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3,079,210

PROCESS FOR THE DYEING OF COPOLYMERS OF ACRYLONITRILE AND VINYL-ACETATE OR VINYL-PYRIDINE

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The dyeing of the copolymer fibers which are produced by copolymerization of 80-90% acrylonitrile and 20-10% vinyl acetate or vinyl-pyridine (e.g. the copolymer of 85% acrylonitrile and 15% vinyl acetate or vinylpyridine manufactured by the Chemstrand Corporation, Decatur, Alabama, U.S.A., under the registered trade mark "Acrilan") has presented a difficult technical problem which still awaits a satisfactory solution. The problem is the same in all the forms in which the fibers are dyed, whether as woven fabric, knitwear, yarn, hank or package, or in blends with other fibers, for example wool.

This invention relates to a process for the dyeing of copolymer fibers which are produced by copolymerization of 80-90% acrylonitrile and 20-10% vinyl acetate or vinylpyridine, more particularly of 85% acrylonitrile and 15% vinyl acetate or vinylpyridine, and for the dyeing of blends of these and other fibers, e.g. wool, using acid wool, chrome or 1:2 metal complex dyestuffs, and particularly 1:2 cobalt and 1:2 chromium dyestuffs. The process consists in treating the material either before, during or after dyeing with a highly sulfonated unsaturated fatty acid of higher molecular weight or with an ester of such an acid, e.g. highly sulfonated oleic acid with a degree of sulfonation of 99% or a highly sulfonated castor oil such as sulforicinate with a degree of sulfonation of 80%, and carrying out the actual dyeing process in a medium acidified with formic, acetic or sulfuric acid.

When the process is performed simultaneously with dyeing, the dyebath is set with a highly sulfonated unsaturated fatty acid of higher molecular weight or with an ester of such an acid and the amount of acid necessary to give a good degree of bath exhaustion. The goods are entered, the dyebath brought to the boil and dyeing continued at the boil for 1 to 2 hours as required. The dyeings obtained are full, penetrated and of brilliant shade, and show good light fastness and very good wet fastness properties (e.g. washing, water, perspiration, milling, crocking).

Equally good results are obtained when the goods are treated before dyeing with a highly sulfonated unsaturated fatty acid of higher molecular weight or with an ester of such an acid. After treatment of the dyed goods with an acid or ester of the said type substantially improves the wet fastness properties without, of course, reducing the depth of the dyeing.

When Acrilan is dyed without the addition of a highly sulfonated unsaturated fatty acid of higher molecular weight or of an ester of such an acid, only the surface of the fiber is dyed (ring dyeing) and consequently the dyeings are weaker, duller, less fast to light and in some cases less fast to wet agencies than the dyeings obtained according to the present process.

When dyeing is carried out in high temperature dyeing machines under pressure, the dyeing times can be considerably reduced by the addition of a highly sulfonated unsaturated fatty acid of higher molecular weight or of an ester of such an acid.

In the following examples the parts are by weight the percentages are calculated on the weight of the goods

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and the temperatures are in degrees centigrade. The dyestuffs used are listed in the Colour Index, vol. I, 2nd edition, 1956, on the pages given in brackets after the names.

EXAMPLE 1

100 parts of a 100% Acrilan fabric are dyed in 5000 parts of a dyeliquor containing the following ingredients:

- 2 parts of Lanasyn Brilliant Green BL (1324),
- 25 parts of a sulforicinate with a degree of sulfonation of 80% and
- 2 parts of 80% acetic acid.

The fabric is entered in the dyebath at 50° and the temperature increased to 98-100° in 30 minutes. 2 parts of 85% formic acid are added and dyeing continued for 1 to 2 hours at the same temperature. The fabric is dyed to an attractive green shade possessing good light fastness and very good washing fastness.

The 2 parts of 85% formic acid can be replaced by 3 to 4 parts of 80% acetic acid.

A dyeing produced under identical conditions without the addition of sulforicinate shows very poor washing fastness and in addition is dull and weak.

In place of Lanasyn Brilliant Green BL (1324) the following dyestuffs can be used:

Xylene Milling Yellow 3GL (1036), Xylene Acid Milling Orange 2G (1081), Sulfonine Scarlet GWL (1140), Brilliant Alizarine Milling Red FBL (1155), Brilliant Alizarine Milling Violet FBL (1213), Alizarine Milling Blue SL (1295), Brilliant Alizarine Milling Blue BL (1265), G (1286), 2RL (1285), RWL (1288), FGL (1292/3) and the red dyestuff of Example 2 of Swiss Patent 316,753.

