-hydroxymethyl-oxazoline and 70 mols of ethylene oxide in a mixing ratio range of 1:1:1 to 8:1:2.

5. A process according to claim 4 wherein said mixing ratio is about 4:1:1.

6. A process according to claim 1 wherein said dispersing agent is added in an amount of about 20 to about 40 grams per liter of said padding bath.

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DONALD LEVY, Primary Examiner

U.S. Cl. X.R.

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