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PROCESS FOR COLORING HYDROPHOBIC FIBER

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1

This invention relates to an improved process for coloring heat-stable, hydrophobic textile fiber such as nylon, polyacrylonitrile fiber, and polyethylene terephthalate fiber. These fibers are well known for their relatively hydrophobic nature; that is an aqueous treatment bath may wet the fibers superficially but has difficulty penetrating the inside of the fiber. As a result of this behavior it is very difficult to color such fibers either by water-soluble dyes or by water-insoluble dyes and pigments, inasmuch as the applied color remains on the surface and is readily removed by the customary rinsing or soaping operations which follow impregnation in the dyeing art. Also, some fibers, especially nylon, have a tendency to produce uneven, streaky dyeings.

It is an object of this invention to provide an improved process for coloring fiber of the foregoing nature whereby to produce strong, even dyeings, well penetrated into the fiber and of good fastness qualities. It is a further object of this invention to provide an improved process as aforesaid, which is adapted for continuous dyeing, that is the dyeing of fabric or yarn off a continuous roll by such methods as padding or printing. Additional important objects of this invention will appear as the description proceeds.

My improved process consists essentially of impregnating the fiber by padding or printing with an aqueous suspension or solution of the selected coloring material (that is, dye, intermediate for dye or pigment), drying the impregnated fiber and then giving it a dry heat treatment at a temperature of between 180° and 230° C. (or in some cases even as high as 250° C.) for a brief interval of time, usually less than 1 minute, and more often of the order of 20 to 40 seconds or even merely 5 seconds. I find that this heat treatment in some manner causes the color particles deposited on the surface of the fiber to penetrate the same, probably by some sort of a solution process, and to distribute the color evenly over the cross section of the fiber. The result is not merely an improved fastness of the color to washing and crocking, but in the case of some fibers, particularly polyethylene-terephthalate fiber there is frequently a surprising improvement in fastness to light. Furthermore, the coloration is generally much stronger than achievable by mere superficial dyeing, and its levelness or uniformity is excellent.

Furthermore, I find that in lieu of the finished dyestuff or pigment I often may employ intermediates adapted to yield the desired coloring compound upon heating. For instance, I may impregnate the fiber with a soluble vat dye

2

(which is usually a salt of a leuco-ester). Then in the heating step the leuco salt becomes converted to the oxidized or keto form. Or again, I may pad the fiber with the components of an azo dye, for instance an azoic coupling component and an aryl amine and subject the impregnated fiber, after drying, to a heat treatment as above described, to effect penetration of the components into the fiber. When the fiber is then treated with an aqueous diazotizing bath, with or without subsequent alkalization (cf. British Patent No. 629,452), an azo dye is formed within the fiber.

Also, where the fiber is of a nature that it requires or is benefited by a heat treatment, such treatment may be combined and achieved simultaneously with the foregoing heat treatment according to this invention. For instance, in the case of nylon fiber or polyethylene terephthalate fiber, the customary setting operation may be achieved simultaneously with the heat treatment for fixing the color according to this invention.

Because of the relatively drastic heat treatment (180° to 230° C.), my invention is naturally limited to such fibers as are capable of withstanding such high temperatures without injury. This rules out, for instance, cellulose acetate, which becomes stiff when heated above 180° C. For the purpose of this specification, therefore, the term heat-stable is to be construed as implying a capacity to withstand a temperature of at least 180° to 230° C. for an interval of time not exceeding 1 minute, without injury to the fiber. Fibers which will withstand higher temperatures or longer intervals of exposure obviously are also well fitted to be treated according to this invention.

The exposure to heat may be achieved in any available apparatus suitable for supplying dry heat at the temperature interval of 180° to 250° C. For operating on a continuous fabric or yarn, a heated drum will naturally be the most convenient form. Other methods, however, may be resorted to, for instance passing the fabric through a molten metallic bath (such as Cerrobend, a low-melting lead alloy), through a flue drier, or under infra-red radiation.

Following the heat treatment, the fabric is preferably subjected to a soaping operation to remove any residual, loosely adhering, superficial pigment particles. The fiber is then rinsed and dried.

