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PROCESS FOR DYEING ACRYLONITRILE POLYMER FIBERS AND THEIR PRODUCTS

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This invention relates to a method of dyeing shaped articles comprising acrylonitrile polymers.

It is known to dye a shaped article comprising an acrylonitrile polymer by padding the article with a liquor containing a dyestuff and treating the wet article with steam to fix the dyestuff into the acrylonitrile polymer article. It is also known (U.S. Patent No. 2,654,652, patented October 6, 1953) to add a cyclic organic ester such as ethylene carbonate, gamma-butyrolactone, etc. in a padding liquor so as to improve the penetration of the dyestuff into the fiber. It is described in U.S. Patent No. 2,512,969 that meta-cresol is a good dye assistant in dyeing acrylonitrile polymer articles with dispersed or basic dyes in a boiling aqueous bath. However, meta-cresol is not effective when used in a pad-dyeing process as admitted in the above mentioned U.S. Patent No. 2,654,652 (column 2, lines 5–6).

The reasons why meta-cresol is not useful in a padding-steaming process while it is effective in a dip-dyeing process may be explained as follows: As is well known a more concentrated dye liquor is required in the case of padding-steaming method as compared with the case of dip-dyeing method, and consequently the concentration of dye assistant in the dye bath or padding liquor must also be higher. However, meta-cresol is comparatively low in water solubility so that when it is added in a large quantity to a padding liquor it will not disperse uniformly therein. When an acrylonitrile polymer article is immersed into such a padding liquor meta-cresol will deposit on the article unevenly so that the article with unevenly deposited meta-cresol is steam-treated resulting in dyeing defects such as uneven dyeing.

Accordingly, it is an object of this invention to provide a novel method for dyeing shaped articles comprising acrylonitrile polymers.

It is a more particular object of this invention to provide a satisfactory method for dyeing shaped articles of acrylonitrile polymers to uniformly and deeply dye the articles while using a cresol-containing padding liquor.

Other objects of this invention will be apparent from the following description.

Briefly, the objects of this invention are accomplished by padding a shaped article comprising an acrylonitrile polymer with an aqueous padding liquor containing a dyestuff and added with a cresol and an aliphatic polyhydric alcohol, and then treating the wet article with steam.

The present invention is applicable to shaped articles comprising acrylonitrile polymers. The polymers include not only polyacrylonitrile but also copolymers and graft copolymers of acrylonitrile with other monomers copolymerizable with acrylonitrile. The monomers copolymerizable with acrylonitrile are well known in the art and include, among others, vinyl acetate, vinyl chloride, vinyl pyridines such as 2-methyl-5-vinyl pyridine, acrylic acid

or its esters such as methyl acrylate, methacrylic acid or its esters such a methyl methacrylate, methallyl sulfonic acid or its salts, and other similar polymerizable hydrocarbons and their derivatives. In any case, it is preferable that acrylonitrile polymers contain at least 40% by weight of acrylonitrile component.

Any shaped articles may be used. Thus, for example, they may be films, fibers, fiber tow, yarns, woven fabrics, knit fabrics, and made-up articles of clothing.

The dye bath or padding liquor may contain any dyestuff which has conventionally been used in dyeing acrylic fibers. Among dyestuffs useful in this invention are cationic dyestuffs, acidic dyestuffs and metal-containing dyestuffs. If desired a mixture of suitable dyestuffs may also be used.

The concentration of dyestuff in the aqueous padding liquor is not critical, although it is preferable to be higher than in the usual dip-dyeing bath. Generally, a concentartion of from 10 to 50 g. per liter is satisfactory, although any higher concentration may be used where such a higher concentration is required to obtain desired shade.

The important feature of the invention is that the padding liquor also contains a cresol and an aliphatic polyhydric alcohol.

Any of the cresols including o-cresol, m-cresol and p-cresol may be used. If desired a mixture of any two or more of these cresols may also be used.

The aqueous dye bath or padding liquor should contain at least 30 g. of cresol per liter of the liquor. Generally, it is preferable that the cresol concentration is 50–100 g. per liter of the padding liquor.

