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# METHOD OF TREATING ACRYLONITRILE SYNTHETIC FIBERS

Yoshimasa Fujita, Saidaiji, and Nobuhiro Tsutsui, Okayama, Japan, assignors to American Cyanamid Company, Stamford, Conn., a corporation of Maine

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The present invention relates to a process for preventing the uneven dyeing and/or improving the whiteness stability of acrylonitrile synthetic fiber containing at least 85% by weight of acrylonitrile by treating the same with an aqueous solution of a multivalent metallic salt so as to restrain the rate of dyeing of same with cationic dyestuffs.

The dyeing of an acrylonitrile synthetic fiber with a cationic dyestuff has a serious disadvantage, for the rate of dyeing is so high that uneven dyeing results when the substrate must be dyed light or medium shades. It is known that uneven dyeing can be prevented by adding a cationic surface active agent to a dye bath as a retarding agent to reduce the dyeing rate. This phenomenon may be explained by the concept of competition between dyestuff and surfactant for active sites on the substrate. According to this theory, the dyeing rate should have to be reduced by the presence of two rivalling factors if a cation other than the dyestuff is present in the fiber. Actually, ordinary cations are relatively slow in penetrating the fibrous structure while the dyestuff may diffuse into the fiber so rapidly that no retarding occurs where such cations are added to the dye bath. Should the aforementioned theory hold true under certain circumstances, however, it is reasonable to expect that dyeing will be retarded when such cations are preliminarily incorporated in the fiber at a stage prior to the dyeing operation.

With the foregoing in mind, we have found that dyeing may be successfully retarded by pre-treating the fiber with an aqueous solution of a polyvalent metallic salt before the dyeing of same. In this connection, it has also been found that the metallic ion so added will not be effective unless it is bivalent or higher instead of univalent. Another discovery is that when the fiber is thus treated with a multivalent metal salt, the stability of whiteness of the fiber is also improved. Heretofore, various processes have been proposed for improving the whiteness of acrylonitrile synthetic fibers, but nost of them are not conducive to the stability of whiteness even if the degree of whiteness is improved. Thus, being heated as in a wet-thermal treatment, the fiber is prone to discoloration. However, the fiber treated with multivalent metallic salt of the mentioned type according to this invention does not discolor even after prolonged exposure under hot wet conditions; therefore said treatment improves the stability of whiteness of the fiber, although the underlying mechanism has not yet been theoretically established. Metallic salts which exhibit strong acidity but no color upon being dissolved in water, e.g., aluminum salts, are particularly suited for the purposes stated.

To describe the invention in further detail, the fiber spun from an acrylonitrile polymer dyeable with cationic dyestuffs and containing at least 85% by weight of acrylonitrile is treated with an aqueous solution of a multivalent metallic salt, preferably an aluminum salt, at any desired stage of processing from after spinning to the final fiber, and preferably during a stage wherein the fiber is still in a wet gelled state. The preferred concentration of such a metallic salt is from 0.0001 mole/liter to 0.1 mole/liter; for if the salt is present in a concentration of more than 0.1 mole/liter, the effect obtainable will not be proportional to the gain in concentration, the net result being



such that not only economy is sacrificed but depending upon the type of metallic salt, unduly high concentrations may impart objectionable color to the treated fiber. The pH of the aqueous solution is preferably from 2 to 4. Those metallic salts which do not exhibit acidity or which are only weakly acidic in water may be adjusted to a suitable pH by adding an acid to the solution. Though the optimum pH range varies according to the type and concentration of salt, pH values over 5 could impair the whiteness of fiber and should, therefore, be avoided. It is preferable that the treatment be effected over a sufficiently long period of time, but it may be shortened, if required, by increasing the salt concentration or the treating temperature, or both. Since the treating solution can penetrate easily into a gelled swollen fiber containing water, such a fiber can be satisfactorily treated at room temperature in a matter of seconds. In contrast, it takes several to scores of minutes at high temperatures in the case of hot stretched fiber which is hard to penetrate. Care must be used, however, for the treatment for a sustained time at high temperature might be detrimental to the whiteness of the fiber.