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

Some of these examples report actual runs in

3

the laboratory to test the chemical validity of the process. Because of the laboratory scale of the test, the experiments were done on a limited quantity of fabric by a batch process, and the heating was done in most cases by apparatus best suited for laboratory-scale operation (e. g. a flue drier). The adaptability, however, of the process in each instance of being converted into continuous operation on a plant scale (using apparatus appropriate for plant scale operation) is obvious from the short period of time required for the heat treatment.

Example 1

20 parts of a commercial 10% paste of the violet anthraquinone dye, C. I. 1161, and 80 parts of water were stirred together at 60° C. until the dye was completely dispersed.

A strip of polyethylene terephthalate fabric was then padded with the above dispersion in usual manner (i. e. by feeding the fabric through the aqueous bath and then through squeeze rolls to a pick-up of 20%), dried and then passed slowly through a flue drier maintained at 230° C., the rate of feed being regulated to give an exposure time of forty seconds. The fabric was then soaked for five minutes at 82° C. in a solution containing 5 g./l. of sodium oleate. A medium red-violet shade was obtained which exhibited very good washing-, light- and crocking-fastness. When the fiber was cross-sectioned, it was found that the color had penetrated the fiber completely. In contrast to this, dyeings prepared with a similar dispersion of this color but without subsequent heating according to this invention produced essentially no coloration even after prolonged boiling.

In a similar manner, fast, uniform and strong dyeings of shades as indicated were obtained on polyethylene terephthalate filament with the following colors:

Color Employed	Shade obtained
Vat Red, C. I. 1162.....	red.
Vat Violet, C. I. 1104.....	violet.
Vat Blue, C. I. 1099.....	blue.
4,4'-dimethyl-6,6'-dichloro-thioindigo (U. S. P. 1,243,171, Example 3.)	brilliant pink.

Example 2

A 2% aqueous dispersion of 4-nitro-9(10)-acridone, prepared by the aid of 0.2% sodium oleate and warming at 60° C., was padded onto a polyethylene terephthalate fabric. The fabric was dried and then passed between two metal surfaces maintained at 180° C., in such a way that the exposure time was five seconds. The fabric was soaked as described above. There was produced a bright yellow dyeing showing excellent crocking-, washing- and light-fastness. Penetration of the fiber was found to be 100%.

Other colors giving equally good results by the same procedure were:

Color Employed	Shade Obtained
4-(4'-nitro-phenylazo)-aniline.....	Orange.
N-ethyl-N-hydroxyethyl-4-(4'-nitro-phenylazo)-aniline.....	Red.
1,4-diamino-anthraquinone.....	Violet.

Example 3

A 3% aqueous dispersion of 4-nitro-9(10)-acridone, prepared as above, was padded onto polyethylene terephthalate tow and then dried. It was then passed continuously between two metal

4

surfaces maintained at 225° C. in such a way that the exposure time was 20 seconds. The tow was soaped for 5 minutes at 82° C. with 5 g./l. sodium oleate solution. A bright yellow dyeing was obtained which exhibited excellent crocking-, washing- and light-fastness. Preparation of the fiber was 100%.

A similar dyeing is obtained using raw stock instead of tow by the above procedure.

Example 4

A 5% dispersion of 1,4,5,8-tetra-amino anthraquinone, prepared as above, was padded onto a modified polyethylene terephthalate fiber, in the manufacture of which 5 mol percent of the ethylene glycol had been replaced by diethylene glycol. The fabric was dried and then passed continuously between two metal surfaces maintained at 220° C. in such a way that the exposure time was 20 seconds. The fabric was soaped as described above. A heavy blue shade was obtained which was equivalent in strength and fastness to a similar dyeing on polyethylene terephthalate fiber.

Example 5

2-nitro-diphenylamine-4-sulfonamide was applied to polyethylene terephthalate fiber by padding a 5% dispersion of the dye in water, drying, passing continuously between two metal surfaces maintained at 220° C. in such a way that the exposure time was 20 seconds, and finally soaping as in Example 3. A bright yellow shade was obtained which exhibited excellent light-, washing- and crocking-fastness. Penetration of the fiber was 100%.

Other dyes applied by the same procedure were:

Color Employed	Shade Obtained
α-2'-nitro-4'-tolylazo-acetoacetanilide.....	Yellow.
The dye made according to Example 35 of U. S. P. 2,212,928 by using 1-amino-4-anilino-anthraquinone as starting material.....	Scarlet.
The nickelized azo dye from o-hydroxy-aniline and 1-phenyl-3-methyl-5-pyrazolone.....	Yellow.

