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2,955,008

DYEING OF POLYACRYLONITRILE FIBROUS MATERIAL

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This invention relates to the dyeing of polyacrylonitrile fibrous material with vat dyestuffs, and more particularly to the use of ester salts of leuco vat dyestuffs for such dyeings.

The dyeing of fibrous material 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 material but the results have not been completely satisfactory. This has been particularly true with respect to attempts made to dye such fibrous material with vat dyestuffs.

It is an object of this invention to produce acceptable dyeings with vat dyestuffs on fibrous material having a basis of polyacrylonitrile. Another object of this invention is the provision of a vat dyestuff composition useful for dyeing such fibrous material. Other objects and advantages will appear as the description proceeds.

The above objects are attained by the instant invention which is based upon the discovery that a dye bath containing an ester salt of a leuco vat dyestuff and a polymerized N-vinyl lactam produces commercially acceptable and highly improved dyeings on polyacrylonitrile fibrous material.

In general, the dye bath of this invention should contain an ester salt of a leuco vat dyestuff, a polymerized N-vinyl lactam, and sodium formaldehyde sulfoxylate. The use of such a bath for dyeing polyacrylonitrile fibrous material has been found to produce dyeings of uniform shade and very good wash fastness as compared with dyeings obtained without the use of the polyvinyl lactam which have poor wash fastness and are uneven in shade due to a too rapid rate of exhaust. The polyvinyl lactam in the dye bath acts as both a dispersing agent and protective colloid to prevent the dyestuff from precipitating out, and as a retarding agent to lower the rate of exhaust. In addition the dyeings obtained in accordance with this invention have exceptionally good light fastness properties and are surprisingly durable in wet processing. They satisfactorily withstand a #3 Felling Test (AATCC, 1950, p. 94) so that the dyed polyacrylonitrile fibrous material may be readily admixed with wool.

The dye bath of the invention is usually employed in a fiber-liquor ratio of from about 1:10 to 1:40, depending mainly upon the form of the fibrous material being dyed. The dye bath, which is an aqueous solution, will generally contain from about 0.02 to 0.2 percent by weight of the polymerized N-vinyl lactam and from about 0.2 to 1 percent by weight of sodium formaldehyde sulfoxylate. Since the dyeing process operates by exhaustion, the amount of dyestuff in the dye bath will depend upon the amount of fibrous material being dyed. The desired depth of shade may usually be obtained by use of from about 0.2 to 2 percent of the dyestuff by weight of the fiber or about 0.005 to 0.2 percent by weight of the dye bath. The selection of the proper amounts of dyestuff, polymerized N-vinyl lactam and

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sodium formaldehyde sulfoxylate in any particular operation may be readily determined by the worker skilled in the art.

In carrying out the process of the instant invention for dyeing polyacrylonitrile fibrous material, the material is treated with the aforementioned dye bath for a short period of time, the temperature raised to at least 180° F., and held at that temperature for from about ½ to 1 hour after the addition of acid. Following this dyeing period, the fibrous material may if desired be rinsed in cold water, then developed in the usual manner with nitrous acid, rinsed, neutralized and scoured with soda ash and a detergent such as soap, acyl alkyl taurates and other synthetic surfactants. The process may be carried out in any suitable dyeing equipment, continuous or batch.

The temperature of the dye bath should be maintained at from about 180° F. to the boiling point during the dyeing operation. However, an acid should first be added to the dye bath in order to assist in driving the dyestuff on their fiber. For this purpose sulfuric acid is preferably used, in amounts of about 5 to 10%, preferably about 6 to 7% by weight of the fiber, but other organic or inorganic acids may also be employed in acidic equivalent amounts, as for example, formic, phosphoric, acetic, glycolic, sulfamic acids, and the like. The developing process is carried out in the usual manner, best results being obtained at temperatures of about 190° F. However, for certain purposes developing temperatures as low as 100° F. may be employed. In some instances, dyeing results may be further improved by incorporating a small amount of thiourea and Glauber's salt (about 2 to 5 percent of each by weight of the fiber) to the dye bath.

Ester salts of leuco vat dyestuffs are well known in the art. The alkali-metal salts of the leuco sulfuric acid esters of the following vat dyestuffs, given for illustrative purposes only, may be employed in accordance with this invention. The term "AATCC" refers to the Technical Manual and Year Book of the American Association of Textile Chemists and Colorists.

Prototype 9, AATCC, 1951
 Prototype 291, AATCC, 1951
 Prototype 116, AATCC, 1951
 Prototype 109, AATCC, 1951
 Prototype 503, AATCC, 1951
 Prototype 293, AATCC, 1951
 Prototype 118, AATCC, 1951
 Prototype 295, AATCC, 1951
 C.I. 1098
 C.I. 1217
 C.I. 1104
 C.I. 1184
 C.I. 1185
 C.I. 1113
 C.I. 1178
 C.I. 1101

The polymerized N-vinyl lactams useful in the instant invention may be produced in known manner as disclosed in U.S. Patents 2,265,450 and 2,335,454. The preferred N-vinyl lactam is vinyl pyrrolidone (1-vinyl-2-pyrrolidone, N-vinyl pyrrolidone, N-vinyl- α -pyrrolidone). Other polymerized N-vinyl lactams which may be employed are the polymerization products of N-vinyl caprolactam, N-vinyl piperidone, N-vinyl hexahydrophthalimidine, and the like. Copolymers of the aforementioned N-vinyl lactams with other monomers may also be employed. The N-vinyl lactams and its copolymers must be soluble or readily dispersible in water. Polymers having a K value of from about 10 to 90, preferably 25 to 35, may be employed. The K value of any particu-

lar mixture of polymers is calculated from viscosity data and is useful as an indication of the average molecular weight of such mixture. Its determination is fully described in "Modern Plastics," 23, No. 3, 157-61, 212, 214, 216, 218 (1945) and is defined as 1000 times k in the empirical relative viscosity equation:

$$\frac{\log_{10} \eta_{rel}}{C} = \frac{75k^2}{1 + 1.5kC} + k$$

wherein C is the concentration in grams per hundred cc. of polymer solution and η_{rel} is the ratio of the viscosity of the solution to that of pure solvent.