Aliphatic polyhydric alcohols which are used in this invention contain not more than 6 carbon atoms. Among aliphatic polyhydric alcohols useful in this invention are dihydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, pentamethylene glycol, hexamethylene glycol, etc., trivalent alcohols such as glycerine, butane triol, pentane triol. etc., tetra-valent alcohols such as erythrite, pentaerythrite, etc., among which, however, ethylene glycol, diethylene glycol and propylene glycol are preferable. In order to uniformly disperse cresol in the padding liquor the amount of the polyhydric alcohol should be at least two times (by weight) that of cresol. Generally, the use of a polyhydric alcohol in an amount from 2 to 3 times by weight based on cresol is satisfactory, but no adverse effect is seen when a larger amount is added. Of course, a mixture of any two or more of the above mentioned aliphatic polyhydric alcohols may also be used.

The temperature of the padding liquor is not critical. Thus it may be room or ordinary temperature. However, when the dye concentration is high it is preferable to heat (e.g. 30–40° C. and up to about 60° C.) the padding liquor to prevent precipitation of the dyestuff.

In carrying out the method of this invention, a shaped article comprising an acrylonitrile polymer is padded with the above mentioned padding liquor. This may be conducted in a known manner for example by immersing the article in the padding bath.

The amount of dye or padding liquor to be picked up by the article may vary depending upon the desired depth of shade, concentration of the dye in the liquor and generally the pick-up may be within a range from 70 to 120%, but usually a pick-up of about 100% is satisfactory.

Then the article thus padded with the aqueous dye liquor is subjected to a steam treatment. The wet steam treat-

ment is carried out in steam of a temperature of from 100° C. to 150° C. The time of this steam treatment may vary depending upon the particular steam temperature and should be sufficient to obtain the desired result. Generally the steam treatment of at least 30 seconds is necessary. For example, when the steam treatment is carried out at a temperature of from 100° C. to 105° C. a satisfactory result would be obtained in about 0.5–2 minutes.

After the steam treatment, the dyed article is finished in a usual manner. Thus the dyed article is washed with water to remove any dye, cresol and alcohol which remain on the article surface. In case of deep dyeing, it is preferable to treat the dyed article with an aqueous liquor containing soap or non-ionic surfactant in an amount of 0.5 g./l. at about 60° C. for about 15 minutes and then to wash with water. The washed article is then dried, e.g. at about 80–100° C. for about 5–10 minutes.

According to this invention, shaped articles comprising acrylonitrile polymers can readily be dyed deeply and uniformly without using any special apparatus.

The invention will be better understood when referred to the following examples which are given for illustrative purposes only and are not limitative in any way. In these examples, all parts and percentages are by weight. The colorimetric test was carried out by dissolving 0.02 g. of the dyed sample in 20 g. of gamma-butyrolactone and measuring the light absorbency of the solution with a photoelectric colorimeter (FPW–III type colorimeter of Hitachi Seisakusko) with the filter indicated.

Example 1

In 1000 parts of water was dissolved 25 parts of C. I. Basic Yellow 23 to prepare an aqueous dye solution. Then a mixture of 100 parts of a mixture of o-, m- p-cresols and 300 parts of ethylene glycol was added to the above dye solution.

A tow of fibers prepared from a copolymer of 90% acrylonitrile and 10% methyl acrylate was immersed in the above mentioned padding liquor and squeezed to a pick-up of 100%. The wet padded tow was treated for 30 seconds to 10 minutes with steam of 100° C. and then washed with water and dried.

The same procedure was repeated except that the mixture of cresols and ethylene glycol was not added to the padding liquor.

The dyed fibers thus obtained were subjected to a colorimetric examination and the following results were obtained.

Steaming time (minutes)	Control, no dye assistant added	Cresol and ethylene glycol added
0.5	0.096	0.395
1.0	0.252	0.510
2.5	0.362	0.608
5.0	0.478	0.650
7.5	0.500	0.670
10.0	0.581	0.685

Remarks: A filter of 430 mμ was employed.