Example 6—Mixed pigments

A suspension containing 3 grams of 1-nitro-acridone and 2.4 grams of vat violet (C. I. 1161) in 100 cc. of water was prepared as in Example 1. Polyethylene terephthalate fabric was impregnated with this dispersion by padding and then dried. It was then passed through a flue drier, maintained at 220° C., in such a way that the exposure time was thirty seconds. The fabric was soaked for five minutes at 82° C. with 5 g./l. sodium oleate solution. In this way a medium orange-brown shade was obtained which had very good washing-, light- and crocking-fastness. Penetration of the fiber was 100%. The acetate dye and vat dye have been proven to be completely miscible by the method of this invention.

Example 7—Printing

A paste containing the following was prepared:

	Parts
Vat Yellow, C. I. 1132.....	10
Water.....	26
"Pine Solvent XX" (pine oil and emulsifying agent).....	4
"Keltex" (a sodium alginate).....	60
Total	100

5

Polyethylene terephthalate fabric was printed with this paste and dried. It was then passed continuously between two metal surfaces maintained at 225° C. in such a way that the exposure time was forty seconds. The fabric was soaped as described above. A yellow print was obtained which was very much brighter and stronger than a similar print by standard printing methods.

Other colors applied by the same procedure were:

Color Employed	Shade Obtained
Vat Violet, C. I. 1104.....	Violet.
Copper Phthalocyanine Green, Pr. 483.....	Green.
Vat Red, C. I. 1212.....	Red.
4,4'-dimethyl-6,6'-dichloro-thioindigo.....	Brilliant pink.

Example 8

A 1% solution of anilide of beta-oxy-naphthoic acid in "Cellosolve" (ethylene glycol monoethyl ether) was padded onto polyethylene terephthalate fiber and dried. A 5% solution of m-nitro aniline in 95% ethanol was over-padded on the above padding and dried. The fabric was then passed between two metal surfaces maintained at 200° C. in such a way that the exposure time was 20 seconds. It was then treated for five minutes at 100° C. with a solution of 3 g./l. sodium nitrite and 3.7 g./l. hydrochloric acid. A medium orange shade was obtained which exhibited excellent crock-fastness.

The same fiber was also dyed by the same procedure except for selecting different amines, with the following results:

Amine Selected	Shade Obtained
2-nitro-p-toluidine.....	Red.
4,4'-di-o-anisidine.....	Violet.

It will be clear from the above examples that my invention is applicable with a wide variety of pigments and dyestuff or, indeed, with organic substances which are not dyestuffs per se but are convertible into dyestuffs when heated by themselves or in the presence of oxidizing agents. Of particular interest, however, are the water-insoluble organic coloring materials such as vat dyes (including in this term vat dyes of the anthraquinone, indigo and thioindigo series), cellulose-acetate dyes, azo dyes, metallic azo dyes and phthalocyanine pigments.

Not all of these dyestuffs are applicable with equal advantage to all classes of hydrophobic fiber. Thus, vat dyes are of special interest in connection with polyethylene terephthalate fiber; cellulose-acetate dyes and leuco-esters of vat dyes are preferred for polyacrylonitrile fiber; acid dyes, metallized azo dyes and cellulose-acetate dyes are preferred for nylon. Sulfur dyes and some basic dyes may be applied satisfactorily to all fibers. But in all cases, heat-treatment according to my invention produces important unforeseen advantages and improvements, even though the nature of the gain may depend on the particular combination of fiber and color under consideration.

Thus, polyethylene-terephthalate fiber becomes dyeable with vat pigments, with essentially complete penetration. By the orthodox dyeing methods this fiber cannot be dyed with vat pigments at all. When using cellulose-acetate dyes on the mentioned fiber, some degree of penetration is possible by the ordinary aqueous disper-

6

sion method; but my novel method gives highly improved penetration and achieves a given depth of shade in a much shorter time. Combining the two advantages, polyethylene terephthalate fiber may also be dyed by mixed pigments, for instance a mixture of a vat color and a cellulose acetate dye, according to this invention.

To summarize all the above, the practice of my invention achieves a broadening of the base of applicable colors in the case of some fibers, improved penetration and stronger dyeings in other cases or in the case of certain colors, faster fixation in nearly all cases, and improved levelness in the case of nylon when dyed with acid wool colors.

