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DYEING OF POLYACRYLONITRILE WITH VAT DYES

Jerry M. Mecco, Somerville, and Joseph W. Creely, East Bound Brook, N. J., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

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This invention relates to a process of dyeing certain types of polyacrylonitrile synthetic fibers with vat dyes.

Polyacrylonitrile fibers both in filament and staple form have achieved extensive commercial success. In general, there are two types of spinning processes. In the one, the polymer is dissolved in an organic solvent such as diethyl formamide and forced through the spinnerette opening into an atmosphere which results in rapid evaporation of the solvent. This spinning process is used, for example, by the DuPont Company in producing their fiber under their trade-mark "Orlon." Another process of spinning is a wet process in which the polymer is dissolved in a strong aqueous thiocyanate solution and extruded into a suitable bath. The wet spinning process is applicable both to pure polymerized acrylonitrile and to copolymers of acrylonitrile with small amounts of other substances such as acrylates, vinyl pyridine and the like. Although polyacrylonitrile whether spun by the organic solvent or dry method or the aqueous thiocyanate method, is probably chemically the same substance, the surfaces appear to be different which difference may be physical or chemical or both.

It has been attempted in the past to dye polyacrylonitrile fibers produced by either wet or dry spinning with vat dyes, in order to obtain the important advantages of vat dyes such as high light fastness and fastness to many other treatments. In the past, however, the ordinary vat dyeing procedure has not been applicable at all to fibers spun from solutions in organic solvents and has not been entirely satisfactory, at least for deep shades even with wet spun polyacrylonitrile.

The present invention relates to a new process of dyeing various polyacrylonitrile fibers, both pure polymers and copolymers when spun from concentrated thiocyanate solutions. It has been found that excellent results are obtainable provided the dyeing is effected in a very narrow pH range of from 6 to 8 and preferably between about 6.5 and 7.5. In this range the reduced or leuco form of the vat dyestuff exists in the form of the compound with free hydroxyl groups and not in the form of the sodium salt as is in ordinary vat dyeing procedures at higher pH's. The free hydroxy leuco form has been sometimes referred to rather loosely as a "vat acid," although it is only an acid in the sense that it is capable of forming compounds with strong bases which is true of most phenols.

The pH range of the present invention is extremely critical, particularly at its upper limit. The moment that the pH is high enough to form the sodium salt of the vat acid, the advantages of the present invention cease and effective dyeing, particularly of a dark shade is impossible. On the other hand, within the pH range of the present invention, excellent dyeing permitting the production of dark shades is possible. It is not known why the nature of the spinning process should be so decisive in the effectiveness of the present process. Obviously, the surface of the fiber has been affected by the spinning process used, and it is not desired to limit the present invention to any

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theory of action or of chemical or physical constitution of the surfaces of the spun fibers.

While the pH range is the most critical and the most important feature of the present invention, it has been found that temperature is also an important factor, and in general, quite high temperature should be used with some dyes and particularly in the case of some of the acrylonitrile copolymer fibers it is possible to dye at temperatures below the boiling point of water down to as low as 160° F. Improved results are, however, normally obtained by dyeing at the boil and with many dyes still better results are obtained at higher temperatures up to or around 300° F. or even slightly higher. In general, the top temperature limit is not one which is determined by dyeing efficiency but is dictated by the temperature at which damage to the fiber results. In general, it may be considered that 325° F. will represent a top limit at which some damage may be noticeable but can be tolerated if the dyeing is effected very readily.

The critical limitation as to pH range can be met by any method desired, thus it is even possible to maintain the pH range with dilute solutions of a strong alkali such as sodium hydroxide. However, such methods of maintaining the pH range while effective require very careful control because within the pH range close to neutral a very small amount of alkali will make a great pH change. The reduction of the dye itself tends to lower the pH because the sodium hydrosulfite used is oxidized to sodium bisulfate which is distinctly acid and therefore results in a lowering of the pH. The necessity of careful control makes it desirable to use a buffer rather than to maintain the pH by very careful addition of alkali, and accordingly, in its preferred embodiment the present invention includes the use of suitable buffers. The two best buffers which have been found are sodium tripolyphosphate and sodium tetrphosphate, the former giving the most reliable and complete buffering action. It should be understood that the buffers do not appear to act chemically other than the control of pH because the dyeing procedure appears to depend on the pH regardless of how it is maintained.

It is an important advantage of the present invention that more dye and reducing agent can be added at any time during the dyeing process which is often difficult or not feasible at all with the ordinary vat dyeing procedure. A very delicate and continuous control is thus made possible.

