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RESERVED POLYAMIDE FIBERS AND A PROCESS FOR DYEING THE SAME

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The present invention concerns a dyeing process for textiles made up from synthetic polyamide fibres and other textile fibres and also the dyed material obtained according to the new process. In particular it is concerned with the reservation of the synthetic undyed or pre-dyed part of the fibres when dyeing mixed textiles made up of synthetic polyamide fibres and natural protein fibres with acid wool and chrome dyestuffs.

Mixed spun yarns and mixed weaves made up from natural textile fibres and synthetic polyamide fibres and the textiles made up therefrom enjoy an ever increasing popularity because they combine the proved properties of the natural fibre, e. g. the heat insulating properties of the wool which the artificial product has not yet attained, with the improved physical properties of the synthetic polyamide fibres, e. g. the improved tensile strength. Also, processes gain in importance which are concerned with the dyeing of such mixed textile fibres.

By the expression "synthetic polyamide fibres" are meant those high molecular artificial products which arise from organic bifunctional amino-, hydroxy-, carboxyl-, amino-hydroxy-, and carbonyl compounds by amide-like linkage, which have also been called synthetic protein fibres, linear-polymeric amides, superpolyamides, superpolyurethanes or synthetic polyamides and which today are known in the textile industry under partly registered names such as "Nylon" or "Perlon." Because of the similar chemical construction, these artificial fibres behave in a similar manner to wool on dyeing, and can be dyed with typical wool and chrome dyestuffs from an acid aqueous dye liquor. However, according to their chemical composition, physical condition and type of technical production, they show decided differences to a greater or lesser degree. Generally, with good affinity, the saturation point for wool dyestuffs is different from that for natural fibres so that components of synthetic fibres are dyed to varying depths. For this reason, the problem of the level dyeing of mixed textiles made up from wool and synthetic polyamide fibres is very difficult to solve. Also according to constitution and number of sulphonic acid groups, the wool dyestuffs show considerable differences in affinity. A process is now known in which organic sulphonic and carboxylic acids having affinity for the artificial fibre and therefore partly reserving them, are made to act on the synthetic fibre component before or during dyeing with the wool dyestuff, whereby a more level dyeing of mixed fabrics is attained. As trials have shown, however, a true white reservation of the undyed artificial fibres has not been attained by the above agents in the usual concentrations.

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In contrast to this, it has now been found that according to the usual dyeing methods, the synthetic fibre component can be largely, if not completely, reserved when dyeing mixed material made up from natural and synthetic protein fibres with wool dyestuffs, in which process also an after-treatment with suitable chrome dyestuffs is understood. This can be done by subjecting the synthetic fibre component, either before or during dyeing, alone or with the natural fibre component, in a weakly acid, preferably organic acid, medium to the action of synthetic tanning agents of the naphthalene monosulphonic acid, dihydroxydiphenyl sulphone and formaldehyde condensation product classes. According to the new process it is possible, for example, to obtain wool dyeings with pure white or coloured effect threads of synthetic polyamide fibres.

By the expression "natural protein fibre" silk, preferably wool, and by "synthetic protein fibres" the artificial fibres described above are meant. The condensation products used according to the above invention are already known as synthetic tanning agents. They are obtained by condensation of naphthalene monosulphonic acids (preferably 2-naphthalene sulphonic acid or its admixture with 1-naphthalene sulphonic acid), and 4.4' - dihydroxydiphenyl sulphones (which can also be substituted in the phenyl radicals if required, but if so preferably methyl substituted), with formaldehyde in an aqueous acid medium by application of a molecular ratio of 1:0.7–1.5:0.7–1. Surprisingly, it has been shown that, from among the synthetic tanning agents which are mostly sulphonic acids of formaldehyde condensation products of aromatic hydroxyl compounds, just those condensation products applied according to the invention are excellent because of a particularly marked reservation action on synthetic polyamide fibres. Even in the usual amounts of a few per cent, calculated on the weight of fibres to be treated, a very good if not complete white reservation of the undyed synthetic polyamide fibres, and a very pure shot effect on dyeing pre-dyed synthetic polyamide fibres mixed with wool with wool dyestuffs is obtained. The reserving agents according to this invention are best used for reserving synthetic polyamide fibres alone in a weakly acid, e. g. acetic or formic acid, dyebath after which the artificial fibres are spun or woven with the natural fibres. It is also possible to subject finished mixed spun or woven fabrics to a pretreatment with the reserving agents according to this invention in a weakly acid medium, rinse well and then dye with acid wool dyestuffs. Finally, the reserving agents according to this invention can also be added direct to the dyebath with the acid wool dyestuff and the goods dyed

in the usual manner. If possible, the first method is to be preferred to the others to attain the best possible reservation because it can be easily controlled.