EXAMPLE 2

A dyeliquor is prepared with:

- 6000 parts of water,
- 2 parts of Lanasyn Brown RL (1340),
- 25 parts of a sulforicinate with a degree of sulfonation of 80%,
- 2 parts of 80% acetic acid,
- 2 parts of 85% formic acid and
- 2 parts of 66% sulfuric acid.

An Acrilan fabric is entered, the dyeliquor heated to the boil in 30 minutes and maintained at this temperature for 2 hours. The pleasing brown shade obtained possesses very good light and washing fastness, while a comparative dyeing produced in the absence of the sulforicinate is weak, dull and of poor fastness to washing.

The 25 parts of sulforicinate with a degree of sulfonation of 80% can be replaced by an equal amount of a sulfoleate with a degree of sulfonation of 99%.

The dyeing can also be carried out in a dyebath acidified with 2.5 to 3 parts of 66% sulfuric only or with 3 to 4 parts of 85% formic acid only.

In place of Lanasyn Brown RL (1340) the following dyestuffs can be used: Lanasyn Yellow 3GL (1048), Yellow GLN (1049), Yellow 2RL (1086), Orange RLN (1087), Red 2GL (1182), Red BL (1182), Bordeaux BL (1183), Brown 3RL (1341), Dark Violet RL (1221) and Grey BL (1397).

EXAMPLE 3

The dyebath is set with the ingredients given in Example 2, and dyeing is carried out in a high temperature laboratory dyeing machine for 30 minutes at 115°. The brown dyeing is well penetrated and has good fastness to light and washing. The same good results are obtained when the dyeing is carried out at 110° for about 45 minutes or at 120° for about 20-25 minutes.

EXAMPLE 4

100 parts of 100% Acrilan fabric are treated for 30 minutes with a boiling solution of 4 parts of a sulforicinate with a degree of sulfonation of 80% in 6000 parts of water. The well impregnated fabric is then rinsed with water and entered in a dye bath at 50° made up with 6000 parts of water, 2 parts of 80% acetic acid and 2 parts of Lanasyn Grey BL (1397). The bath is brought to 100° in about 30 minutes, 15 parts of 10% formic acid are added and dyeing continued for 1 hour at 100°. The dyed fabric is removed, rinsed with water and dried. A dyeing of full depth is obtained which is notable for the good penetration of dyestuff and its good light fastness and very good fastness to washing, milling and perspiration.

The preliminary treatment can also be carried out at 80°.

The same dyeing procedure with the omission of the preliminary treatment results is a dyeing of light depth which is not penetrated and lacks washing fastness.

With the process described in this example full, penetrated dyeings fast to light and wet treatments can be obtained with the dyestuffs named in Examples 1 and 2.

EXAMPLE 5

An Acrilan fabric is dyed with 2% Lanasyn Brown RL (1340) in an acid dye bath for 1 hour at 100°. The dyeing is thin and dull in shade and has insufficient washing fastness. It is treated for 30 minutes in a bath at 98-99° containing 0.5 part of a highly sulfonated castor oil in 1000 parts of water (goods to liquor ratio 1:60), upon which a more attractive dyeing of the same depth is obtained but with much better wet fastness properties.

In the same way the wet fastness properties of dyeings on Acrilan fabric produced with the dyestuffs named in Examples 1, 2 and 5 without the addition of a highly sulfonated ester of a higher molecular unsaturated fatty acid can be substantially improved by an aftertreatment of the above nature.

EXAMPLE 6

100 parts of an Acrilan-wool fabric, blended in the ratio of 1:1 or 3:2 are entered in a bath of

5000 parts of water,
25 parts of a sulforicinate with a degree of sulfonation of 80% and
2 parts of 80% formic acid.

The bath is brought to the boil and after boiling for 15-20 minutes cold water is run in to cool it to room temperature. The impregnated fabric is removed, rinsed and entered in a dye bath set with

5000 parts of water,
2 parts of Lanasyn Brown RL (1340),
5 parts of a sulforicinate with a degree of sulfonation of 80% and
2 parts of 80% acetic acid.

The dye bath is brought to the boil in 30 minutes and maintained at the boil for 45 minutes. 2 parts of 66% sulfuric acid are added and dyeing continued for 2 hours at the boil. The fabric is then removed, rinsed and dried. The Acrilan and the wool components are dyed to equal depth in the same attractive brown shade (tone-in-tone dyeing). Without preliminary treatment and without the addition of sulforicinate in the dye bath the fabric is not penetrated by the dyestuff and the wool is dyed more heavily than the Acrilan, the dyeing as a whole being dull in shade and without fastness to washing.