Polyacrylonitrile fibers are subject to yellowing or dulling which will often result in producing a relatively dull dyed material. These two undesirable changes are of two types. One, which results when the fiber is exposed to alkali which is a reversible result and can be removed by acidification. It is no problem in the present invention which is not carried out at a high pH. The second form of yellowing appears to be a temperature and time phenomenon and is not reversible. Although the dyeing is extremely rapid at high temperatures in the process of the present invention, still there may be some yellowing due to heat. It has been found that fibers which are copolymers, particularly acrylate copolymers, may be protected from heat yellowing or the yellowing greatly reduced by the addition to the dye bath of compounds of polyvalent metals in the state of oxidation in which they exert no oxidizing effect. The most important element is zirconium, the compounds of which exert a maximum anti-yellowing effect. Other effective elements are manganese and magnesium while somewhat less effective compounds are those of calcium and aluminum.

In a more specific aspect of the present invention when used for dyeing acrylonitrile copolymer fibers the addition of anti-yellowing compounds is also included. It is not known why the metal compounds referred to above exert

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such a marked effect on heat yellowing with the acrylonitrile copolymer fibers and yet do not appear to have any practically useful effect with pure polyacrylonitrile. It is not desired therefore to limit the invention to any theory of how these metal compounds act.

The polyvalent metal compounds referred to above should not be confused with the use of cuprous compounds in the so-called cuprous ion method of dyeing. This is a method in which a cuprous ion is formed in the dye bath and has been extensively employed in introducing various dyestuffs in a nonbasic polymerized synthetic fibers which would not otherwise have affinity for the fiber. Therefore, the term polyvalent as used in the present invention should be interpreted in its normal restricted meaning, namely, that the metal will unite with more than one equivalent of a monobasic anion. Cuprous compounds show copper with a net valence of 1, that is to say, when a compound with a monobasic anion such as chlorine is formed there are as many atoms of chlorine as of copper. Although in the actual structural formula of the compounds, copper is usually assumed to have a valence of 2, 1 valence being connected to the other copper atom. In the present invention, however, only the net valence toward anion is considered and the term "polyvalent" is used in this sense only. It does not include cuprous compounds which are just as ineffective in the present invention as any other monovalent metals.

The invention will be described in greater detail in conjunction with the following specific examples, the parts being by weight except where otherwise specified.

Example 1

A dye bath was prepared containing 0.15 part of a green vat dyestuff Color Index 1101, 1 part of sodium tripolyphosphate, 0.75 part of sodium hydrosulfite and 200 parts of water. This bath was heated to 160° F. and then 5 parts of a 10% solution of manganous chloride with 6 moles of water of crystallization added. In the bath was dyed 5 parts of thiocyanate spun filament yarn of acrylonitrile copolymerized with a small amount of methyl acrylate. The dyeing was continued at 160° C. until complete and the bath then slowly cooled. Thereupon the material was removed, boiled in 400 parts of an aqueous solution containing 5 parts of sodium carbonate and 0.5 part of soap. The yarn was then rinsed and dried.

The resultant dyeing was an excellent green shade being much stronger and brighter than a corresponding dyeing prepared under identical conditions but without the manganous chloride in the bath.

Example 2

A dye bath was prepared containing 15 parts of a 1% aqueous slurry of paste of a vat dye of Example 1, 1 part of sodium tripolyphosphate, 0.75 part of sodium hydrosulfite and 200 parts of water. The bath was heated to the boil and 5 parts of a 10% solution of zirconium oxychloride added.

In the bath there was dyed 5 parts of acrylonitrile copolymer filament yarn as described in Example 1. After the dyeing was complete, the material was removed from the bath and boiled with a 1% aqueous solution of sodium carbonate. Thereupon the material was boiled in a 0.1% soap solution, rinsed and dried.

The resultant dyeing was much greener than a corresponding dyeing prepared under identical conditions except that the zirconium oxychloride was not present in the dye bath.

Example 3

A dye bath was prepared with 15 parts of a 1% slurry of a green vat dyestuff, Color Index 1101, described in Example 2, 1.3 parts of sodium tripolyphosphate and 200 parts of water. This bath was heated to the boil and 0.1 part sodium hydrosulfite and 3.3 parts of a 10% aqueous

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solution of manganous chloride with 6 molecules of water of crystallization was added.

In the bath 5 parts of a acrylonitrile copolymer described in Example 1 was dyed at the boil until dyeing was complete whereupon it was transferred to another bath and boiled in a 1% aqueous sodium carbonate solution. After rinsing and drying, the resulting dyeing was compared with a dyeing under identical conditions without the manganese present in the bath. A much stronger dyeing resulted from the presence of the manganous chloride.

Example 4

The procedure of Example 3 was followed but the boiling was continued for three times as long as in Example 3. The results were identical. This shows that the relatively better results obtained with the manganous chloride were not due to an insufficient dyeing time of the dyeing which did not have the manganous chloride present.

