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DYEING OF ACID-MODIFIED ACRYLIC AND POLYESTER FIBERS

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This invention relates to processes of dyeing acid-modified acrylic and polyester fibers with cationic dyes. By acid-modified acrylic fiber, throughout this specification and claims, is meant acrylic fiber having acid sites; for instance, the sulfonate modified acrylic fibers described in U.S.P. 2,837,500 and 2,837,501. By acid-modified polyester fiber, is meant polyethylene terephthalate fiber containing metal-sulfonate groups, as described more fully in British Patent No. 826,248, accepted December 31, 1959. By cationic dyes are meant organic dyes which are free of sulfo and carboxy groups but are water-soluble by virtue of having at least one positively charged, pentavalent nitrogen atom associated with a water-soluble anion such as Cl^-, SO_4H^-, acetate, etc. For the purpose of this invention it makes no difference whether the cationic N-atom is part of a heterocyclic ring (as in oxazine or methine type dyes), is a substitutent on a cyclic C-atom (as for instance in triphenylmethane dyes) or is located on an alkyl side chain (as in the azo dyes of S. N. Boyd, U.S.P. 2,821,526).

It is an object of this invention to provide a practical and reasonably rapid method for dyeing acid-modified synthetic fibers as aforementioned with cationic dyes at relatively low temperatures. Additional objects and achievements of this invention will become apparent as the description proceeds.

Hithereto, the normally accepted procedures for dyeing acid-modified polyester and polyacrylic fibers with cationic dyes involved the use of an aqueous dyebath and required a dyeing time of at least 1 to 2 hours, and temperatures of at least 100° C. Faster exhaust times are possible in some cases, but are undesirable because of lack of levelness in the dyeing obtained. For this reason, retarders have to be used with many dyes.

Prolonged dyeing procedure is obviously unsuitable for continuous dyeing (for instance, dyeing of piece goods) and is costly from the viewpoint of time and energy consumed. Furthermore, the heating of polyester fibers at high temperatures for prolonged periods tends to injure the fiber by hydrolysis or other adverse chemical or physical effects. Attempts to improve the dyeing of the above fibers with assistants and carriers have often lead to unsatisfactory results, such as plasticizing or shrinking the fibers or imparting thereto a harsh hand, and/or degrading the fastness of the dyes.
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Now, according to this invention, the aforenoted problems are eliminated and the dyeing of acid-modified acrylic and polyester fibers with cationic dyes is effected neatly and rapidly by adding pyridine or a homolog of pyridine to the aqueous dyebath. In other words, according to my invention the color is dissolved in an aqueous solution of pyridine (or a homolog thereof) generally of 5 to 50% strength (and in special cases of up to 80% or 90% strength), and the acid-modified fiber is dyed in said solution at a temperature of about 80° to 105° C. for a very short period (usually less than 15 minutes), whereupon the fiber is removed from the dyebath, rinsed with water and dried.

As a result of both the lower dyeing temperature and the very short dyeing period, the dyes employed do not decompose, and they give even, level dyeings with rapid build-up, despite the short dyeing time. Also, the solvent is easily removed from the dyed fabric by rinsing with water. In addition, by my novel process it becomes possible to extend the range of useful dyes to those which lack adequate buildup or have insufficient solubility in the known aqueous systems. Finally, the accelerated dyeing time enables my novel process to be used in the continuous dyeing of piece goods.

The dyeing time in my novel process may vary from a few seconds to 15 minutes depending on the shade desired. Both acid-modified acrylic and acid-modified polyester fibers are dyed in extremely level shades with the good fastness properties inherent in the respective dyes.

Any normally liquid pyridine base may be used in my invention, including pyridine itself, the picolines and the lutidines, and in particular, liquid commercial mixtures sold generally under the name of pyridine bases.

As for the quantity of pyridine base, 5% by weight of the dyebath produces an appreciable reduction in the dyeing time or, conversely, will produce a noticeable increase in depth of dyeing in a fixed dyeing period of, say, 5 minutes. The degree of improvement increases up to 10% pyridine concentration (by weight). Then it begins to level off reaching a maximum somewhere between 10 and 25% of pyridine. From thereon, normally there is no special improvement in using higher concentrations of pyridine; nor is there any special loss, except the cost of the pyridine, and concentrations up to 50% are considered practical.