It will be apparent from the above table that when cresol and ethylene glycol are added to the padding liquor the dye absorbency of the fiber is remarkably improved and the time required for steaming is substantially reduced as compared with the case where no such cresol and ethylene glycol was added.

When only cresol was added and ethylene glycol was not added in the above example, the fibers were dyed too unevenly to be of commercial value.

Example 2

In 1000 parts of water was dissolved 25 parts of C. I. Basic Red 14 to prepare an aqueous dye solution. Then a mixture of 100 parts of m-cresol and 300 parts of ethylene glycol was added to the above dye solution.

A tow of fibers prepared from a copolymer of 90% acrylonitrile and 10% methyl acrylate was immersed in the above prepared padding liquor and then treated in the same manner as in Example 1.

The same procedure was repeated but without adding the mixture of m-cresol and ethylene glycol to the padding liquor.

The dyed fibers thus obtained were subjected to a colorimetric examination and the following results were obtained.

Steaming time (minutes)	Control, no dye assistant added	Cresol and ethylene glycol added
0.5	0.072	0.407
1.0	0.165	0.480
2.5	0.302	0.688
5.0	0.462	0.780
7.5	0.490	0.790
10.0	0.505	0.800

Remarks: A filter of 500 mμ was employed.

Example 3

In 1000 parts of water was dissolved 25 parts of C. I. Basic Blue 54 and a mixture of cresol (o- p-, m-cresols mixture) 100 parts and diethylene glycol 300 parts was added thereto to prepare a padding liquor.

A tow of fibers prepared from a copolymer of 90% acrylonitrile, 9.5% methyl acrylate and 0.5% sodium methallyl sulfonate was immersed in the above padding liquor and squeezed to a pick-up of 100%. The wet padded fiber tow was treated for 2 minutes with steam at 105° C., and then washed with water and dried. The fiber was evenly dyed in a deep blue shade.

Example 4

A fabric prepared from yarn of a copolymer of 90% acrylonitrile, 5% vinyl acetate and 5% 2-methyl-5-vinyl pyridine was a padded with an aqeous padding liquor containing 100 g. of C. I. Acid Blue 23 (C. I. No. 61,215), 20 g. of sulfuric acid (98%), 100 g. of cresol (o-, m- and p-cresols mixture) and 300 g. of propylene glycol per liter of the bath. The fabric with a pick-up of 100% was treated for 2 minutes with steam at 105° C., and then washed with water and dried. The fabric was evenly dyed in a deep blue shade.

Example 5

A fabric prepared from yarn of a copolymer of 90% acrylonitrile and 10% methyl methacrylate was padded with an aqueous padding liquor containing 5 g. of C. I. Basic Orange (C. I. No. 48,035), 5 g. of C. I. Basic Blue 45, 10 g. of acetic acid, 50 g. of (o-, m- and p-cresols mixture) cresol and 150 g. of ethylene glycol per liter of the bath. The fabric was squeezed to a pick-up of 100% and treated for 3 minutes with steam at 105° C. Then the steam treated fabric was soaped with nonionic surface active agent, washed with water and dried. The fabric was evenly dyed in an exceptionally vivid khaki shade.

What we claim is:

1. A method for dyeing a shaped article comprising an acrylonitrile polymer which comprises padding the article with a padding liquor containing (1) dyestuff selected from the group consisting of cationic dyestuffs, acidic dyestuffs and metal-containing dyestuffs, (2) cresol selected from the group consisting of m-cresol, o-cresol and p-cresol and (3) at least twice by weight based on the cresol of aliphatic polyhydric alcohol having not more than 6 carbon atoms, and then treating the wet padded article with steam.

2. A method as claimed in claim 1 in which the amount

of the cresol is at least 30 grams, per liter of the padding liquor.

3. A method as claimed in claim 1 in which the amount of the cresol is from 50 to 100 grams per liter of the padding liquor.

4. A method as claimed in claim 1, in which the steaming is carried out at a temperature of from 100° C. to 150° C.

5. A method as claimed in claim 1 in which the aliphatic polyhydric alcohol is selected from the group consisting of ethylene glycol, diethylene glycol and propylene glycol.

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