United States Patent

Smith et al.

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[54] METHOD FOR IMPROVING THE DYEABILITY AND FOR HEAT SETTING SYNTHETIC LINEAR POLYESTERS

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[51] **Int. Cl.** **D06p 3/00**

[58] **Field of Search** 8/130.1, 4, 166, 179, 94, 174, 8/175

[56] **References Cited**

UNITED STATES PATENTS

2,999,002	9/1961	Dayvault	8/94
3,154,374	10/1964	Gruschke	8/130.1
3,512,913	5/1970	Day et al.	8/4

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[57] **ABSTRACT**

A method is provided for improving a dyeability and for heat setting synthetic linear polyesters, wherein the polyester in fibrous or film form is contacted at an elevated temperature, for example, 120° to 200° C. for about 1 to 20 seconds with a monocyclic or bicyclic halogenated aromatic hydrocarbon. The halogenated aromatic hydrocarbon is extracted from the polyester after treatment. The polyester fibers and films treated in accordance with the method of this invention exhibits superior dyeing properties being readily dyed to deep shades in the absence of a carrier. The polyester fibers and films treated in accordance with the present invention likewise exhibit improved dimensional stability.

13 Claims, 1 Drawing Figure

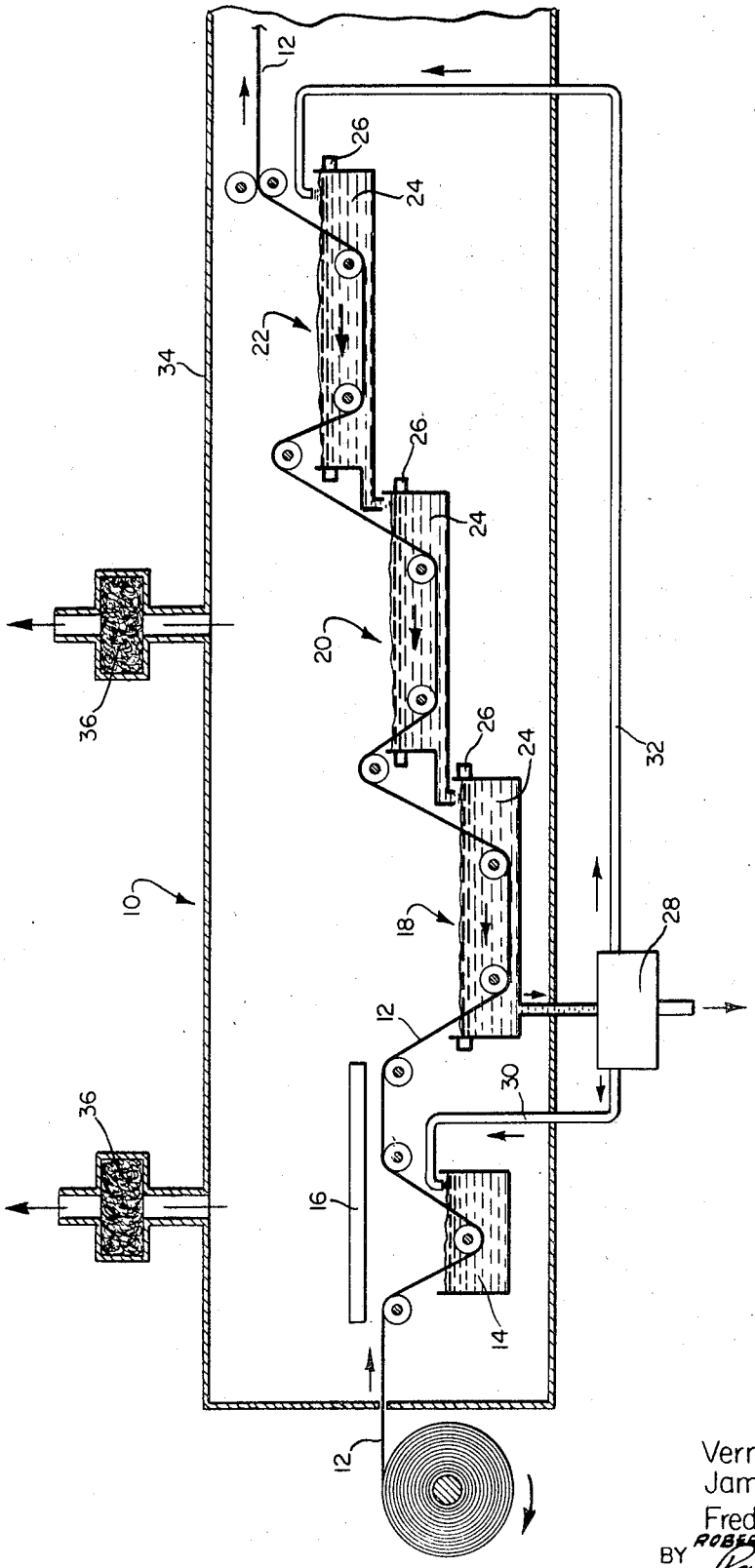


Fig. 1

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METHOD FOR IMPROVING THE DYEABILITY AND FOR HEAT SETTING SYNTHETIC LINEAR POLYESTERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is concerned with a method for modifying the properties of synthetic linear polyesters. More particularly this invention is concerned with a method for improving the dyeability and dimensional stability of polyester fibers and films.

2. Description of the Prior Art

The synthetic linear polyesters which are prepared from dibasic aromatic acids and glycols such as the polyesters of the polyethylene terephthalate type possess many properties which make them especially valuable for employment in the form of fibers and films. However, due to a combination of the relative chemical inertness of the polyester polymers and the hydrophobic nature of the polyester polymers and the high degree of compactness of the fibers and films made from the synthetic linear polyester, considerable difficulty is encountered in dyeing polyester fibers and films.

Various suggestions have been made to improve the dyeability of the polyesters. One such suggestion was to dye the polyesters with dyestuffs having a relatively small molecular size. The resultant polyester dyeings, however, had poor fastness especially to laundering. An additional suggestion was to employ high temperature high pressure dyeing techniques. This suggestion was not satisfactory in that it required the use of special pressure dyeing apparatus, and necessitated the use of batch dyeing techniques.

