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PROCESS FOR DYEING POLYESTER ARTICLES

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This invention is an improved process whereby polyester articles may be more efficiently colored. More particularly, it relates to such a process for improving the efficiency of the dyeing and for providing such articles of improved lightfastness.

The coloring of synthetic man-made fibers and filaments is frequently beset by troublesome problems. These have not been eased by the increased use in recent years of finishing agents, such as stabilizing resins, water repellents, agents to improve wrinkle resistance, and others, which sometimes adversely influence dyefastness. Concurrently the demands have increased for improved fastness to washing, sunlight, dry cleaning, perspiration, ozone, and gas fumes, as well as to fibers and filaments having improved physical and chemical properties.

The polyesters, such as polyethylene terephthalate, are among the more difficult synthetic man-made fibers to color effectively. Dope dyeing is generally unsatisfactory performancewise in addition to the inherent disadvantages of that technique. Three general methods have been found to be suitable for dyeing polyester terephthalate. Aqueous dyeing with or without carriers at temperatures near the boil; aqueous pressure dyeing at elevated temperatures, and the "Thermosol" technique. All of these procedures require the use of elevated temperature and/or applied pressure. Regardless of the technique used, the dyes that have been found to be operable in coloring polyethylene terephthalate and other polyesters include the disperse dyes, such as azo and anthraquinone, the vat dyes and certain naphthanil dyes, and, more recently, certain of the cationic dyes. Most of the dyestuffs that have been found useful commercially are relatively expensive, are somewhat specific, and in general require careful selection for use with the polyesters.

Accordingly, it is the principal object of this invention to provide an improved process for coloring polyesters including polyethylene terephthalate.

It is a further object to provide such a process which results in increased dye pickup of the polyester article.

It is a still further object of the invention to provide such a process which will result in objects having increased colorfastness.

The above and related objects are accomplished in the process whereby an article composed of at least a characterizing amount of a polyester condensation of polymer is exposed to and contacted with a liquid dyebath containing as an essential constituent from 0.1 to 5.0 percent by weight of said article to be dyed of an agent selected from the group consisting of isobutyl o-(5-chlorosalicyloyl)benzoate; 5-chloro-2-hydroxy-4'-t-butylbenzophenone; 4-benzoyl-3-hydroxyphenyl salicylate; and 4-benzoyl-3-hydroxyphenyl stearate.

The present invention finds greatest utility with the filamentary articles prepared from polyester condensation polymers and such articles are accordingly preferred. In the fiber and filamentary form the commercially accepted products have generally been limited to polyethylene terephthalate. However, the present invention finds use with any dyeable polyester. By the term, characterizing amount, is meant that the filamentary article (or other article) be composed of sufficient polyester that the dyeing characteristics of the article are determined by the

polyester. Thus, fiber blends of polyesters with other natural or man-made fibers are utilizable.

The invention is applicable to dyeing raw stock, fiber, filament, fabric, yarns in rope form, sewing thread, and any other continuous, coherent articles, such as films and molded articles, which are formed from a characterizing amount of the stated polyester. In this specification and claims the term, article, is intended to connote all such shaped forms.

The invention is operable with all of the known processes and techniques for dyeing filamentary articles in which the article is brought into contact with a dispersion of the dyestuff. The nature of the dispersion will vary somewhat with the dyeing method or technique. For the present invention, however, the salient feature is that the dyebath or paste include one of the four indicated compounds as a protective screener.

The amount of the agent to be used should fall within the range of from about 0.1 to 5 percent of the weight of the article to be dyed. Preferably, the amount to be employed should fall in the range of from 0.5 to about 1.5 percent of the weight of filamentary article. Amounts of agent less than about 0.1 percent will usually be insufficient to assist in the dyeing and to improve the colorfastness. More than about 5 percent is wasteful of the protective screener.

Common to all of the known dyeing procedures useful with polyester filamentary articles is preparation of the article prior to the actual dyeing step. It is commonplace in the dyeing art to scour the filamentary article preparatory to dyeing to remove dirt, soil, stains, loom grease, sizings, finishing agents, etc. It is sometimes desirable to employ an additional pre-scour step in a bath of a surface-active agent together with other materials commonly used for this purpose. Included among these materials are sodium polyphosphate, sodium metasilicate, and carboxymethyl cellulose. A typical scouring bath might include equal parts of soap, a surface-active agent, and trisodium phosphate. Occasionally it is necessary to include an organic solvent in one of the scour baths. In such an event, great care must be exercised to remove all such solvents since these materials frequently affect the dyeing, as well as the dyefastness.