The choice of suitable dyestuffs also plays a part in the dyeing process according to this invention, because as already mentioned above, the chemical constitution and number of sulphonic acid groups of the wool dyestuff influences the affinity for synthetic polyamide fibres. As a rule it can be said that in the process according to this invention simply constructed dyestuffs are generally more suitable than complicated ones, i. e. monoazo dyestuffs are better than polyazo dyestuffs and the dyestuff with more sulphonic acid groups generally gives better effects than monosulphonic acids. However, there are very suitable dyestuffs available in all the most known classes of wool dyestuffs, for instance, among the acid anthraquinone, acid triphenylmethane, azo and azochrome wool dyestuffs. According to the present invention mixed textile fabrics made up of synthetic and natural protein fibres are dyed with wool dyestuffs according to the usual methods by heating in an acid, preferably an organic acid, dyebath containing Glaubers salt. Chrome dyestuffs can be converted into the metal complex in the usual way by treatment with chrome salts. On the other hand those prepared chrome complexes of azochrome dyestuffs which need a strong mineral acid dyeing process are less suitable for the process according to this invention. On dyeing mixed fabrics made up of synthetic polyamide fibres and cellulose fibres with direct dyestuffs, a certain reservation is attained by the synthetic tanning agents used according to this invention, however not nearly so good effects are attained as by the process claimed according to this invention.

The following examples illustrate the dyeing process according to this invention without limiting it in any way. Parts are given as parts by weight and temperatures in degrees centigrade.

A. RESERVATION OF THE FIBRES

Example 1

(*a*) Nylon fibres in the skein are kept moving for half an hour at boiling temperature in an aqueous treatment bath (liquor ratio 1:30) which contains 3% of a synthetic tanning agent calculated on the weight of the fibres, consisting of acid condensed resin from 1 mol of a technical mixture of about 85% naphthalene-2- and about 15% naphthalene-1-sulphonic acid, 1 mol 4.4'-dihydroxy-diphenyl sulphone and 1 mol formaldehyde, and 3% formic acid. The fibres are then well rinsed and dried. The fibres so prepared are incorporated as effect threads in undyed woollen fabric and then dyed as described in the following examples.

(*b*) The same procedure as under (*a*) is followed, but a synthetic tanning agent consisting of acid condensed resin from 1 mol of the technical mixture of about 85% naphthalene-2- and about 15% naphthalene-1-sulphonic acid, 1.5 mol 4.4'-dihydroxy-diphenyl sulphone and 1 mol formaldehyde is used.

(*c*) The same procedure as under (*a*) is followed, but a synthetic tanning agent consisting of acid condensed resin from 1 mol of the technical mixture of about 85% naphthalene-2- and ca. 15% naphthalene-1-sulphonic acid, 0.7 mol 4.4'-dihydroxy-diphenyl sulphone and 0.75 mol of formaldehyde is used.

(*d*) The same procedure as under (*a*) is followed but a synthetic tanning agent prepared from 1 mol naphthalene-2-sulphonic acid, 1 mol 4.4'-dihydroxydiphenyl sulphone and 1 mol formaldehyde is used.

Example 2

Perlon L, a polyamide fibre produced from the polymerisation product of ε-aminocaprolactam is reserved with a synthetic tanning agent according to the process described in Examples 1*a–d*.

Example 3

Perlon U, a synthetic fibre produced from polyurethane is reserved with a synthetic tanning agent according to the process described in Examples 1*a–d*.

Example 4.—Reservation of mixed fabrics

A union consisting of 50% wool and 50% nylon is boiled for half an hour in an aqueous treatment bath which contains 2% of a synthetic tanning agent as described in Examples 1*a–d* calculated on the total fibre mixture, and 3% formic acid in a liquor ratio of 1:30. It is then well rinsed and finally dyed as described in Example 13.