An additional suggestion was to include in the aqueous dye bath compounds referred to as carriers to assist the application of the dyestuffs onto the polyester fibers and films. Various types of compounds were suggested as carriers. These compounds included, for example, phenolic compounds, such as, o- or p-phenylphenol, esters such as methylsalicylate and halogenated compounds such as the dichlorobenzenes and the trichlorobenzenes. The amount of the carriers that were added were dependent to some extent on the depth of the shade desired. However, the amount of carrier that was generally employed was in the range of approximately 10 percent by weight of the dye bath. The carrier dyeing technique was not satisfactory. Initially the use of the carriers substantially increased the cost of dyeing the polyesters. The rate of dyeing was substantially improved, however, the rate of dyeing was still relatively slow requiring approximately 60 minutes of dyeing time for exhaustion of the dye bath under normal dyeing conditions. This length of dyeing time precluded the use of continuous dyeing methods when dyeing polyesters using the carrier dyeing technique.

A further difficulty of the carrier dyeing method is that it can result in substantial air and water pollution. At the dyeing temperature of approximately 100° C. substantial amounts of certain of the carriers tend to steam distill off into the atmosphere. Since many of the carriers have rather distinct and obnoxious odors they cause substantial air pollution problems when discharged into the air. A further difficulty encountered is control of water pollution. Since the spent dye liquors contain substantial amounts of carriers, the dye liquors must be given extensive treatment to prevent the discharged material from polluting water sources. With the recent increase in legislation concerning control of air and water pollution, it is evident that the carrier dyeing techniques may be prohibited in many areas in the near future for the dyeing of polyester fibers.

Attempts have been made to improve the dyeability of the polyesters by pretreating the polyesters before dyeing. It was reported, for example, by A. H. Brown, and A. T. Peters in American Dyestuff Reporter of Apr. 22, 1968, that when polyester fibers were pretreated with aqueous dispersions of carriers that the resulting pretreated fibers had better dyeability in the absence of the carrier than the untreated fibers. However, it was further reported that the pretreated fibers did not exhibit the same dyeability as untreated fiber dyed in the presence of a carrier. Accordingly, the pretreatment with the aqueous dispersions of the carriers was not a satisfactory solution.