The polymers to which the present invention is applicable are not limited to polyacrylonitrile (homopolymer) but may be any member of the group consisting of those copolymers, graft polymers, and block polymers composed of acrylonitrile and at least one monoethylene-type monomer copolymerizable therewith and containing more than 85% by weight of acrylonitrile. In addition, it is necessary that these polymers must contain acid groups which can act as dye sites for cationic dyestaffs.

The monoethylene-type monomers copolymerizable with acrylonitrile include, for example, acrylic acid esters, methacrylic acid esters, vinyl acetate, styrene, vinylchloride, methacrylonitrile, etc., acrylic acid, methacrylic acid, allylsulfonic acid, methalylsulfonic acid, styrene-sulfonic acid, etc. and the salts thereof.

The multivalent metallic salts which can be employed in the process of the invention include, for example, inorganic salts such as the nitrates, sulfates, chlorides, etc. of alkaline earth metals such as magnesium, calcium, barium, etc. of transition metals such as chromium, zinc, cobalt, nickel, etc., or of such other metals as aluminum, tin, lead, etc., as well as the salts of said metals and organic acids, it being understood that said salts must be soluble in water.

The invention will be further illustrated by reference to the following examples, wherein all percentages given are by weight and the dyeing tests and the measurements of yellowness were made in the following manner:

## DYEING TEST: DYESTUFF—SEVRON BRILLIANT RED 4G (E. I. DU PONT DE NEMOURS & CO.)

Samples were dyed in a bath composed of a suitable amount of Sevron Brilliant Red 4G (E. I. du Pont de Nemours & Co.), 1% O.W.F. of acetic acid, and 3% O.W.F. of sodium acetate at a bath ratio of 100 to 1 and a bath temperature of 98° C. The exhaustion of dyestuff was colorimetrically determined based on the residual liquor.

## MEASUREMENT OF YELLOWNESS

Percent reflectance of aligned fibers at the wavelengths of 453, 553, and 595 mμ were determined by a spectrophotometer using the magnesium oxide plate as reference, and the yellowness of the fibers were calculated according to the following formula:

$$\text{Yellowness} = \frac{R_{595} - R_{453}}{R_{553}} \times 100$$

wherein $R_{453}$, $R_{553}$, and $R_{595}$ are the percent reflectance

at the wavelengths of 453, 553 and 595 mμ respectively. For determination of the stability of whiteness, samples of organic fiber and samples of fiber bleached with chlorite were boiled in drinking water (tap water) for 30 minutes, and the samples before and after boiling were compared as to yellowness.



solution (pH 3) of nitric acid at room temperature for 15 seconds. The filament was then stretched under heat, heat-treated, and dried as in Example 1. Upon treatment with an aqueous solution of aluminum nitrate, the filament had improved retarding effect and stability of whiteness.

| | Gel treatment | Dye adsorption (percent) | | Yellowness | |
|---|---|---|---|---|---|
| | | 15 min. | 60 min. | Raw filament | Boiling |
| A | Aluminum nitrate 0.0013 mole/l. pH 3 | 42.8 | 85.7 | 2.0 | 4.7 |
| B | Aluminum nitrate 0.013 mole/l. pH 3 | 35.0 | 71.8 | 1.2 | 3.8 |
| C | Nitric acid pH 3 | 93.4 | 99.6 | 7.2 | 10.2 |

(Dyestuff concentration in dye bath: 4% O.W.F.)

*Example 1*

A sodium thiocyanate solution of a copolymer comprised of 90% of acrylonitrile and 10% of methyl acrylate polymerized in the presence of a redox catalyst of sodium chlorate and sodium sulfite was spun in a dilute aqueous solution of sodium thiocyanate. After washing, the filament was extracted with a solvent, and the resultant wet gelled filament was immersed in an aqueous solution of aluminum nitrate [(A) 0.001 mole/liter, pH 2, (B) 0.001 mole/liter, pH 4, (C) 0.01 mole/liter, pH 2, (D) 0.01 mole/liter, pH 4] or (E) an acid aqueous solution (pH 3) of nitric acid, for about 15 seconds at room temperature. Thereafter, the filament was stretched under heat and heat-treated. The filament was finally dried.