In the procedure utilizing aqueous dyebath at temperature above boiling, the filamentary article as a tow, skein, package, or other form is immersed in the dyebath which is then exhausted. The dyebath commonly is composed of the dye to be used, a small amount of an inorganic acid, a water-soluble colloidal material, such as carboxymethyl cellulose, a carrier, and, for the present invention, the protective screener. Each of the elements other than the protective screener of the dyebath is conventional in its chemical composition and in its proportion.

The procedure for dyeing at elevated temperature under applied pressure is similar to the above in that the filamentary article is immersed in the dyebath and the dyebath exhausted. The components of the dyebath and their proportion are conventional and will be known to the skilled worker. As with the previous technique, the protective screener should be dispersed directly into the dyebath.

Another procedure useful with the polyesters is the "Thermosol" technique. This is described in the American Dyestuff Reporter, 42, pages 1 to 2 (1953). In this procedure the dyestuff is formed into a paste dispersion which is padded onto the filamentary article, the padded article subjected to both elevated temperature and relatively high pressure, and the paste then removed.

Following the dyeing step, it is commonplace and conventional in the dyeing art with all dyeing procedures to scour the filamentary article to remove excess dyestuff and any other undesirable materials.

The dyeing of films, molded articles, and other non-filamentary shaped forms is achieved in similar manner to any of these described above. In such cases the time to achieve dyebath exhaustion and other conditions may have to be altered slightly. However, the improvement of this invention will result in equal benefits and advantages to those noted for the filamentary articles.

The present procedural improvement results in improved dyebath exhaustion and dye penetration and in improved colorfastness of the filamentary articles over a comparable process omitting the protective screener. These benefits and advantages, as well as others, will be illustrated with the following example wherein all parts and percentages are by weight.

EXAMPLE

The utility of the compounds of this invention were evaluated as protective screeners and as dye assistants in the dyeing of a polyester fabric. The fabric used in all cases was a polyethylene terephthalate sold commercially as "Dacron." Test specimens of approximately 5 inches wide by 7 inches long were cut from the fabric. These test specimens weighed 3.5 grams on the average. The dyes employed were Sevron Orange G (CI 48,035), Sevron Blue 5G (CI 51,004), Basic Fuchsin (CI 42,500), and Brilliant Green Crystals (CI 42,040). Employed as the protective screeners and dye assistants were the compounds of this invention and, for comparison, monobenzoyl resorcinol monobenzoate and 2,2'-(dihydroxy)-4,4'-(dimethoxy)benzophenone sold commercially as Uvinul D-49.

All of the test specimens were pre-scoured for 45 minutes at 180° F. in 300 milliliters of a solution containing 2 grams per liter of a long chain alcohol ethylene oxide condensate sold commercially as "Alkanol HC," 2 grams per liter of sodium tripolyphosphate, and 2 grams per liter of sodium metasilicate. The pre-scoured samples were washed free from the scour with cold water.

The fabric dyeing was carried out in tubes attached to reflux condensers by rubber stoppers. A combined percolator and volume displacer was employed in the tube during the dyeing procedure. The dye carrier solutions were first prepared by adding 95 cubic centimeters of an aqueous solution containing 0.5 gram per liter Alkanol HC, 1.5 grams per liter of a long chain hydrocarbon composition sold commercially as "Avitone T," and 5 grams per liter of sodium sulfate at 55° C. while vigorously stirred to 3 cubic centimeters of a 15 percent solution of an organic ester/amide mixture sold as "Latyl Carrier A" in dimethyl formamide. Where a protective screener was employed, the desired amount was added to this carrier solution prior to addition of the dye. The dye was dissolved in one cubic centimeter of 10 percent acetic acid and added to the carrier solution. Finally, the pH was adjusted to 4 using 10 percent acetic acid.

After the dye solution was placed in the dyeing tube, the wet fabric was wrapped around the percolator and inserted into the dyeing tube. The temperature was raised to the boil over a period of 25 to 30 minutes and was maintained at the boil for an additional 2 hours. The fabric was water washed following completion of the dyeing procedure.

After dyeing, each fabric specimen was after-scoured for 20 minutes at 180° F. with 300 cubic centimeters of a solution containing 0.5 gram per liter Alkanol HC and 0.25 gram per liter acetic acid. The samples were rinsed with cold water and air dried.