Various methods were suggested, in the prior art, wherein the surfaces of synthetic linear polyester fibers were made more dyeable. One such method was disclosed by D. S. Adams, U.S. Pat. No. 3,155,754, wherein the surfaces of polyester fibers were treated with semisolvents for the polyester to form a layer of more dyeable polyester material on the outer surface of the fibers. The resulting fibers had a sheath-core structure. The outer sheath of the fibers accepted the dyestuff more readily than the untreated fibers. The resultant dyeings were not, however, satisfactory in that the fibers were "ring dyed" because of the difference in dyeability of the sheath and the core. Fibers that are "ring dyed" are unsatisfactory in that as the fiber wears or is abraded the color changes noticeably.

Another method of treating the surfaces of polyester fibers to improve their dyeability is disclosed by Gruschke, et al., U.S. Pat. No. 3,154,374. In the Gruschke, et al. process polyester fibers are treated at high temperatures, for example 200° to 350° C. for short periods of time, for example 10^{-4} seconds to 10 seconds, with certain selected esters, ethers or ketones. Typical treating agents employed in the Gruschke, et al. process are for example, sebacic acid dimethylester, benzophenone and phenylbenzoate. The process taught by Gruschke, et al. was not a satisfactory solution to the problems of dyeing polyesters. At the temperatures at which the Gruschke, et al. process was conducted the polyesters shrunk considerably. The increase in the dyeability of polyester fibers was at best only a surface effect which caused the "ring dyeing" of the fibers which had the well-known disadvantages noted above. In addition, the Gruschke, et al. process at best only increased the rate of dyeing the pretreated polyesters to that obtainable with the use of a carrier which limited the dyeing of the polyesters to the batch type dyeing rather than continuous methods of dyeing.

Despite all of the various methods suggested in the prior art for improving the dyeability of the polyesters, it was still not possible to satisfactorily obtain printed polyester fabrics in relatively heavy shades, especially on heavy weight materials. The inability to satisfactorily print heavy weight polyester fabrics considerably limited the use of the polyester fibers in certain high volume fabrics, such as, printed carpeting.

An additional area wherein some difficulty was encountered with the polyester fibers was the manufacture of texturized yarn and fabrics. Texturized yarns and fabrics are employed in order to obtain special effects, such as, high bulk or to impart elastic properties to the fabrics. Various well known methods are employed to make texturized yarns, such as, twist-untwist, false twisting, knit deknit, and so forth. In the various processes the yearn or fabric are heat set at least once in order to set the texturized effect in the yarn or fabric. The heat-setting step has caused considerable problems especially with regard to both the cost and the uniformity of the treatment. Depending on the process employed, the yarn may be subjected to several coneing and also to batch-type autoclaving for extended periods of time which increase the process costs. The ends comprising a given fabric may receive substantially different treatment in heat setting. The difference in the treatment causes variations in both the dyeability and the appearance of the final fabric. The variations in the heat set treatment cause defects in the finished product as barre marks and unlevelness in the dyeing of the fabrics.

It is an object of the present invention to overcome the forementioned problems and difficulty encountered in the prior art methods.

It is a further object of this invention to provide a process for improving the dyeability of synthetic linear polyester fibers and films.

It is a still further object of this invention to provide a method of pretreating synthetic linear polyester fibers and

films so that they can be dyed in the absence of a carrier in a time which is substantially less than that required for the dyeing of untreated polyester in the presence of a carrier.

It is an additional object of this invention to provide a method for dimensional stabilizing texturized yarns and fabrics comprised of synthetic linear polyester fibers in which the treatment is substantially uniform to all of the fibers comprising the fabric or yarn and is conducted in a short period of time in a continuous manner.

Other objects and advantages of the present invention will become further apparent from a review of the attached drawing and a reading of the specification and subjoined claims.

SUMMARY OF THE INVENTION

The objects of this invention have been achieved by providing a method wherein the synthetic linear polyester fibers or films are treated with a halogenated aromatic hydrocarbon at a temperature of about 120° to 200° C. for about 1 to 20 seconds and then the halogenated aromatic hydrocarbon is extracted from the polyester.