The fibrous material to the dyeing of which the instant invention is directed should have a basis of at least 75 percent by weight of polyacrylonitrile copolymerized if desired with other polymerized monomers such as disclosed in U.S. Patents 2,527,863, 2,548,282, 2,558,735, 2,595,848, etc. Fibrous material containing about 85 percent of polyacrylonitrile is particularly suitable for dyeing in accordance with this invention. Other modifying agents may of course be present in the fiber. Exceptionally good results are obtained in dyeing Acrilan (product of Chemstrand Corp.) in accordance with this invention. The fibrous material may be in any of the usual forms, as for example, staple fiber, continuous filament, tow, rope, yarn, fabric, felt, and the like, and treated as a wound package, running lengths, fibrous stock, bulk, etc.

The following examples are illustrative of the instant invention and are not to be regarded as limitative.

Example I

A 5 gram skein of yarn having a basis of polyacrylonitrile was scoured and worked in an aqueous dye bath containing 0.1 gram of the leuco disulfuric acid ester sodium salt of 3,4,8,9-dibenzpyrene-5,10 quinone, 1 cc. of a 30 percent by weight aqueous solution of polyvinylpyrrolidone, and 0.5 gram of sodium formaldehyde sulfoxylate, at 140° F. for about ten minutes. The fiber-liquor ratio was 1:40. The temperature was then raised to 190 to 200° F. and after another ten minutes at this temperature 0.2 cc. of sulfuric acid (66° Bé.), diluted to 20 cc., was added slowly over a period of ten minutes. Working of the yarn in the dye bath was continued for 45 minutes at the same temperature, after which the dyeing, without rinsing, was developed in an aqueous bath containing 1 gram of sodium nitrite and 20 cc. of sulfuric acid (66° Bé.) per liter at 100 to 110° F. for five to ten minutes. The dyeing was then rinsed, neutralized, and scoured at the boil for about ten minutes in an aqueous bath containing sodium N-oleoyl-N-methyl taurate and soda ash. The resulting dyeing was an even, pleasing shade of golden-yellow with very good light fastness, and excellent wash resistant properties.

Example II

About 80 pounds of staple fiber stock having a basis of polyacrylonitrile were treated in a Smith-Drum machine for 15 to 20 minutes at 160° F. in an aqueous bath containing ½ percent (by weight of fiber) of sodium

oleoylmethyl taurate and then rinsed with water. An aqueous dye bath containing 1.5 pounds of the leuco disulfuric ester sodium salt of the dyestuff C.I. 1104, 14 ounces of a 30 percent by weight aqueous solution of polyvinylpyrrolidone and 5 pounds of sodium formaldehyde sulfoxylate per 100 gallons was then introduced into the machine at 160° F., the temperature raised to 180° F. and 2 pounds of sulfuric acid (66° Bé.) previously dissolved in 8 to 10 gallons of cold water, added gradually over a period of ten minutes. The temperature was then raised to 190 to 200° F. and the dye bath recirculated through the fiber stock for 45 minutes. Sufficient cold water was then added as a running rinse to bring the temperature down to 100° F. 14 ounces of sodium nitrite in solution were then introduced followed by 2 gallons of sulfuric acid (66° Bé.). After 5 to 10 minutes running, the fiber stock was rinsed, neutralized and scoured with sodium oleoyl methyl taurate and soda ash at 200° F. for 15 minutes. The dyed fiber stock had a pleasing, even shade of violet having very good light fastness, and excellent wash resistant properties.

Other modifications and variations will be obvious to the person skilled in the art and it is to be understood that such modifications and variations are included within the purview of this application and the spirit and scope of the appended claims.

I claim:

1. An aqueous dye bath comprising about 0.005 to 0.2% by weight of an ester salt of a leuco vat dyestuff, about 0.02 to 0.2% by weight of a water-soluble polymer of an N-vinyl lactam selected from the group consisting of N-vinyl pyrrolidone, N-vinyl caprolactam, N-vinyl piperidone, and N-vinyl hexahydrophthalimidine, and having a K value of about 10 to 90, and about 0.2 to 1% by weight of sodium formaldehyde sulfoxylate.
2. A dye bath as defined in claim 1 wherein the N-vinyl lactam is N-vinyl pyrrolidone.
3. In a process for dyeing fibrous material having a basis of at least about 75% by weight of polyacrylonitrile, the steps comprising treating such material with an aqueous dye bath comprising about 0.005 to 0.2% by weight of an ester salt of a leuco vat dyestuff, above 0.02 to 0.2% by weight of a water-soluble polymer of an N-vinyl lactam selected from the group consisting of N-vinyl pyrrolidone, N-vinyl caprolactam, N-vinyl piperidone, and N-vinyl hexahydrophthalimidine, and having a K value of about 10 to 90, and about 0.2 to 1% by weight of sodium formaldehyde sulfoxylate, and adding to said bath before the completion of treatment of said fibrous material therewith an amount of acid equivalent to about 5 to 10% of sulfuric acid by weight of said fibrous material.
4. A process as defined in claim 3 wherein the N-vinyl lactam is N-vinylpyrrolidone.
5. A process as defined in claim 3 in which the fiber-liquor ratio is from about 1:10 to 1:40.

References Cited in the file of this patent

- Amer. Dyestuff Reporter for February 1, 1954, pp. P72-P75.