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DYEING ACRYLIC FIBERS

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This invention relates to the dyeing of acrylic fibrous material, and more particularly to the dyeing of such materials by an improved method with vat dyestuffs and sulfur dyestuffs.

The dyeing of fibrous materials having a basis of polyacrylonitrile has for some time been a problem encountered by workers skilled in the art. Various methods and expedients have been proposed for producing dyeings on such fibrous materials but the results have not been completely satisfactory and/or the methods employed have been objectionable. This has been particularly true with respect to attempts made to dye such fibrous materials with vat and similar dyestuffs. These fibers are well known for their relatively hydrophobic nature whereby an aqueous treatment bath may wet the fiber superficially but has difficulty penetrating the inside of the fiber. The most common expedient employed for dyeing such fibrous materials has involved the use of pressure and temperatures of at least about 250° F. Under such conditions, such fibrous materials become plastic and take up the dye, but tend to pack down under the pressure to such an extent that only by careful operation in special equipment are acceptable level dyeings possible. Even then, the deleterious effects of packing, channeling of dye solution and the like are difficult to eliminate. Further, many vat and sulfur dyestuffs are unstable under such drastic conditions.

It is an object of this invention to provide a method for dyeing polyacrylonitrile fibrous materials with vat or sulfur dyes which can be carried out without the use of special pressure equipment. Another object of this invention is the provision of a method for dyeing polyacrylonitrile fibrous materials with vat or sulfur dyes in a simple manner to produce commercially acceptable dyeings. Still another object of this invention is the provision of a vat or sulfur dye composition which can be employed to dye polyacrylonitrile fibrous materials in a simple manner. Other objects and advantages will appear as the description proceeds.

The above objects are made possible by the instant invention which includes the improvement comprising impregnating fibrous materials, the fiber content of which is composed of at least 75% by weight of polyacrylonitrile, with the reduced form of a dyestuff selected from the group consisting of vat and sulfur dyestuffs stable at temperatures of about 205 to 220° F., from an aqueous alkaline hydrosulfite vat in the presence of about 8 to 25% of sodium tetraborate by weight of the fiber at a temperature of about 205 to 220° F. The instant invention eliminates the necessity for employing high pressure equipment and its attendant disadvantages while enabling

the attainment of commercially acceptable dyeings having good properties with respect to lightfastness, wash fastness, perspiration fastness, and/or fastness to dry cleaning and/or crocking.

The instant invention is applicable to fibrous materials having a basis of polyacrylonitrile in any suitable form as for example in the form of staple or continuous filaments, yarns, slubbings, warps, fibers, and the like. The fiber content may be composed principally of acrylonitrile homopolymer or of heteropolymers of acrylonitrile and up to 25% by weight of other polymeric material such as vinyl chloride or acetate, styrene, methacrylic acid, chloroacrylic acid, and their amides, chlorides, nitriles and the like. Other modifying agents may of course be present in the fiber. Such materials, and their methods of manufacture are disclosed for example in U.S. Patents 2,527,863, 2,548,282, 2,558,735, 2,595,848, etc. As examples of such fibers available on the market, there may be mentioned Acrilan (modified polyacrylonitrile fiber of Chemstrand Corp.), the modified polyacrylonitrile fiber of Dow Chemical Co., and the like.

In carrying out the process of the instant invention, almost any vat dyestuff (e.g. of the quinoid or indigoid series) or sulfur dyestuff may be employed. Such dyestuffs are well known in the art, and the following dyestuffs operative in the instant invention are given only by way of illustration:

Indanthrene Brilliant Green BN pure double paste conc.	C.I. 1101
Indanthrene Orange RRTA paste	C.I. 1098
Indanthrene Navy Blue BRP paste	C.I. 1100
Indanthrene Olive Green BA double paste	Pr. 293
Indanthrene Golden Orange GA double paste	C.I. 1096
Indanthrene Golden Yellow RKA double paste	Pr. 292
Algol Yellow GCA paste	Pr. 9
Brilliant Indigo 4B conc. paste fine	C.I. 1184
Indanthrene Brilliant Pink RAP paste	Pr. 109
Indanthrene Brilliant Pink RN paste CF	Pr. 109
Indo Carbon CLGS paste fine	Pr. 126

The identity of the above-mentioned dyestuffs is given in the 1954 Technical Manual and Year Book of the American Association of Textile Chemists and Colorists (AATCC). The term "C.I." refers to Rowe's Colour Index. The term "Pr." refers to the number of the foreign prototype.