BRIEF DESCRIPTION OF THE DRAWING

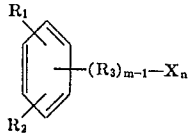
FIG. 1 is a schematic illustration of a continuous treating apparatus suitable for employment in the method of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The synthetic linear polyesters which are preferably treated in accordance with the present invention are the condensation polymerization products of dicarboxylic acids and polyhydric alcohols. The repeating structural units of the polymer chain include at least one divalent carbocylic ring containing at least six carbon atoms which is present as an integral part of the polymer chain and have a minimum of four carbon atoms between the points of attachment of the ring in the polymer chain. The preferred synthetic linear polyesters are of the polyethylene terephthalate type. Other types of polyesters are likewise employable such as those obtained by polymerizing a dicarboxylic acid such as terephthalic acid, bromoterephthalic acid, 4,4'-benzophenonedicarboxylic acid and so forth with glycols such as those of the formula $HO(CH_2)_nOH$ wherein, n is a whole number from two to 10, diethylene glycol, neopentylene glycol and the like.

The synthetic linear polyesters that are treated may be formed in various physical shapes. The polyesters may, for example, be treated in the form of an extruded continuous film. More commonly, however, the polyesters are treated in the fibrous form. When referring to fibers and to the fibrous form this is intended to include, unless otherwise indicated, fibers per se such as continuous filaments and chopped tow and also to include fibers which have been manufactured into yarns and fabrics. With regard to the fabric, it should be noted that the terminology fabric includes woven fabrics, knitted fabrics and nonwoven materials. When referring to yarns this is intended to include filament yarns, spun yarns, slit yarns and fibralated yarns. The yarns and fabrics that are treated according to this invention preferably consist of only polyester fibers. However, it is possible to treat polyesters in blends with other fibers by the present invention providing the other fibers are not adversely affected.

The halogenated aromatic hydrocarbons which are employed in the present invention may be monocyclic or bicyclic hydrocarbons with the monocyclic hydrocarbons being preferred. The halogenated aromatic hydrocarbons are represented by the formula



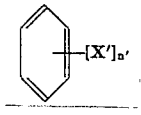
Formula I

wherein R_1 and R_2 are the same or different and represent hydrogen, an alkyl having one to four carbon atoms such as methyl, ethyl, n-propyl, isopropyl, and n-butyl or an alkenyl having two to four carbon atoms such as vinyl, 1-propenyl and 2-butenyl. When R_1 and R_2 are attached to vicinal carbon atoms they may be attached to each other to form a five to six-membered aliphatic or aromatic ring when taken together with the vicinal carbon atoms of the aromatic ring of the compound of formula I, with the naphthalene ring system being the preferred ring system R_3 is a lower alkylene having one to four carbon atoms such as methylene, ethylene, propylene and butylene when R_1 and R_2 are joined together. The symbol X in the above formula stands for a halogen such as fluorine, chlorine, bromine or iodine, n is a whole number from one to three and when n is two or more X can stand for the same or different halogens.

The halogenated aromatic hydrocarbon employed in the method of the present invention should have a melting point below 120° C. and advantageously should be a liquid at the treating temperature, however, it is possible to conduct the present process in the vapor phase. The ideal compound for employment in the present invention should melt at a point below 130° C. and should have a boiling point above 160° and more preferably above 200° C. The halogenated aromatic hydrocarbon should be substantially anhydrous, however, it can contain minor amounts of water and will tend to pick up small amounts of water from the polyester being treated. Since the treatment is conducted at elevated temperatures, the water is volatilized and removed from the treating bath.

Blends of halogenated aromatic hydrocarbons can be employed if desired, however, it is preferable to employ a single compound as it facilitates the separation and recovery of the halogenated aromatic hydrocarbon from the extraction media as will be more specifically set out below.

The preferred halogenated aromatic hydrocarbons for employment in this invention are represented by the formula



wherein X' is chlorine or bromine and n' is 2 and more preferably 3.

The mono-halogenated compounds wherein R_1 and R_2 are hydrogen, that is the mono-halo-benzenes, are generally not employed in the present invention because of their relatively low boiling points. However, the mono-halogenated benzenes can be employed if the process is conducted at a temperature below their boiling point or if the process is conducted in the vapor phase or under pressure conditions. Even if the process is conducted at normal pressures, compounds such as bromobenzene and iodobenzene can be employed to some advantage.