Example 5

The procedure of Example 3 was followed. The boiling time was 12 times as long. No substantial difference in dyeing result was noted over Examples 3 and 4.

Example 6

The procedure of Example 3 was repeated with 4 different amounts of manganous chloride, namely, 5 parts, 2.5 parts, 0.5 part and a control with no manganous chloride present. Oxidation was effected by dipping in a 1% sodium carbonate solution, followed by treatment with a hot 1% solution of sodium perborate. The appearance of the dyeing showed a regular improvement from a rather poor violet color when no manganous chloride was present to a green of maximum strength when 5 parts of the solution were present.

Example 7

The procedure of Example 6 was followed replacing the manganous chloride with 3.3 parts of a 10% solution of calcium chloride. Results were obtained which were very similar to those of Example 6.

Example 8

The procedure of Example 7 was followed using Vat Yellow GC (1,2,5,6-anthraquinone-C-diphenyl dithiazole). Excellent results were obtained much stronger than the corresponding dyeing under identical conditions in the bath in which the calcium chloride was omitted.

Example 9

The procedure of Example 8 was followed replacing the Vat Yellow GC with Vat Olive T (6-benz-1-dianthraquinonylamino BzN2,2'-acridine). Again two dyeings were made, one without calcium and one with calcium. The dyeing with calcium in the bath showed markedly improved strength.

Example 10

The procedure of Example 7 was repeated using Vat Red BN Color Index 1162. Here again the dyeing in the bath containing the calcium chloride was markedly better than the corresponding dyeing in which the calcium chloride was omitted.

Example 11

The procedure of Example 1 was followed omitting the manganous chloride and the sodium tripolyphosphate and substituting for the latter one part by volume of a 30° Bé. of aqueous sodium hydroxide. The results obtained were the same as with the sodium tripolyphosphate.

Example 12

Four parts of a commercial paste of Vat Violet 6R Color Index 1212 was mixed with 30 parts by volume of a 10% solution of sodium tripolyphosphate and 2 parts of sodium hydrosulfite. The mixture was brought

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to a boil and water added to make up a total volume of 200 parts, the mixture being cooled to room temperature. Five parts of a skein of filament of pure polyacrylonitrile spun from concentrated aqueous thiocyanate solution was introduced as a skein. The bath was raised slowly to the boil, the boil continued until dyeing was complete. The yarn was taken from the bath, washed in warm water and then boiled for five minutes in a 5% soda ash solution. This was followed by washing with warm water and finishing with a wash of a solution of 2.5 parts of sodium dodecyl sulfate per gallon. This last wash was effected at the boiling temperature. The yarn dyed a strong violet showing good fastness.

Example 13

The procedure of Example 12 was followed using staple fiber instead of filament. Excellent penetration and a level shade was obtained.

Example 14

An acrylonitrile copolymerized staple spun as described in Example 1 was dyed with 10% dimethoxydibenzanthrone, Jade Green, in a bath containing 3% sodium tripolyphosphate and 2% sodium hydrosulfite. The temperature was 250° F. and after dyeing the dye was oxidized on the fiber by boiling with 1 part by volume of hydrogen peroxide containing 1% acetic acid. A well-penetrated, level medium green dyeing resulted.

We claim:

1. A method of dyeing with vat dyes polyacrylonitrile fibers which are copolymers of acrylonitrile and a small amount of methyl acrylate and spun from a concentrated aqueous thiocyanate solution, which comprises heating at a temperature between 160°–325° F. the said fibers in an aqueous dyebath containing an unesterified leuco vat dyestuff, a reducing agent and a sufficient amount of zirconium oxychloride to substantially reduce heat yellowing of said fiber, the dyebath having a pH between 6 and 8, maintaining the pH of said aqueous dyebath between 6 and 8 during said heating until the dyeing is complete and oxidizing the dyestuff on the fiber.

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2. As a method of dyeing polyacrylonitrile fibers containing copolymers of a major amount of acrylonitrile and a minor amount of methyl acrylate copolymerized together and spun from a concentrated aqueous thiocyanate solution of said copolymers, with vat dyes, the improved method which comprises heating said fibers in an aqueous dyebath having a pH between 6 and 8 and containing an unesterified leuco vat dye, a reducing agent, a sodium polyphosphate buffer and a soluble, non-oxidizing, polyvalent metal chloride which is capable of reducing the heat yellowing of said fibers, at a temperature between 212° and 300° F., maintaining the pH of said aqueous dyebath between 6 and 8 during said heating thereof by means of said buffer until the dyeing is complete and oxidizing the dyestuff on the fiber.

3. The process of claim 2 wherein the said polyvalent salt is zirconium oxychloride.

4. The process of claim 2 wherein the said polyvalent salt is manganous chloride.

5. The process of claim 2 wherein the said polyvalent salt is calcium chloride.

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