In the special case of dye mixtures, for instance blacks composed of green, yellow and perhaps other component dye, the dyeing acceleration effect of a given concentration of pyridine is often greater for one of the component colors than for the others. Therefore, to give each component the fullest chance for going onto the fiber in the shortened dyeing time, it is recommended to use a concentration of pyridine of 80 to 90% by weight of the aqueous dye-bath. Dye-baths, however, of less than 10% water-content are not recommended, inasmuch as cationic dyes require the presence of water for dissolution.

Without limiting this invention, the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

Example 1

A dyebath is prepared by dissolving 1.2 parts of the oxazine dye, C.I. Basic Blue 4 (C.I. 51004), in 100 parts of 50% aqueous pyridine in a glass-lined steel vessel and is brought to the boiling point. Acid-modified polyester fabric is stirred in the boiling solution for a period of time ranging from 15 seconds to 1 minute, depending on the depth of shade desired. The fabric is then removed from the dyebath, rinsed with water, scoured for 5 minutes with an aqueous solution of a surfactant (e.g. 1 part of the sodium sulfate of the 1:20-mole condensation product of oleyl alcohol and ethylene oxide in 1000 parts of water) and dried.

The resultant blue dyeing is level and deeply colored, the depth of shade increasing with dyeing time. It has good fastness properties and a soft hand.

If an acid-modified acrylic fiber is substituted for the polyester fiber in this example, medium blue, level dyeings are obtained.

Example 2

A dyebath is prepared as in Example 1, using 4 parts of [p-(1-amino-4-hydroxy-2-anthraquinonyloxy)benzyl]-triethylammonium ethyl sulfate (U.S.P. 2,888,467) and 100 parts of a 50% aqueous pyridine solution. Acid-

modified polyester fabric is dyed in the boiling bath for a period of time between 15 seconds and 5 minutes, as desired. The fabric is then removed and treated as in Example 1. The fabric shows good buildup in level, red shades, the exact shade depending on the length of dyeing, and that obtained in the five-minute dyeing, being almost a maroon color.

Example 3

The procedure is as in Example 1 except that the 50% aqueous pyridine dyebath is replaced by a 50% aqueous solution of 3-picoline. Deep, level and fast blue dyeings are obtained, the shade being deeper than that obtained in the corresponding dyeing time using the aqueous pyridine dyebath of Example 1.

Example 4

The procedure, color and fabric are as in Example 1, but instead of the 50% aqueous pyridine bath there specified, a 10% aqueous solution of 3-picoline is here employed. Deep, level and fast blue dyeings are obtained.

Similar results are obtained by the above procedure if the dyebath employed is a 10% aqueous solution of pyridine, 2-picoline, 4-picoline or 2,4-lutidine, using a dyeing period of 1 minute. All the dyeings are level and deep with rapid buildup. Pyridine, 2-picoline and 4-picoline give approximately equivalent dyeings. The use of 3-picoline results in a higher dyeing rate and buildup, while 2,4-lutidine has the strongest effect of all.

Example 5

The procedure, color and fabric are as in Example 1, but instead of the 50% aqueous pyridine bath there specified, a 5% aqueous solution of 3-picoline is employed. The dyeing period may vary from 6 seconds to 5 minutes, level and fast dyeings being obtained, varying from light to medium shades, depending on the length of the dyeing period.

Example 6

A dyebath is prepared by dissolving 0.7 part of C.I. Basic Yellow (C.I. 48055), 0.09 part of C.I. Basic Blue 4 (C.I. 51004), 0.34 part of C.I. Basic Violet 14 (C.I. 42510) and 0.95 part of C.I. Basic Green 1 (C.I. 42040) in 96 parts of an 80% aqueous pyridine solution in a glass-lined steel vessel and is heated to boiling. Acid-modified polyester fabric is stirred in the boiling solution for a period of time between 15 seconds and 5 minutes. The fabric is then taken out of the dyebath, rinsed with water until free of excess dye solution, and scoured for 5 minutes with a surface-active solution as in Example 1. The resulting dyed fabric is deeply and evenly colored black, the depth of shade increasing with the length of the dyeing period.

It will be noted, by contrast, that presently accepted carrier dyeing procedures for the production of black shades on acid-modified polyester fibers require dyeing times of two hours.

It will be noted further that complete solubility of the cationic dye in the aqueous pyridine base is not necessary for rapid and level dyeing according to this invention. A continuous dyeing method is therefore possible, by passing the fabric through a hot dyebath in which the dye-loss, due to exhaust, is compensated for by maintaining the concentration of the dye at the saturation point and regulating the depth of shade by the residence time of the fabric in the dyebath.

The process of this invention may also be readily applied by a pad-steam method, and illustrated by the following example.