The dihalogenated benzenes are, on the other hand, quite useful in the process of the present invention and are one of the preferred class of compounds. For example, all of the isomers of the dihalogenated benzenes such as the dichloro, the dibromo and the diiodo benzenes give excellent results. The mixed dihalogenated compounds, such as, m- and p-bromochlorobenzenes and the iodobromobenzene compounds, such as the ortho and meta isomers are likewise useful in the present invention.

The most important class of compounds for employment in the process of the present invention are the trihalogenated benzenes. All of the isomers of the trichloro benzenes, such as the 1,2,4-trichloro, 1,2,5-trichloro and the 1,3,5-trichloro benzenes are the most preferred compounds for employment in the present invention. The other trihalogenated benzenes, such as the trifluoro, the tribromo and the triiodo and the various mixed halogen compounds are likewise useful and are in the preferred class compounds.

Of the compounds wherein R_1 or R_2 represent alkyls having one to four carbon atoms, by far the most important class of

compounds are the halogenated toluenes and halogenated xylenes compounds, with even the monohalogenated compounds, such as the chlorotoluenes and bromoxylenes, being quite suitable.

Of the compounds wherein R_1 and R_2 are attached to each other to form a five to six-membered ring, particular attention is directed to the halogenated compounds of the naphthalene series such as the monohalogenated naphthalene such as 1-bromo-, 2-bromo-, and 1-chloro naphthalenes and the dihalogenated naphthalenes such as 1,2-dichloro, 1,3-dichloro and 1,4-dichloro naphthalenes.

Of the compound where R_3 is a lower alkylene and *m* is 2 particular attention is directed to compounds such as αchlorotoluene, α-o-dichlorotoluene bromotoluene and bromoα-o-xylene.

The selection of the particular halogenated aromatic hydrocarbon is dependent on various factors such as the desired treatment temperature, cost and commercial availability of the compound, and the resulting improvement in the properties of the polyester. By comparing all of these factors it has been found that the trichlorobenzenes are clearly the preferred compounds for employment in the present invention.

In the method of this invention the synthetic linear polyester is treated with the halogenated aromatic hydrocarbon for a short period of time at an elevated temperature. More particularly, the polyester is passed through a bath of the halogenated aromatic hydrocarbon at a temperature of 120° to 200° C. at a speed such that immersion time in the halogenated aromatic hydrocarbon is from 1 to 20 seconds. Generally, a treatment temperature between 130° and 160° C. is sufficient in order to obtain the desired improvement in both the dyeability and dimensional stability and does not cause shrinkage or degradation of the polyester polymers. Shorter immersion times can be employed, however it has been found that 10 seconds gives the optimum results. Immersion times in excess of 20 seconds can be employed but no advantage is obtained with the longer treatment times.

After the immersion step the halogenated aromatic hydrocarbon is extracted from the polyester. The extraction is advantageously conducted by passing the treated polyester through a solvent with which the halogenated aromatic hydrocarbon is miscible and which has a boiling point which is substantially different and preferably lower than the boiling point of the halogenated aromatic hydrocarbon in order to facilitate the separation and recovery of the materials. Solvents which have proven to be especially valuable as extraction media are the halogenated aliphatic hydrocarbons, such as methylene chloride, trichloroethylene, 1,1,1-trichloroethane, perchloroethylene and mixtures thereof.

In order to further explain the process of this invention, reference is made to FIG. **1** which schematically illustrates a treating apparatus which is suitable for treating polyesters in accordance with the method of the present invention. A synthetic linear polyester **12**, which may be in the form of a film, continuous filaments, yarn or fabric, is fed into the treating bath **14** which contains a halogenated aromatic hydrocarbon, for example trichlorobenzene. The bath **14** is heated to 120° to 200° C. and the feed is regulated so that the immersion time in the bath **14** is from 10 to 20 seconds. A cooler **16** is positioned over the bath **14** in order to prevent the vapors of the halogenated aromatic hydrocarbon from escaping. After immersion in the treating bath **14**, the polyester **12** advances through a series of extraction baths **18, 20, 22** through which an extraction media **24** is flowing counter to the direction of advancement of the polyester **12**. The first extraction bath **18** removes a substantial portion of the halogenated aromatic hydrocarbon from the polyester with the remainder being removed in the second and the third extraction baths. As the polyester **12** leaves the third extraction bath **22**, it contains only the extraction media **24** which, because of its low boiling point, is easily removed by conventional drying methods (not shown) such as can dryers. The extraction baths **18, 20, 22** advantageously have cooling coils **26** positioned about their perimeter to limit as much as possible the escape of fumes from the extraction baths.