The above dyestuffs are applied to the polyacrylonitrile fibrous material in their reduced solubilized form as obtainable by treatment thereof in an aqueous alkaline vat with an alkali metal hydrosulfite or equivalent reducing agent. The amount of caustic and sodium hydrosulfite required in any particular instance to maintain the dyestuff in the reduced from during the dyeing process will be obvious to the worker skilled in the art and will in general be dependent upon the fiber:liquor ratio, the particular dyestuff employed, and the amount thereof, the particular method of impregnation selected, and the like. For example, at a fiber:liquor ratio of about 1:12, about 5 to 8% of each of caustic soda and sodium hydrosulfite by weight of the fiber is usually sufficient. The dyestuff is employed in amounts dependent upon the depth of shade desired, and the like. In general, about 0.5 to 10% of the dyestuff, with the usual diluents, dispersing agents and the like, prescribes the usual limits.

As stated above, the dyeing of the polyacrylonitrile

fibrous material is carried out in the presence of about 8 to 25 percent of sodium tetraborate by weight of the fiber. Generally, amounts of about 8 to 15% are sufficient in most cases. If desired, potassium tetraborate or ammonium tetraborate may be used in place of sodium tetraborate. The sodium tetraborate should be distributed throughout and/or impregnated in the polyacrylonitrile fibrous material prior to application of the reduced form of vat or sulfur dyestuff. This may be accomplished by pretreatment with an aqueous solution of the sodium tetraborate followed by treatment with an aqueous bath containing the prereduced dyestuff at a temperature of about 205 to 220° F., or the dyestuff in pigment form may be added to a bath containing the fibrous material previously treated with sodium tetraborate followed by reduction with caustic and sodium hydrosulfite in the same bath. Alternatively, the fibrous material may be treated in an aqueous bath containing the sodium tetraborate and the vat or sulfur dyestuff in pigment form followed by addition of the caustic and sodium hydrosulfite to the bath to reduce the dyestuff in situ. While the treatment with the sodium tetraborate may be carried out at any temperature up to about 220° F., the application of the reduced form of vat or sulfur dyestuff must be carried out at temperatures of from about 205 to 220° F. in order to achieve the desired results.

After the fibrous material has been uniformly and thoroughly impregnated with the reduced dyestuff in the above-described manner, which usually takes about ½ to 1½ hours, the fibrous material is oxidized in a manner well known in the art. Thus, aqueous solutions of various oxidizing agents may be applied to oxidize the dyestuff to the final form, as for example sodium perborate, hydrogen peroxide and acetic acid, sodium persulfate, sodium chlorite, sodium nitrite and sulfuric acid, sodium bichromate and acetic acid and the like. Rinsing should be carried out before and after the oxidizing treatment, in known manner, with the usual final treatment with detergent.

As another feature of this invention, it is sometimes expedient to provide a composition containing 1 part of the vat or sulfur dyestuff, in pigment or reduced form, combined with from about 1 to 4 parts by weight of sodium tetraborate. Such a composition may be conveniently employed for dyeing polyacrylonitrile fibrous material in accordance with the process described above, if desired with adjustment of the proportions of dyestuff to sodium tetraborate where required to achieve the desired depth of shade, and the like.

In the following examples, which are only illustrative of the instant invention, a vessel was charged with water and fibrous material, the fiber content of which was composed of about 85 to 95% polyacrylonitrile, in a ratio of 12:1, the water containing about 10% of sodium tetraborate by weight of the fiber. The solution was circulated through the fibrous material at 120 to 130° F. for about 10 minutes, the dyestuff composition given in the example added to the bath, and the temperature raised to about 150° F. Caustic soda and sodium hydrosulfite were then added in amounts of about 8% each by weight of the fiber, the temperature raised to 212° F., and the dye solution circulated through the material for about 60 to 80 minutes. The impregnated material was then rinsed with hot water till clear, oxidized in a solution containing 4% sodium perborate and ½% acetic acid (28% conc.) for 20 to 30 minutes at 130° F., rinsed, dried at the boil in a detergent solution containing 2% soda ash, rinsed and dried. Commercially acceptable dyeings were obtained, as determined by 40 to 160 hour tests for light fastness in the Fadeometer, AATCC Wash Tests Nos. 3 and 4, fastness to dry cleaning, acid and alkaline perspiration tests, and resistance to crocking. Proportions given above and in the table below are based upon the weight of the fiber, unless otherwise indicated.

