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COMPOSITION AND PROCESS FOR DYEING POLYETHYLENE TEREPHTHALATE FIBERS

Hans Luttringhaus, Chatham, N. J., and Alex Anthony Arcus, Bellerose, N. Y., assignors to General Dyestuff Corporation, New York, N. Y., a corporation of New York

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The invention relates to a composition and improved process for producing fast dyeings on polyethylene terephthalate fibers.

The aromatic polyesters with which the present invention is concerned are the highly polymer esters obtained by heating glycols of the series $HO(CH_2)_nOH$, where n is an integer from 2 to 10 with terephthalic acid or with an ester-forming derivative thereof, for example, an aliphatic (including cycloaliphatic) or aryl ester or half-ester, an acid halide or ammonium or amine salt, under conditions which yield the esters in a highly polymerized condition. Examples of such highly polymeric linear esters are those obtainable from terephthalic acid or an ester-forming derivative thereof and ethylene glycol, trimethylene glycol, tetra, hexa, and decamethylene glycol. These polyesters are highly melting, difficultly soluble, colorless or substantially colorless, materials, which can be formed into filaments which can be extended by drawing into strong flexible fibers, showing by characteristic X-ray patterns, molecular orientation along the fiber axis. Of these polyesters, polyethylene terephthalate is preferred on account of its availability and its outstanding utility as a textile material. A commercial type, known as "Fiber V" is manufactured by the duPont Company.

Polyethylene terephthalate is not easily dyed by ordinary dyeing methods. Some of the methods which have met with some success include the application of vat dye pigment followed by treatment with high temperatures, such as 350° F. Another method which has been used involves the application of acetate colors at 212° F. in the presence of a carrier such as benzoic or salicylic acid. The function of the carrier is to promote the exhaust of the dyestuff on to the fabric. The use of carriers may permit the dyeing at lower temperatures than is possible in the absence of the carrier. This is practically impossible where dyeings would otherwise be required to be carried out at temperatures substantially above boiling because the usual equipment is not designed for dyeing above boiling temperatures. The results obtained with benzoic acid have been satisfactory only to a limited degree.

It is therefore an object of the present invention to provide an improved process for dyeing polyethylene terephthalate.

It is a further object of the present invention to provide a process for dyeing polyethylene terephthalate in deep fast shades.

It is a further object of the present invention to provide a process for dyeing polyethylene terephthalate deep fast shades with acetate or vat dyes.

It is a further object of the present invention to provide an improved process for fast dyeing

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polyethylene terephthalate by utilizing a new dye bath composition.

These and other objects are attained by the present invention which comprises a composition of an acid-vat dye or an acetate dye, a carrier selected from the group consisting of xylene, naphthalene, chlorobenzene, orthodichlorobenzene, and trichlorobenzene, and an emulsifying agent. The invention further relates to a process of dyeing polyethylene terephthalate by combining these ingredients in an aqueous dye bath and dyeing at temperatures in the range 165 to 212° F.

Since the carriers are hydrophobic, emulsifying agents are employed to make them dispersible in water. Any of a very wide variety of emulsifying agents may be used. Those which have been found particularly useful include sulfonated castor oil, triethanolamine stearate, alkyl or aromatic sulfonate, and polyalkoxy alkyl phenol. Such emulsions, however, should have only a limited stability in water at higher temperatures. If the affinity between the carrier and emulsifier is greater than the affinity between the carrier and the fiber the depth of the shade will be influenced adversely.

With the help of such composition, it is now possible to produce shades several times heavier and brighter than could be obtained heretofore with acetate colors. While only weak or medium shades could be obtained with carriers suggested heretofore, we are now able to produce shades of any desired depth and brightness. It should be especially noted that with our method for the first time a black on polyethylene terephthalate can be produced, even at temperatures below boiling.