B. DYEING WITH ACID AZO DYESTUFFS

Example 5

A piece of wool flannel which contains a nylon effect thread reserved according to Example 1*a* is dyed for an hour at boiling temperature in a dyebath (liquor ratio 1:50), which contains 10% of the weight of the fibres of Glaubers salt, 2% of the dyestuff from diazotised 1-aminonaphthalene coupled with 2-hydroxynaphthalene-6,8-disulphonic acid=Krystallponceau 6B (Schultz, Dyestuff Tables, VII, Edition, No. 126) and 5% formic acid. It is then well rinsed and dried. A red wool dyeing is obtained with a pure white nylon effect.

Very similar dyeings of wool flannel with nylon effect threads are obtained, the effect threads having been reserved with similar synthetic tanning agents according to Examples 1*b–d* or with Perlon U effect threads which have been reserved with various synthetic tanning agents according to Example 3.

If, in the above example, a dyestuff from diazotised 4-acetamino-1-amino benzene coupled with 1-amino - 8 - hydroxynaphthalene - 3.6 - disulphonic acid=Amidonaphthol red 6B (Schultz, VII, No. 110) is used, bluish-red wool dyeings with white nylon or Perlon effects are obtained.

Example 6

A piece of wool flannel with Perlon L effect threads reserved according to Example 2 is dyed at the boil for three quarters of an hour in a dyebath (liquor ratio 1:30) which contains 10% Glauber's salt calculated on the weight of the fibers, 4% formic acid and 2% of the monazo dyestuff from diazotised 1-amino-8-hydroxynaphthalene-3.6-disulphonic acid coupled with 1-phenylamino-naphthalene - 8 - sulphonic acid= Sulphone Acid Blue R (Igfa). A reddish-blue wool dyeing with white Perlon L effects is obtained.

Similar good white effects are obtained with nylon or Perlon U fibres reserved according to Examples 1*a–d* or Example 3.

If, in the above example, a dyestuff from diazotised 1-aminonaphthalene-4-sulphonic acid coupled with 2-hydroxynaphthalene-3.6-disulphonic acid=Azorubin S (Schultz, VII, No. 212)

is used, bluish-red wool dyeings with white polyamide thread effects are obtained.

Example 7

White wool flannel with nylon effect threads reserved according to Example 1 is dyed at the boil for an hour in a dyebath (liquor ratio 1:30) which contains 10% Glauber's salt calculated on the weight of the fibres, 3% formic acid and 2% of the diazo dyestuff from diazotised amino-azo benzene monosulphonic acid coupled with 2-hydroxynaphthalene - 6 - sulphonic acid=Wool Fast Scarlet R (Schultz VII, No. 565). A red dyeing is obtained with good white effect threads. If, in the above example, a dyestuff from diazotised aniline coupled with 1-aminonaphthalene-6-sulphonic acid diazotised and coupled with 1-phenylamino-naphthalene-8-sulphonic acid=Sulphone Cyanine 5R (Schultz VII, No. 552) is used, a deep blue wool dyeing with white nylon effect threads is obtained.

C. DYEING WITH CHROME AZO DYESTUFFS

Example 8

Undyed wool flannel with Perlon L effect threads reserved according to Example 2 is dyed for 45 minutes at the boil in a dyebath (liquor ratio 1:30) containing 10% Glauber's salt, 3% formic acid and 2% of the chrome azo dyestuff from diazotised 2-amino-4-sulpho-3'-carboxy-4'-hydroxydiphenyl sulphone coupled with 2-amino-8-hydroxynaphthalene - 6 - sulphonic acid=Diamond Red 3B (Igfa). It is then rinsed and chromed at the boil for half an hour in a fresh bath containing 3% formic acid, 10% Glauber's salt and 1.5% bichromate. A bluish-red wool dyeing is obtained with only faintly yellowish-white effect threads.

A similar result is obtained with Perlon U effect threads.

A yellow dyeing with white effect threads can be obtained if, in the above example, a dyestuff from diazotised 2-aminobenzene - 1 - sulphonic acid coupled with 1 - [2' - (3'' - carboxy - 4'' - hydroxyphenyl sulphonyl) -5'-sulphonic acid]-3-methyl-5-pyrazolone=Acid Chrome Yellow 3GL (Säurechromgelb 3GL) is used.

Example 9

Wool flannel with nylon effect threads reserved according to Example 1 is dyed for 45 minutes at the boil in a dyebath (liquor ratio 1:30) containing 2% of a chrome dyestuff from diazotised 4-chloro-2-aminophenol coupled with 1.8-dihydroxynaphthalene - 3.6 - disulphonic acid=Fast Mordant Blue B (Igfa), 10% Glauber's salt and 3% formic acid, and then chromed in a fresh bath containing 3% formic acid, 10% Glauber's salt and 1.5% bichromate for half an hour at the boil. A blue dyeing with pure white nylon effects is obtained. White effects will also be obtained with Perlon U fibres mordanted according to Example 3.