Example	Dye Composition	Dyeing
1	10% Algol Yellow GCA Double Paste	Greenish-yellow.
2	10% Indanthrene Golden Orange GA Double Paste.	Golden Orange.
3	10% Indanthrene Orange RRTA Paste	Brownish-orange.
4	10% Indanthrene Brilliant Pink RN Paste Fine.	Reddish-Pink.
5	10% Indanthrene Navy Blue BRP Paste.	Deep Violet.
6	10% Brilliant Indigo 4B Paste Fine	Blue.
7	10% Indanthrene Olive Green BA Double Paste.	Dark Green.
8	10% Brilliant Indigo 4B Extra conc. Paste Fine. 5% Indo Carbon CLGS conc. CF	Black.
9	10% Indanthrene Golden Yellow RKA Double Paste.	Greenish-yellow.
10	10% Brilliant Green BN Pure Double Paste conc.	Bright Bluish-green.
11	8% Indo Carbon conc. CF 5% Brilliant Indigo 4B Paste Fine 2% Indanthrene Golden Orange GA Double Paste.	Black.
12	8% Indo Carbon CLGS conc. CF 6% Brilliant Indigo 4B Paste Fine 2% Indanthrene Golden Yellow RKA Double Paste Fine.	Do.
13	15% Brilliant Indigo 4B Paste Fine 2% Indo Carbon CLGS conc 0.4% Indanthrene Brilliant Green BN Pure Double Paste conc.	Navy Blue.
14	12% Brilliant Indigo 4B Paste Fine 20% Indo Carbon CLGS Paste Fine CF. 1% Indanthrene Olive-Green BA Double Paste.	Do.
15	40% Indo Carbon CLGS Paste Fine	Black.

In the last example, the dyeing was carried out at about 200° F. for 50 minutes, then at 212° F. for 10 minutes.

This invention has been disclosed with respect to certain preferred embodiments, and various modifications and variations thereof will become obvious to the person skilled in the art. It is to be understood that such modifications and variations are to be included within the spirit and purview of the application and the scope of the appended claims.

I claim:

1. In a process for dyeing fibrous materials containing fibers composed of at least 75% by weight of polyacrylonitrile, the improvement comprising pretreating said material with an aqueous solution containing about 8 to 25% of sodium tetraborate by weight of the fiber, and then impregnating the pretreated material with an aqueous alkaline hydrosulfite vat at a temperature of about 205 to 220° F., said vat containing dissolved therein the reduced form of a vat dyestuff stable at the temperature of the vat.

2. In a process for dyeing fibrous materials containing fibers composed of at least 75% by weight of polyacrylonitrile, the improvement comprising pretreating said material with an aqueous solution containing about 8 to 25% of sodium tetraborate by weight of the fiber, adding to said solution containing the pretreated material a vat dyestuff soluble in reduced form in an aqueous alkaline hydrosulfite vat and stable at about 205 to 220° F., and then adding to said solution sufficient caustic soda and sodium hydrosulfite to form and maintain the dyestuff in reduced form in the bath while dyeing the pretreated material in the bath at about 205 to 220° F.

3. A process for dyeing fibrous material containing fibers composed of at least 75% by weight of polyacrylonitrile, comprising pretreating said material with an aqueous solution containing about 8 to 25% of sodium tetraborate by weight of the fiber, then impregnating the pretreated material with an aqueous alkaline hydrosulfite vat at a temperature of about 205 to 220° F., said vat containing dissolved therein the reduced form of a vat dyestuff stable at the temperature of the vat, and then oxidizing the dyestuff on the fiber.

4. A process for dyeing fibrous material containing fibers composed of at least 75% by weight of polyacrylonitrile, comprising pretreating said material with an aqueous solution containing about 8 to 25% of sodium

tetraborate by weight of the fiber, adding to said solution containing the pretreated material a vat dyestuff soluble in reduced form in an aqueous alkaline hydrosulfite vat and stable at about 205 to 220° F., then adding caustic soda and sodium hydrosulfite to the bath in an amount sufficient to form and maintain the dyestuff in reduced form while dyeing the pretreated material in the bath at about 205 to 220° F., and then oxidizing the dyestuff on the fiber.

5. A composition devoid of reducing agents and suitable for use in dyeing fibrous material, the fiber content of which is composed of at least 75% by weight of polyacrylonitrile, comprising 1 part by weight of a vat dyestuff soluble in reduced form in an aqueous alkaline hydrosulfite vat and stable at about 205 to 220° F., and about 1 to 4 parts by weight of sodium tetraborate.

References Cited in the file of this patent

Journal of Textile Institute Proceedings, pp. 544–545, August 1951.