Each of the fabric specimens was mounted on a tester frame and heatset for 5 minutes at 165° to 170° C. in a circulating air oven.

The weighed fabric samples dyed with Sevron Orange G and Basic Fuchsin were extracted with dimethyl formamide and the extract analyzed spectrophotometrically for the percent dye. This was compared with a control in which no screener was employed in the dyebath to determine the relative dye pickup. The Sevron Blue 5G and Brilliant Green Crystals dyes appear to undergo degradation when subjected to prolonged contact with dimethyl formamide. As a result, fabric samples dyed with these dyes could not be rated for dye pickup by extraction and spectrophotometric analysis. With these two dyes the change in dye pickup was determined by visually rating the fabrics containing these dyes. In the results listed below the average increase or decrease in dye pickup for the four dyes is indicated qualitatively. The quantitative measurement in the runs employing Sevron Orange G and Basic Fuchsin of increase in dye pickup caused by inclusion of the compounds of this invention in the dyebath and likewise for the decrease in dye pickup caused by the comparative compounds is indicated in the table below.

Swatches of 1.5 inches by 5 inches were cut from each fabric specimen and mounted on standard exposure cards which were exposed in an Atlas Fadeometer for from 2 to 35 hours. The improvement in lightfastness on the average for the four dyes tested was rated qualitatively and is indicated as such in the table below. For Sevron Orange G and the Basic Fuchsin the number of hours to reach a given discoloration was determined and the specimen rated as a percentage increase or decrease in lightfastness relative to the control containing no protective screener. In addition, the percentage concentration of protective screener required to achieve a given discoloration was determined so as to indicate the amount of compound required to increase the lightfastness by 40 percent. By that is meant to extend the time required for the fabric specimen to reach that given discoloration by 40 percent. The results of these determinations for each of these two dyes is given in the table below.

The results for Sevron Blue 5G and Brilliant Green Crystals exhibited the same improvement in dye pickup and in lightfastness noted for the Sevron Orange G and Basic Fuchsin.

Table

Compound	Average for the Four Dyes		Sevron Orange G and Basic Fuchsin		
	Improvement in Lightfastness	Dye Pickup	Percent Increase in Lightfastness at 1% Conc.	Percent Change in Dye Pickup	Percent Compound Required to Increase Lightfastness by 40%
This Invention:					
4-benzoyl-3-hydroxyphenyl stearate	Excellent	Slight increase	58.5	+0.6	0.37
isobutyl o-(5-chlorosalicyloyl)benzoate	Very good	Marked increase	52.5	+27.2	0.80
5-chloro-2-hydroxy-4'-t-butylbenzophenone	do	do	46.5	+22.1	0.77
4-benzoyl-3-hydroxyphenyl salicylate	Good	do	41.0	+22.9	0.96
For Comparison:					
2 2'-(dihydroxy)-4 4'-(dimethoxy)benzophenone	do	Slight decrease	24.4	−3.9	1.45
4-benzoyl-3-hydroxyphenyl benzoate	do	Marked decrease	19.0	−13.6	>1.5

What is claimed is:

1. In the process for dyeing an article composed of a polyester condensation polymer wherein said article is exposed to and contacted with a liquid dyebath, the improvement consisting of including in said dyebath from 0.1 to 5.0 percent by weight of said article to be dyed of an agent selected from the group consisting of 4-benzoyl-3-hydroxyphenyl stearate; isobutyl o-(5-chlorosalicyloyl) benzoate; 5-chloro-2-hydroxy - 4' - t - butylbenzophenone; 4-benzoyl-3-hydroxyphenol salicylate.

2. The improvement claimed in claim 1 in the process wherein said article is a filamentary article.

3. The improvement claimed in claim 2 in the process

wherein said polyester condensation polymer is polyethylene terephthalate.

4. The improvement claimed in claim 3 wherein the dyeing is accomplished by exposure and contact of said filamentary article to the dyebath at the boil.

5. The improvement claimed in claim 1 wherein said liquid dyebath contains as the sole colorant a cationic dye.

References Cited in the file of this patent

UNITED STATES PATENTS

2,081,117	Hall	May 18, 1937
2,568,894	Mackey	Sept. 25, 1951
2,916,345	Hees	Dec. 8, 1959
2,965,578	Pestemer et al.	Dec. 20, 1960