Finally, it is well known that nylon generally requires a heat-setting treatment to set the fiber. Polyethylene terephthalate fiber is also improved by heat-setting to produce a non-shrinking fabric. In ordinary practice, this operation requires special handling in a special setting of apparatus. By the process of my invention, however, this extra operation may be dispensed with, since it is possible to achieve both dyeing and heat-setting in one continuous operation.

The above examples illustrate the fact that heating periods of less than 1 minute will generally suffice to effect penetration and fixation of the color. This is a very important factor, because it is on this short heating period that the adaptability of my process to be used in continuous plant-scale operation depends. Thus, certain attempts have been made in the art heretofore to cause fixation of color on certain fibers by heating. U. S. Patent No. 2,080,254, for instance, suggests a heating period for the dyeing of cellulose acetate. But because cellulose acetate fiber cannot be heated to a temperature over 180° C. without damage to the fiber, and because the mentioned process demanded very long heating periods (15 minutes), its application to continuous dyeing on a plant-scale was out of question, and the process has, to the best of my knowledge, not found any practical application in the industry.

Notwithstanding all the foregoing, my invention is not limited to a heating period of 1 minute, inasmuch as I find that the fibers herein dealt with will withstand the prescribed range of temperature for considerably longer periods. It is therefore possible to practice my invention with a longer heating period, up to 2 or even 3 minutes, provided the system of apparatus available is such as to make continuous operation under these conditions economical.

The fibers to which my invention is applicable is any synthetic fiber which can withstand temperatures of 180° C. or over. Nylon, polyethylene terephthalate and acrylonitrile fibers have already been mentioned. But this invention may be applied also to modified or plasticized variations of such fibers; for instance, linear polyesters of ethylene glycol and terephthalic acid which have been modified by the addition of up to 10% of other glycols and/or dibasic acids; and polyethylene terephthalate which is mixed with other materials such as plasticizers, modifiers, etc. These fibers are all well known in the literature, and many of them are common commercial products. See for instance, Carothers, U. S. P. 2,071,250, 2,071,253 and 2,130,948; and Whinfield et al., U. S. P. 2,465,319.

My invention is of particular interest in connection with melt-spun hydrophobic fiber, that is, nylon, polyethylene-terephthalate fiber, and

the aforementioned modified forms of the latter. These fibers have the property in common of being rather difficult to dye uniformly in filament form; they also have the further property in common of requiring or being benefited by a heat-setting treatment, as hereinabove mentioned.

I claim as my invention:

1. A process for continuously coloring polyethylene terephthalate fiber, which comprises impregnating the same continuously with an organic coloring material from an aqueous medium, drying continuously the impregnated fiber and then exposing the same continuously to dry heat at a temperature between 180° and 230° C. for a period of 5 to 60 seconds, whereby to effect fixation of said coloring materials on the fiber and uniform distribution thereof within the fiber.
2. A process as in claim 1, the impregnation being effected by padding the textile fiber in an aqueous suspension of said coloring material.
3. A process as in claim 2, followed by soaping of the fiber to remove superficially disposed surplus coloring material.
4. A process as in claim 1, the coloring matter being an anthraquinone vat dye.
5. A process as in claim 1, the coloring matter being a thioindigoid vat dye.
6. A process as in claim 1, the coloring matter being a cellulose-acetate dye.
7. A process for coloring a continuous length of fabric made from polyethylene terephthalate fiber, which comprises impregnating continuously fresh portions of said fabric with an aqueous suspension of a water-insoluble, organic coloring matter at a temperature not exceeding 60° C., drying continuously the impregnated portions and then exposing continuously the dried portions to dry heat at a temperature between

180° and 225° C. and for a period of time from 20 to 60 seconds, whereby to effect penetration of said coloring matter into the fiber, and continuously soaping the treated portions to remove superficially disposed surplus coloring matter.

8. A process for coloring polyethylene terephthalate fabric, which comprises printing the same with an aqueous printing paste comprising an organic coloring material, drying the printed fabric, heating the dried fabric at a temperature between 180° and 230° C. for a period of 20 to 60 seconds to effect fixation of the color upon the fabric, and then washing the fabric to remove surplus color and the water-soluble printing paste ingredients.

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