In the following table some further dyestuffs are listed which can be applied according to the procedures described in Examples 1 to 6 and give dyeings of particularly good light fastness on Acrilan. Column 1 contains the commercial names of the dyestuffs, column 2 the page in the Colour Index, vol. I, 2nd edition, on which

they are listed and described, and column 3 the shade of the dyeing on Acrilan.

Table

Example	1	2	3
7	Lanasyn Yellow GLN	1049	yellow.
8	Xylene Fast Orange P	1072	orange.
9	Azo Rubinoles 3GS	1108	red.
10	Azo Rubinoles 3GP	1107	red.
11	Xylene Fast Red P	1143	red.
12	Sulfonine Scarlet GWL	1140	scarlet.
13	Lanasyn Red BL	1182	red.
14	The dyestuff of Example 2 of Swiss Patent 316,753.		red.
15	Lanasyn Brilliant Yellow 5GL (Pattern card No. 1279 of Sandoz Ltd.)		yellow.
16	Xylene Fast Bordeaux P (Pattern card No. 1314 of Sandoz Ltd.)		bordeaux

Having thus disclosed the invention what I claim is:

1. Process for dyeing copolymer and a blend containing same, said copolymer being composed of from 80 to 90% acrylonitrile and from 20 to 10% of a polymerizable compound selected from the group consisting of vinyl acetate and vinyl pyridine, with a dyestuff selected from the group consisting of 1:2-cobalt dyestuff, 1:2-chromium dyestuff, and acid dyestuff without metallizable groups, in shades fast to wet treatments, which consists in treating a member selected from the group consisting of the copolymer and the blend with a sulforicinate of 80% sulfonation degree, and carrying out the actual dyeing in an acidified medium.

2. A process according to claim 1, wherein the treatment is carried out before dyeing.

3. A process according to claim 1, wherein the treatment is carried out during dyeing.

4. A process according to claim 1, wherein the treatment is carried out after dyeing.

5. A process according to claim 1, wherein the treatment is carried out at elevated temperatures.

6. A process according to claim 1, wherein the treatment is carried out at temperatures ranging from 80 to 120° C.

7. A process according to claim 1, wherein the treatment is carried out in a medium acidified with formic acid.

8. A process according to claim 1, wherein the treatment is carried out in a medium acidified with acetic acid.

9. A process according to claim 1, wherein the treatment is carried out in a medium acidified with sulfuric acid.

10. A process according to claim 1, wherein the treatment is carried out in a medium acidified with a mixture of acids.

11. A process for dyeing with acid dyestuff from 80/20 to 90/10 copolymer of acrylonitrile with the member selected from the group consisting of vinyl acetate and vinyl pyridine, which process consists essentially of contacting the copolymer with a sulforicinate of 80% sulfonation degree and carrying out the actual dyeing in an acidified medium.

12. A process for dyeing in shades fast to wet treatments with acid dyestuff from 80/20 to 90/10 copolymers of acrylonitrile with a member selected from the group consisting of vinyl acetate and vinyl pyridine, which process consists essentially of contacting the copolymer with a sulforicinate of 80% sulfonation degree and carrying out the actual dyeing in an acidified medium.

13. A process for dyeing in shades fast to wet treatments with 1:2 cobalt complex dyestuff from 80/20 to 90/10 copolymers of acrylonitrile with a member selected from the group consisting of vinyl acetate and vinyl pyridine, which process consists essentially of contacting the copolymer with a sulforicinate of 80% sulfonation degree and carrying out the actual dyeing in an acidified medium.

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14. A process for dyeing in shades fast to wet treatments with 1:2 chromium complex dyestuff from 80/20 to 90/10 copolymers of acrylonitrile with a member selected from the group consisting of vinyl acetate and vinyl pyridine, which process consists essentially of contacting the copolymer with a sulforicinate of 80% sulfonation degree and carrying out the actual dyeing in an acidified medium.

15. 80/20 to 90/10 copolymer of acrylonitrile with a member selected from the group consisting of vinyl acetate and vinyl pyridine dyed in an acidified medium with an acid dyestuff and intimately contacted with a member selected from the group consisting of a sulforicinate of 80% sulfonation degree, the shade of said copolymer being fast to wet treatment.

16. 80/20 to 90/10 copolymer of acrylonitrile with a member selected from the group consisting of vinyl acetate and vinyl pyridine dyed in an acidified medium with a 1:2 metal complex dyestuff said metal being a member selected from the group consisting of cobalt and chromium and intimately contacted with a sulforicinate

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of 80% sulfonation degree, the shade of said copolymer being fast to wet treatment

17. A member selected from the group consisting of copolymer composed of from 80 to 90% acrylonitrile and from 20 to 10% of a polymerizable compound selected from the group consisting of vinyl acetate and vinylpyridine and blends containing such polymers dyed according to the process claimed in claim 1.

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