A violet dyeing with white Perlon U or nylon effects can be obtained if, in the above example 2% of a dyestuff from diazotised 4-chloro-2-aminophenol-6-sulphonic acid coupled with 1-hydroxynaphthalene - 5 - sulphonic acid = Acid Chrome Blue 2R (Säurechromblau 2R) is used.

Example 10

Wool flannel with nylon effect threads reserved according to Example 1 is dyed for half an hour at the boil in a dyebath (liquor ratio 1:30) containing 10% Glaubers salt calculated on the weight of the fibres, 3% formic acid and 2% of the chrome azo dyestuff from diazotised 4-chloro-2-aminophenyl-6-sulphonic acid coupled with 1-hydroxynaphthalene-4-sulphonic acid=Acid Chrome Blue 5R (Igfa) (Säurechromblau 5R). The dyeing so obtained is then chromed for half an hour at the boil in a fresh bath containing 3% formic acid and 1.5% bichromate. A violet dyeing with white effects is obtained.

A green dyeing with white effects is obtained according to the above process when a dyestuff from diazotised 5-nitro-2-aminophenol coupled with 1-amino-8-hydroxynaphthalene-3.6-disulphonic acid=Eriochrome Green H (Schultz VII, No. 135) is used.

D. DYEINGS WITH ACID WOOL DYESTUFFS OF OTHER CLASSES

Example 11

Wool flannel with white nylon effect threads reserved according to Example 1, is dyed at the boil for an hour in a dyebath (liquor ratio 1:30) containing 10% Glauber's salt calculated on the weight of the fibre, 4–5% formic acid and 2% 1.5-dihydroxy - 4.8 - diamino-anthraquinone-2.6-disulphonic acid = Alizarine Saphirol B (Schultz VII, No. 1187). A blue dyeing with white effects is obtained. Similar effects are obtained with Perlon U fibre mordanted according to Example 3.

Example 12

Wool flannel with Perlon L effect threads reserved according to Example 2 is dyed for half an hour at the boil in a dyebath (liquor ratio 1:30) containing 10% Glauber's salt calculated on the weight of the fibre, 3% formic acid and 2% triphenylmethane dyestuff from 4-chloro-2-sulphobenzaldehyde and ethylbenzyl aniline sulphonic acid=Erioglaucin A (Schultz VII, No. 770). A luminous greenish-blue wool dyeing with white effects is obtained.

Similar white effects are obtained with nylon fibres treated according to Example 1 and Perlon U fibres treated according to Example 3.

E. DYEING OF RESERVED MIXED FABRICS

Example 13

A union fabric of 50% nylon and 50% wool pretreated according to Example 4 is dyed in a dyebath (liquor ratio 1:30) containing 10% Glauber's salt calculated on the weight of the fibres, 3% formic acid and 2% dyestuff. White nylon effects are obtained.

Dystuff	Wool dyeing	Effects
Azo rubine S (Schultz VII, No. 212)	red	white.
Amidonaphthol red 6B (Schultz VII, No. 110).	blue-red	Do.

Example 14.—Reservation and dyeing in the same bath

A dyebath is prepared containing 10% Glauber's salt calculated on the weight of the fibres, 1.5% of a synthetic tanning agent from 1 mol naphthalene-2-sulphonic acid, 1 mol 4.4'-dihydroxydiphenyl sulphone and 1 mol formaldehyde and 2% of the azo dyestuff Azorubin S (Schultz VII, No. 212), liquor ratio 1:50. Wool flannel which contains about 20% nylon effect threads is entered into the bath at 75°. The bath is brought to the boil within about 10 minutes and dyeing takes place for an hour at the boil. A red

wool dyeing is obtained with pure white effects.

A blue-red dyeing with pure white effects is obtained in the same way with Amidonaphthol Red 6B dyestuff (Schultz VII, No. 110) on wool flannel which contains 20% Perlon U effect threads.

Example 15.—Reserved polyamide thread effects in silk

Bleached material from unweighted silk which contains Perlon L effect threads reserved according to Example 2 is dyed for an hour at 80–100° in a bath containing 2% Erioglaucine A (Schultz, VII, No. 770), 4% acetic acid and 10% Glauber's salt, liquor ratio 1:30. A pure blue dyeing with white effect threads is obtained.