Dyeings with the new carriers are not only deeper and brighter, i. e. they show a higher chroma, but they also show the important feature of a completely penetrated single fiber. Microscopical studies have shown that carriers so far only could produce a ring dyeing. Since our new methods produce excellent penetrations, we can produce superior fastness properties. Acetate dyes applied to polyethylene terephthalate with our new carriers show in the deepest shades an excellent fastness to crocking. They also are fast to acid and alkaline perspiration, fast to four and one-half hours of fulling, and even fast to wash test No. 4 of AATCC which constitutes a washing at 185° F. in the presence of soda ash and chlorine. Such fastness properties are very unusual for acetate colors and could not be expected by anyone familiar with these types of dyestuffs.

Furthermore, we have found that we can dye mixtures of polyethylene terephthalate and wool with the help of these compositions in such a way that minimum of acetate colors is precipitated on the wool. This is of great importance

since acetate colors on wool do not possess any wet fastness properties at all and crock to an objectionable degree. Since the new assistants carry the acetate colors almost entirely to polyethylene terephthalate, the entire piece will show fastness properties that are required for men's wear after the wool is cross dyed with suitable dyestuffs. Considering the physical properties of polyethylene terephthalate, our new dyeing method makes the manufacture of high class sportswear possible for any mill with regular dyeing equipment, while such mills heretofore only could use polyethylene terephthalate in the undyed state.

Furthermore, we have been successful in producing a new dyeing method for vat colors on polyethylene terephthalate with our new dye composition. When we added emulsions of the above-mentioned carriers to a dyebath at 80–100° F., we found that the original turbidity of the bath disappeared increasingly with time and also with increasing temperature. The affinity of the new carriers to polyethylene terephthalate was so great that all of the carrier exhausted on polyethylene terephthalate when the emulsion was prepared correctly. When such a dyebath was a regular alkaline vat prepared with caustic soda and sodium hydrosulfite, the dyestuffs in general did not exhaust on polyethylene terephthalate. When, however, the solubility of the vat color was reduced by the addition of an acid, we found that the solubility of the free acid of the leuco compound had a greater solubility in the new carriers than in water. Thus we succeeded in concentrating the acid leuco compound in our composition that had exhausted on polyethylene terephthalate. The composition in turn carried the vat dyestuff into the very center of the fiber. The exhaustion could be regulated with acid and temperature. Thus we succeeded in dyeing polyethylene terephthalate with vat colors at temperatures of 165–200° F. which could not be accomplished so far.

The following examples illustrate preferred embodiments of the invention, but it will be understood that variations and modifications may be made within the scope of the claims:

Example 1

100 parts by weight of polyethylene terephthalate piece goods were immersed in 4,000 parts of water containing 20 parts xylene, dispersed with 2 parts of a sulfonated castor oil, at room temperature. After 15 minutes 2 parts of a blue acetate dye comprising a lower 1,4-dialkylamino anthraquinone was added and the temperature was raised slowly to 180° F. The temperature was kept at 180° F. for 30 minutes and was raised then to 205° F. After 20 minutes a deep, bright blue dyeing was obtained, which surpassed by far a corresponding dyeing carried out with benzoic acid, which so far has been recognized and accepted as the best carrier. A comparative measurement carried out with a spectrophotometer with automatic tristumulus integrator attachment established the following Munsell notations, which clearly show the improved strength and brightness of our dyeing:

Benzoic Acid	Xylene
2.9 PB 4.0/6.8	4.9 PB 3.1/8.1

Visually this would amount to about 2.5 to 3 times the strength.

Example 2

100 parts by weight of polyethylene terephthalate tricot were entered into 4,000 parts of water containing 20 parts monochloro-benzene, dispersed with 2 parts of a sulfonated castor oil at 90° F. After 15 minutes 2 parts of a blue acetate dye comprising 1,4,5,8-tetraamino anthraquinone was added and the temperature was raised slowly to 180–190° F. The temperature was kept at 180–190° F. for about 30 minutes and was raised then to about 205° F. After 20 minutes a deep blue was obtained which appeared about 5 times stronger visually than a corresponding dyeing carried out with benzoic acid. The Munsell notation measured and calculated as in Example 1 shows the extent of increase in depth and brightness.