*Example 3*

A copolymer composed of 90% of acrylonitrile, 10% of methyl acrylate and less than 1% of methacryl sulfonate was spun in the same manner as in Example 1. The resulting gelled filament was treated with an aqueous solution of aluminum nitrate (Sample A: 0.001 mole/liter, pH 3; Sample B: 0.01 mole/liter, pH 3; Sample C: 0.1 mole/liter, pH 3) or an aqueous solution (pH 3) of nitric acid as in Example 1. The filament was then after-treated.

| | Gel treatment | Dye adsorption (percent) | | | Yellowness | |
|---|---|---|---|---|---|---|
| | | 10 min. | 30 min. | 60 min. | Raw filament | Boiling |
| A | Aluminum nitrate 0.001 mole/l. pH 3 | 63.1 | 98.4 | 99.5 | 3.2 | 7.6 |
| B | Aluminum nitrate 0.01 mole/l. pH 3 | 50.0 | 95.2 | 99.6 | 3.6 | 6.3 |
| C | Aluminum nitrate 0.1 mole/l., pH 3 | 43.7 | 87.6 | 99.0 | 3.3 | 6.2 |
| D | Nitric acid pH 3 | 97.1 | 99.8 | 99.8 | 3.2 | 11.6 |

(Dyestuff concentration in dye bath: 4% O.W.F.)

It was observed that both the retarding effect and the stability of whiteness has been improved.

*Example 4*

Each sample of the gelled filament spun from a copolymer similar to the one employed in Example 1 was treated with an aqueous solution of zinc nitrate (Sample A: 0.01 mole/liter, pH 2; Sample B: 0.01 mole/liter pH 4) or an aqueous solution (pH 3) of nitric acid under the same conditions as in Example 1. The filament is then drawn under heat and after-treated.

| | Gel treatment | Dye adsorption (percent) | | | Yellowness | | | |
|---|---|---|---|---|---|---|---|---|
| | | 10 min. | 30 min. | 60 min. | Raw filament | Boiling | Bleaching | Boiling after bleach. |
| A | 0.001 mole/l. aluminum nitrate pH 2 | 91.3 | 99.3 | 99.5 | 4.0 | 7.9 | 3.2 | 11.9 |
| B | 0.001 mole/l. aluminum nitrate pH 4 | 66.0 | 98.3 | 99.5 | 4.3 | 7.4 | 2.8 | 8.6 |
| C | 0.01 mole/l. aluminum nitrate pH 2 | 66.8 | 98.3 | 99.4 | 4.0 | 6.4 | 2.3 | 9.5 |
| D | 0.01 mole/l. aluminum nitrate pH 4 | 64.1 | 92.4 | 99.3 | 3.2 | 6.2 | 1.6 | 8.8 |
| E | Nitric acid pH 3 | 96.7 | 99.5 | 99.5 | 7.4 | 9.8 | 2.0 | 15.8 |

(Dyestuff concentration in dye bath: 4% O.W.F.)

*Example 2*

A copolymer composed of 90% of acrylonitrile, 10% of methyl acrylate and less than 1% of methacrylic acid was spun in the same manner as in Example 1. The resulting gelled filament was immersed in an aqueous solution of aluminum nitrate (Sample A, 0.0013 mole/liter, pH 3; Sample B, 0.013 mole/liter, pH 3) or an aqueous

| | Gel treatment | Dye adsorption (percent) | | | Yellowness | | | |
|---|---|---|---|---|---|---|---|---|
| | | 10 min. | 30 min. | 60 min. | Raw filament | Boiling | Bleaching | Boiling after bleach |
| A | Zinc nitrate 0.01 mole/l. pH 2 | 65.9 | 95.9 | 98.8 | 5.6 | 8.4 | 1.9 | 11.5 |
| B | Zinc nitrate 0.01 mole/l. pH 4 | 61.0 | 91.1 | 98.8 | 12.3 | 13.0 | 2.0 | 14.4 |
| C | Nitric acid pH 3 | 95.3 | 99.4 | 99.5 | 5.8 | 10.1 | 2.3 | 15.3 |

(Dyestuff: 2% O.W.F.)