In order to make the present method commercially feasible, it is important to recover essentially 100 percent of the materials employed in the process. This both prevents air and water pollution and makes the process feasible from an economic standpoint. In this regard it should be noted that the liquor from the first extraction bath **18**, which contains the greatest amount of the halogenated aromatic hydrocarbon, is drained from the extraction bath **18** and fed into a fractionater **28**. In the fractionater **28**, the mixture received from the extraction bath **18** is separated into a halogenated aromatic hydrocarbon fraction which is fed back along the supply line **30** into the treating bath **14** and the extraction media **24** is fed along the supply line **32** into the third extraction bath **22**. Any remaining material such as extracted impurities for example the spinning oils on the polyesters are discarded.

The use of the cooling coil **16** over the treatment bath **14** and use of the coolers **30** on the extraction baths **18, 20, 22** eliminates substantially all of the vapor loss. However, in order to insure complete recovery of all of the materials employed, the process is conducted in a closed chamber **34** and the fumes in the chamber vented through activated charcoal filters **36**. Periodically the charcoal filters **36** are removed and steamed distilled to recover all the material trapped by the activated charcoal filters.

The synthetic linear polyesters treated in accordance with the present invention are equivalent to the untreated polyesters with regard to their physical properties, such as tensile strength. There is no substantial gain or loss in weight due to the treatment of the present invention. However, the polyesters treated in accordance with this invention can readily be dyed in the absence of a carrier at normal pressures. The most suitable dyestuffs for dyeing the polyesters treated in accordance with this invention are the dispersed dyestuffs which include dyestuff in the azo, azomethine, nitroarene and anthraquinone chemical classes. Surprisingly, the dyeing, even though conducted in the absence of a carrier and at normal pressures, can be conducted in a considerably shorter time with a 75 percent reduction in dyeing time being easily obtained. It should be further noted that the dyeing is not surface dyeing but rather the fiber is dyed to its entire volume and the dyeing is level. The exhaustion of the dyestuffs from the dye bath is almost 100 percent. The treated polyester can be dyed continuously because of the possibility of employing relatively short dyeing times using, for example, pad steam continuous type dyeing machines. It is also possible to print the polyesters, even the heavyweight polyesters such as carpeting, and obtain sharp accurate prints in relatively deep shades which exhibit excellent fastness.

The polyester fibers and films which are heat set according to the method of this invention have a uniform set which is resistant even to treatment in boiling water. The heat setting of the polyester is relatively simple to control so as to obtain reproducible results on each run. In addition, all the end of a given warp can be treated at the same time so as to have uniform treatment across the width of the fabric. The heat setting is completed in a matter of a few minutes rather than hours as required with the conventional heat setting methods and with a minimum amount of labor being involved.

In order to illustrate the present invention below are examples showing typical methods of employing the present invention. Percentage referred to in the examples are to be considered the percentages by weight not volume unless otherwise indicated.

EXAMPLE 1

Knit stocking samples made of 1,000 denier polyethylene terephthate fiber, commercially known as Fortrel, were treated with 1,2,4-trichlorobenzene at various temperatures for 10 seconds and the 1,2,4-trichlorobenzene was removed in

a series of three extractions with 1,1,1-trichloroethane and the samples were dried at 90° C. for 30 seconds to remove the residual 1,1,1-trichloroethane. The treated samples, a blank, and a sample which was only subjected to extraction with the 1,1,1-trichlorobenzene were each dyed at 99°–100° C. for 1 hour in a 30:1 liquor ratio dyebath containing

1.0% OWF	CI dispersed blue 73
1.0% OWF	Monosodium phosphate
0.25% OWF	Acetic acid

After dyeing the samples were washed to remove any excess dyestuff. The shades of the dyeing were as follows:

Sample	Depth of Shade
1. Blank	light blue stain
2. 120°	full deep blue shade
3. 140°	as above
4. 160°	as above
5. 180°	full deep blue shade, slight shrinkage
6. 200°	full deep blue shade, considerable shrinkage
7. solvent extracted only	light blue stain somewhat deeper than sample No. 1

Sample 1–7 were deknitted and the yarns were boiled in water for 15 minutes. Sample 1 and 7 did not retain the crimp while sample 2–6 retained the crimp with the samples set at higher temperatures having superior crimp retention properties.