Benzoic Acid	Monochloro-benzene
2.1 PB 4.6/4.4	3.4 PB 2.76/5.6

Example 3

240 parts by weight of polyethylene terephthalate in top form were dyed in 5,120 parts of water containing 48 parts of dispersed monochlorobenzene and a mixture of 9 parts of a brown acetate dye comprising 2,6-dichloro-4-nitro-4'-(N,N - hydroxyethylmethyl) amino-azobenzene and 3 parts of the blue dye of Example 1. The temperature was slowly raised to 185° F. and kept at 185° F. for 45 minutes. Then the temperature was raised to 205° F. and kept there for 30 minutes. After the material was rinsed a dark brown perfectly penetrated top was obtained. The dyeing was fast to a No. 3 washing for wool of the AATCC, fast to 4.5 hours fulling, fast to perspiration, fast to light and therefore suitable for men's wear.

Example 4

100 parts by weight of polyethylene terephthalate in top form were treated in 4,000 parts of water containing 20 parts monochloro-benzene, dispersed with 2 parts of a sodium petroleum sulfonate. 3% of a scarlet acetate dye comprising 4-nitro-4'-(N,N hydroxyethyl-ethyl) amino-azobenzene on the weight of the polyethylene terephthalate were added and dyed at 185° F. for 30 minutes. Then the temperature was raised to about 205° F. and kept at 205° F. for 15 minutes. The resulting dyeing was a deep scarlet shade. The Munsell notation measured and calculated as in Example 1 shows the large increase in depth and brightness compared with benzoic acid. The depth obtained this way could never be reached with any amount of color in the presence of benzoic acid.

Benzoic Acid	Monochloro-benzene
7.5R 4.2/9.4	6.6R 3.30/10.4

Example 5

100 parts by weight glove material of polyethylene terephthalate were treated in 4,000 parts of water containing 20 parts monochloro-benzene emulsified with 3 parts of a polyalkyl ether of an alkylated phenol, 10% of a navy blue acetate dye and 2% of an orange acetate dye (4,4'-diamino-azobenzene) were added to the bath, the temper-

ature was raised to 180° F. for 45 minutes. Then the temperature was raised to 205° F. and kept there for 20 minutes. The polyethylene terephthalate was dyed to a full black shade.

Example 6

100 parts by weight polyethylene terephthalate in top form were treated at 110° F. for 10 minutes in 4,000 parts of water containing 20 parts monochloro-benzene emulsified with two parts of a sulfonated castor oil. Then an alkaline vat of 10 parts of Indigo were added. While the temperature was raised slowly to about 160° F., the alkaline vat was gradually acidified with acetic acid. As the conversion into the acid vat proceeded, the dyestuff started exhausting and could be exhausted completely with mineral acids. The monochloro-benzene was removed by heating the bath up to 205° F. The vat dyestuff was oxidized on the fiber with sodium nitrite in the presence of acid. A bloomy navy blue was obtained which had excellent fastness properties.

Example 7

10 parts by weight polyethylene terephthalate staple fiber was treated in 400 parts of water with 2 parts dichlorobenzene dispersed with 0.2 part of a sulfonated castor oil. Then an alkaline vat of 1 part Indanthrene Brilliant Green B (Color Index 1101) was added to the bath, the temperature was raised to 160° F. and acetic acid was slowly added to obtain gradually the acid vat. Then the temperature was raised to 205° F. and kept there for 20 minutes. After oxidation with sodium nitrite in the presence of acid, a bright and fast full shade of green was obtained.

Example 8

10 parts by weight polyethylene terephthalate in top form was treated in 400 parts of water containing 2 parts of a mixture of 1 part naphthalene and 1 part xylene emulsified with a polyalkyl ether of an alkylated phenol. Then the bath was acidified and an alkaline vat of 1 part Helindon Red BBD (Thioindigo, Color Index 1207) was added converting thus the alkaline vat into an acid vat. Then the temperature was raised to 160° F., kept at 160° F. for 30 minutes, then raised to 200° F. and kept at 200° F. for 20 minutes. After oxidation with sodium nitrite and acid, a brilliant red shade was obtained which had excellent fastness properties.