The filament treated with an aqueous solution of zinc nitrate suffered a loss in the stability of whiteness at high concentrations. Thus, it is advantageous to select lower pH values. Sample A was better than Sample C in retarding effect and the stability of whiteness.

*Example 5*

Samples of the filament spun from a copolymer similar to the one employed in Example 1, drawn under heat, and then heat-treated were treated with an aqueous solution of (A) aluminum nitrate (0.03 mole/liter, pH 3), (B) zinc nitrate (0.03 mole/liter, pH 3), respectively, at the temperature of 98° C. for 40 minutes. The results of dyeing tests for these samples and a control are summarized below. While a slight fading was observed on Samples A and B, the shade itself was not affected.

| Sample | Treating conditions | Dye adsorption (percent) | | |
|---|---|---|---|---|
| | | 10 min. | 30 min. | 60 min. |
| A | Aluminum nitrate 0.03 mole/l. pH 3 | 59.6 | 98.7 | 99.3 |
| B | Zinc nitrate 0.03 mole/l. pH 3 | 43.4 | 78.6 | 97.4 |
| C | Control | 93.1 | 99.1 | 99.4 |

(Dyestuff: 2% O.W.F.)

*Example 6*

Samples of the filament spun from a copolymer similar to the one employed in Example 1 drawn under heat and then heat-treated were treated with an aqueous solution (0.01 mole/liter) of sodium nitrate, potassium nitrate, calcium nitrate, barium chloride, nickel nitrate, and aluminum sulfate, respectively, at the temperature of 100° C. for 30 minutes. While no retarding effect was observed with the samples treated with sodium nitrate and potassium nitrate respectively, the other multivalent metallic salts showed a conspicuous retarding effect.

We claim:

**1.** A process for retarding the dyeability of an acrylonitrile polymer fiber containing acid groups and which is highly substantive to cationic dyes, said process comprising immersing such fiber in an aqueous solution of a water-soluble salt of a multivalent metallic ion selected from the group consisting of magnesium, calcium, barium, chromium, zinc, cobalt, nickel, aluminum, tin, and lead with an anion selected from the group consisting of nitrates, sulfates, chlorides, and organic acid residues prior to exposure of such fiber to cationic dyes.

**2.** A process as defined in claim **1** wherein said aqueous solution has a salt concentration of between 0.0001 mole/liter and 0.1 mole/liter.

**3.** A process as defined in claim **1** wherein said aqueous solution is maintained at a pH between about 2 and about 4.

**4.** A process as defined in claim **1** wherein said fiber is immersed in said aqueous solution after spinning while still in the wet gel state.

**5.** A process as defined in claim **1** wherein said multivalent metallic salt is aluminum nitrate.

**6.** A process as defined in claim **1** wherein said multivalent metallic salt is zinc nitrate.

**7.** In the process of producing dyed fibers from an acrylonitrile polymer fiber containing acid groups and which is highly substantive to cationic dyes comprising spinning said polymer from a solution thereof into a suitable coagulating medium to form a wet gelled filament, drying said wet gelled filament, and dyeing the filament with a cationic dye; the improvement comprising treating the filament after spinning and prior to dyeing with an aqueous solution of a water-soluble salt of a multivalent metallic ion selected from the group consisting of magnesium, calcium, barium, chromium, zinc, cobalt, nickel, aluminum, tin, and lead with an anion selected from the group consisting of nitrates, sulfates, chlorides, and organic acid residues.

**8.** A process as defined in claim **7** wherein the filament is treated with the aqueous solution of a water-soluble multivalent metallic salt while the filament is in the wet gelled state.

**9.** A process as defined in claim **7** wherein said aqueous solution is maintained at a pH between about 2 and about 4.

**10.** A fiber produced by the process of claim **1**.

**11.** A fiber produced by the process of claim **5**.

**12.** A fiber produced by the process of claim **6**.

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NORMAN G. TORCHIN, *Primary Examiner.*

ABRAHAM H. WINKELSTEIN, *Examiner.*

J. C. CANNON, *Assistant Examiner.*