EXAMPLE 2

The procedure described in Example 1 was repeated with the sample being treated at 140° C. with various other halogenated aromatic hydrocarbons as noted below

Sample	Color
1. 1,2,5 trichlorobenzene	deep level blue
2. O-dichlorobenzene	as above
3. O-dibromobenzene	as above
4. P-dichlorobenzene	as above
5. O-bromochloro benzene	as above
6. 1-chloronaphthalene	as above
7. Blank	light blue stain
8. solvent-rinsed sample	as above

As in Example 1 when the samples were deknitted and boiled the samples treated with the halogenated aromatic hydrocarbon retained the crimp.

EXAMPLE 3

The general procedure disclosed in Example 1 was repeated but different commercially available polyethylene terephthate fibers and different type of dyestuff were employed. The difference in shade between a blank and the treated samples were measured colorimetrically

Polyester fiber	1,2,4 trichlorobenzene treatment temp.,° C.	Dispersed dyestuff	Color yield versus untreated sample
Kodel 241	135	C.I. Red 60	2.5 times greater.
Kodel 241	120	C.I. Yellow 54	2.8 times greater.
Kodel 241	150	C.I. Blue 73	6.2 times greater.
Kodel 241	120	C.I. Blue 27	3.4 times greater.
Kodel 241	155	C.I. Blue 27	6.9 times greater.
Kodel 241	120	C.I. Yellow 86	2.4 times greater.
Encron	145	C.I. Blue 27	2.8 times greater.
Fortrel	140	C.I. Blue 27	2.2 times greater.

EXAMPLE 4

A tufted carpet sample made of polyethylene terephthlate fiber (Kodel 241) was immersed in a bath of 1,2,4-trichlorobenzene heated to 150° C. for a period of 20 seconds and then rinsed with trichloroethylene at ambient temperatures. The sample was dried at 80° C. for 30 seconds and dyed for 1 hour at 90°–100° C. with the dye formulation given in Example 1. The dyeing that was obtained was tinctorially four times stronger than a similarly dyed sample of polyester fiber carpet which had not received the 1,2,4-trichlorobenzene treatment.

EXAMPLE 5

Yarn made of 15 denier Polyethylene Terephthlate fiber (Encron Brand) was passed through a bath of 1,2,4-trichlorobenzene maintained at 120° C. at a speed of 12 yards per minute. The immersion distance of the yarn was 2 inches. The yarn was then passed through a second bath of 1,1,1-trichloroethane at ambient temperatures. After subsequent drying, the yarn was readily dyed accordingly with the dye formula given in Example 1 without the use of carriers in the dyebath.

The same excellent dyeings were obtained when trichloroethylene, methylene chloride, perchloroethylene and other halogenated aliphatic solvents were used as the extraction media. The rinse bath of 1,1,1-trichloroethane may be conducted at the reflux temperature of 74° C. and perchloroethylene may be used at the reflux temperature of 121° C.

EXAMPLE 6

A film made of polyethylene terephthalate (Mylar) was fed through a bath of 1,2,4-trichlorobenzene in a manner similar to that in the preceding example. After subsequent drying, the film was dyed according to the dye formula given in Example 1. The film exhibited the same excellent dyeability as the 1,2,4-trichlorobenzene treated polyester fibers exhibited in preceding examples.

EXAMPLE 7

A tufted carpet sample made of Kodel II fibers was immersed in a bath of 1,2,4-trichlorobenzene heated to 145° C. for a period of 10 seconds and then rinsed in three separate portions of 1,1,1-trichloroethane. Subsequently, the carpet was dried at 80° C. for 30 seconds to remove the residual rinse liquid. The carpet was then continuously dyed according to the following procedure:

The carpet sample was immersed in a chemical bath containing

2 g./l. Disodium phosphate
4 g./l. Monosodium phosphate
5g./l. Anionic detergent (Irgapadol P)

and subsequently squeezed between two rubber-coated nip rolls to obtain a wet pickup of about 100 percent. The so-wetted carpet was then advanced through a dye applicator apparatus containing a formulation consisting of