Example 7

A dyebath is prepared by dissolving 1.2 parts of the oxazine dye identified in Example 1 in 100 parts of a 10% aqueous solution of 3-picoline. Acid-modified polyester fabric is immersed into the solution at room temperature for about 1 to 5 minutes, or for a period of time sufficient to achieve complete wetting of the fabric by the dye solution. The fabric is then removed, squeezed free of excess solution, and steamed for an optional period, ranging from 15 seconds to 5 minutes. Light to medium level blue shades are obtained.

In manners similar to the above examples, other cationic dyes may be applied to acid-modified acrylic and polyester fibers to produce thereon rapid dyeings in deep shades. In particular, any of the following classes of dyes or mixtures of any two or more thereof may be used successfully:

N-alkylated triamino triarylmethanes, for instance
- Fuchsine (Lubs, p. 272),
- Malachite green (Lubs, p. 274),
- Brilliant green (Lubs, p. 276),
- Paraosaniline (Lubs, p. 278), or
- Methyl violet B (Lubs, p. 279);

Xanthene dyes, for instance rhodamine B (Lubs, p. 291);

Methine dyes, for instance astrazone yellow 3G (Lubs, p. 250);

Oxazine dyes, for instance the blue dye obtained by reacting 5-diethylamino-2-nitroso-p-cresol hydrochloride with m-phenylenediamine;

Anthraquinone dyes having pendant cationic groups, for instance those described in U.S.P. 2,153,002 and 2,737,517;

Cationic azo dyes, for instance those set forth in U.S.P. 2,821,526;

Quaternized derivatives of the reaction product of a nitrogen-containing heterocyclic hydrazine compound with an aromatic phenol, amine, and enol or indole, for instance those described in U.S.P. 2,832,764; and

Cationic dyes for monazo derivatives of benzothiazole coupled to an aminobenzene compound, such as those set forth in U.S.P. 2,889,315.

In general, all types of cationic dyes may be used. The less soluble dyes are solubilized in the aqueous pyridine system, rendering the process adaptable to the use of dyes heretofore deemed unsatisfactory in the known aqueous carrier systems. Sparingly soluble cationic dyes may be used in the form of dispersions in the aqueous pyridine bases.

It will be understood that the details of the above examples may be varied within the skill of those engaged in this art. Thus, while boiling temperatures have been indicated in most of the examples, other temperatures in the vicinity of the boiling point are useable, for instance 80° to 105° C. The preferred concentration of pyridine base is 80 to 90% by weight where the dye is a composite one, containing components of different colors. Otherwise, a concentration of 5 to 50% by weight in sufficient, with a preferred range of 10 to 25%.

The principal advantages of my novel process have already been pointed out. In addition, the dyeing process of this invention is adapted for using unstandardized dyes, that is, dyes to which no additives have been incorporated, such as dispersing agents, surfactants or standardizing agents. The process of the invention also makes it unnecessary to add carriers, leveling agents or dispersing agents to the dyebath.

I claim as my invention:

1. The method of accelerating the dyeing of textile fiber of the group consisting of acid-modified polyester fiber and acid-modified acrylic fiber with a cationic dye from an aqueous bath, which comprises effecting the dyeing in the presence of a liquid pyridine base.

2. In a process of dyeing textile fiber from an aqueous bath with cationic dyes, said fiber being selected from the group consisting of acid-modified polyester fiber and acid-modified acrylic fiber, the improvement which comprises incorporating in said dyebath a liquid pyridine base of the group consisting of pyridine and its homologs in quantity sufficient to form an aqueous solution thereof of 5 to 90% concentration, and applying said dyebath

to the fiber at a temperature between 80° and 105° C. and for a time period of a few seconds to 15 minutes.

3. In a process of dyeing textile fiber from an aqueous bath with cationic dyes, said fiber being selected from the group consisting of acid-modified polyester fiber and acid-modified acrylic fiber, the improvement which comprises dissolving said cationic dye in an aqueous solution of a liquid pyridine base of 5 to 50% concentration, and applying said dyebath to the fiber at a temperature of 90° to 105° C. and for a time period of 15 seconds to 5 minutes.

4. A process of dyeing a fiber of the group consisting of acid-modified acrylic fiber and acid-modified polyester fiber with a composite cationic dye which contains components of different colors, which comprises dissolving said composite in an aqueous solution of a pyridine base of 80 to 90% strength, and stirring the fiber in said

bath at a temperature of 80° to 105° C. for a period of time in the range of 15 seconds to 5 minutes.

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