Example 9

10 parts by weight polyethylene terephthalate in top form was treated with 2 parts of a mixture of 1 part monochloro-benzene and 1 part trichloro-benzene emulsified with 0.2 part of a polyalkyl ether of an alkylated phenol. Then an alkaline vat of 1 part Indanthrene Golden Orange GA (Color Index 1096) was added and slowly acidified while the temperature was raised to 160° F. After the material had been dyed at 160° F. for 30 minutes, the bath was exhausted with acid while the temperature was raised to 205° F. and kept at that temperature for 20 minutes.

Example 10

100 parts by weight of a fabric containing 50% wool and 50% polyethylene terephthalate were treated in 5,000 parts of water containing 20 parts of monochloro-benzene emulsified with a sulfonated castor oil. A mixture of 3% of the brown acetate dye and 1% of blue acetate dye as in Example 3 was added, the temperature was

raised to 170° F., kept at 170° F. for 30 minutes and then raised to 205° F. for 15 minutes. The material was then washed off and cross-dyed with metallized dyes in the presence of 8% sulfuric acid. Thus a dark brown solid shade, standing the requirements of men's wear fastness properties, was obtained.

Example 11

10 parts by weight of a fabric containing 50% wool and 50% polyethylene terephthalate were treated in 500 parts of water containing 2 parts of monochlorobenzene emulsified with a sulfonated castor oil. The bath was acidified and 1 part of an alkaline vat of Indanthrene Brilliant Green B (Color Index 1101) was added and thus converted into the acid vat. The temperature was raised to 160° F. and dyeing was continued at 160° F. Then the temperature was raised to 205° F. and kept at 205° F. for 20 minutes. The material was washed off, oxidized and the undyed wool was topped with Alizarine Cyanine Green G (Color Index 1078) to a solid shade.

While the proportions of the ingredients in the above examples may be varied, the dispersing agent is usually present in the range .5 to 2 parts for each 10 parts of carrier and preferably one part for each 10 parts of carrier. The dye may be varied widely but is generally in the range .5 to 5 parts of carrier. The acetate dyes are preferably about one part to each 10 parts of carrier, and the vat dyes preferably about 5 parts to each 10 parts of carrier.

We claim:

1. A composition for dyeing polyethylene terephthalate fibers which comprises an acid-vat dye, a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene, and trichlorobenzene, and a dispersing agent therefor.

2. A composition for dyeing polyethylene terephthalate fibers which comprises an acid-vat dye, 20 parts of a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene, and trichlorobenzene, and .5 to 2 parts of a dispersing agent therefor.

3. A composition for dyeing polyethylene terephthalate fibers comprising from .5 to 2 parts of an acid-vat dye, 20 parts of a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene, and trichlorobenzene, and from .5 to 2 parts of a dispersing agent therefor.

4. A composition for dyeing polyethylene terephthalate fibers comprising from .5 to 5 parts of an acetate dye, 20 parts of a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene, and trichlorobenzene, and from .5 to 2 parts of a dispersing agent therefor.

5. A process for dyeing polyethylene terephthalate fibers which comprises heating the fibers in an aqueous bath containing an acid-vat dye, a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene, and trichlorobenzene, and a dispersing agent for said carrier.

6. A process for dyeing polyethylene terephthalate fibers which comprises heating the fibers in an aqueous bath containing an acetate dye, a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene, and trichlorobenzene, and a dispersing agent for said carrier.

7. A composition for dyeing polyethylene terephthalate fibers which comprises an acetate dye, a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene and tri-

chlorobenzene, and a dispersing agent therefor.

8. A composition for dyeing polyethylene terephthalate fibers which comprises an acetate dye, 20 parts of a carrier selected from the group consisting of chlorobenzene, orthodichlorobenzene and trichlorobenzene, and .5 to 2 parts of a dispersing agent therefor.

HANS LUTTRINGHAUS.
ALEX ANTHONY ARCUS.

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