A red dyeing with white effects is obtained in the same manner on silk with nylon effect threads reserved according to Example 1 with 2% Azorubin S (Schultz VII, No. 212).

Example 16.—Cross dyeing of dyed and reserved polyamide fibres to attain shot effects

Nylon is dyed at the boil for an hour with 10% Glauber's salt calculated on the weight of the fibre, 3% formic acid and 2% of the chrome dyestuff from diazotised 6-nitro-4-methyl-2-aminophenol coupled with 1-(4'-sulphophenyl)-3-methyl-5-pyrazolone. It is then cooled somewhat, and chromed for an hour at the boil with 2% sodium bichromate and 3% sulphuric acid. The nylon fibres which have been dyed a yellowish-red colour are then mordanted according to Example 1, and then woven into wool flannel as effect threads. The wool flannel so prepared is then dyed according to Example 9 with 3% of the dyestuff from diazotised 6-nitro-4-methyl-2-aminophenol coupled with 1.8-dihydroxy-naphthalene-3.6-disulphonic acid and chromed with 1.5% sodium bichromate for an hour at the boil. Pure yellow-red effects are obtained on a deep blue background. Yellow-red effects on a blue-red background are obtained when dyeing is performed according to Example 5 with 3% Amidonaphthol Red 6B (Schultz VII, No. 110).

What I claim is:

1. In a process for the dyeing, with a member selected from the class consisting of acid and chrome dyestuffs, of mixed fabric made up of natural protein fibres and fibres prepared from synthetic polyamides of the linear type, the step of applying to the mixed fabric in a dilute aqueous acid medium about 3% by weight of the fibres of an acid condensed resin from 1 mol of naphthalene monosulphonic acid, 0.7 to 1.5 mols of a dihydroxydiphenyl sulphone and 0.7 to 1 mol of formaldehyde, said dilute aqueous acid medium having a concentration of up to about 5% by weight of the aqueous medium and being maintained at an elevated dyeing temperature, the acid in said aqueous acid medium selected from the group consisting of formic acid and acetic acid, in order to reserve said synthetic fibres.

2. In a process for the dyeing, with a member selected from the class consisting of acid and chrome dyestuffs, of mixed fabric made up of natural protein fibres and fibres prepared from synthetic polyamides of the linear type, the step of treating the synthetic fibre component, before dyeing, in a dilute aqueous acid medium with about 3% by weight of the fibres of an acid condensed resin from 1 mol of naphthalene monosulphonic acid, 0.7 to 1.5 mols of a dihydroxydiphenyl sulphone and 0.7 to 1 mol of formaldehyde, said dilute aqueous acid medium having a concentration of up to about 5% by weight of the aqueous medium and being maintained at an elevated dyeing temperature, the acid in said aqueous acid medium selected from the group consisting of formic acid and acetic acid, in order to reserve said synthetic fibres.

3. In a process for the dyeing, with a member selected from the class consisting of acid and chrome dyestuffs, of mixed fabric made up of natural protein fibres and fibres prepared from synthetic polyamides of the linear type, the step of treating the said fabric, when dyeing, in a dilute aqueous acid medium with about 3% by weight of the fibres of an acid condensed resin from 1 mol of naphthalene monosulphonic acid, 0.7 to 1.5 mols of a dihydroxydiphenyl sulphone and 0.7 to 1 mol of formaldehyde, said dilute aqueous acid medium having a concentration of up to about 5% by weight of the aqueous medium and being maintained at an elevated dyeing temperature, the acid in said aqueous acid medium selected from the group consisting of formic acid and acetic acid, in order to reserve said synthetic fibres.

4. In a process for the dyeing, with a member selected from the class consisting of acid and chrome dyestuffs, of mixed fabric made up of wool and fibres prepared from synthetic polyamides of the linear type, the step of applying to the said fabric in a dilute aqueous acid medium about 3% by weight of the fibres of the acid condensed resin from 1 mol of naphthalene monosulphonic acid, 1 mol of 4,4'-dihydroxydiphenyl sulphone and 1 mol of formaldehyde, said dilute aqueous acid medium having a concentration of up to about 5% by weight of the aqueous medium and being maintained at an elevated dyeing temperature, the acid in said aqueous acid medium selected from the group consisting of formic acid and acetic acid, in order to reserve said synthetic fibres.

OTTO FUCHS.

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