3.33 g./l. C.I Disperse Blue 73
1.0 g./l. Anionic detergent (Irgapadol P)
4.0 g./l. Locust Bean Extract (Polygum 260)

and allowed to pickup a concentration of the formulation equal to about a 300 percent wet pickup. The carpet was then moved into a steam chamber maintained at 100° C. for a period of 6 minutes. Complete fixation of the Disperse Blue 73 dyestuff was obtained and there was no washoff of dyestuff in subsequent aqueous treatments of the carpet. A sample of untreated polyester carpet dyed according to the preceding dye procedure resulted in almost no fixation of dyestuff on the carpet fibers. Even when emulsified biphenyl, a well-known carrier for carpet dyeing, was added to the dye liquor in an amount to equal 10 percent based on the weight of the fiber, almost no fixation of dyestuff occurs on the untreated polyester.

EXAMPLE 8

Tufted carpet made of Kodel 241 brand polyester fiber was treated with 1,2,4-trichlorobenzene according to the method of treatment described in Example 7. The carpet was then screen-printed with a printing paste of the following composition:

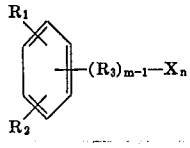
1.5 g./l. wetting agent (Barasol BRM)
1.5 g./l. ammonium sulphate
1.5 g./l. locust bean extract (Polygum 260)
4 g./l. thiodiglycol
1.5 g./l. CI dispersed Blue 73

After applying the printing paste, the carpet was steamed at 100° C. for 6 minutes. Complete fixation of the dyestuff on the

carpet was obtained. A sample of polyester fiber carpet which has not been treated with 1,2,4-trichlorobenzene was printed with the printing paste composition shown above and after subsequent steaming showed almost no fixation of dyestuff.

We claim:

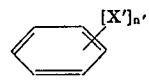
1. The process for improving the dyeability and heat setting of a synthetic linear polyester which comprises: immersing said polyester at an elevated temperature from about 120° to 300° C. for about 1 to 20 seconds in a liquid selected from the group consisting of a substantially anhydrous halogenated aromatic hydrocarbon of the formula:



wherein R_1 and R_2 are the same or different and each stands for a member selected from the group consisting of hydrogen, alkyl having one to four carbon atoms and alkenyl having two to four carbon atoms and R_1 and R_2, when attached to each other and to vicinal carbon atoms stands for a five to six-membered ring, R_3 is an alkylene having one to four carbon atoms X is a halogen selected from the group consisting of fluorine, chlorine, bromine, and iodine, *n* is a whole number from one to three, *m* is a whole number from one to two and mixtures of said halogenated aromatic hydrocarbons; and thereafter extracting said liquid from said polyester.

2. The process according to claim **1** wherein said temperature is about 130° to 160° C.

3. The process according to claim **1** wherein said halogenated aromatic hydrocarbon is represented by the formula



wherein X′ is chlorine or bromine and *n′* is a whole number from two to three.

4. The process according to claim **3** wherein X′ is chlorine.

5. The process according to claim **4** wherein said halogenated aromatic hydrocarbon is 1,2,4-trichlorobenzene.

6. The process according to claim **4** wherein said halogenated hydrocarbon is 1,2,5-trichlorobenzene.

7. The process according to claim **1** wherein said halogenated aromatic hydrocarbon is extracted from the polyester with a solvent having a boiling point lower than and which is miscible with said halogenated aromatic hydrocarbon.

8. The process according to claim **7** wherein said solvent is a halogenated aliphatic hydrocarbon solvent.

9. The process according to claim **8** wherein said solvent is a member selected from the group consisting of methylene chloride, trichloroethylene, 1,1,1-trichloroethane, perchloroethylene and mixtures thereof.

10. The process according to claim **1** wherein the polyester after treatment with and removal of the halogenated aromatic hydrocarbon is dyed.

11. The process according to claim **10** wherein the dyeing is conducted in an aqueous medium in the absence of a carrier.

12. A polyester having improved dyeability prepared by the process of claim **1**.

13. The dimensional stabilized polyester prepared by the process of claim **1**.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,644,079 Dated February 22, 1972

Inventor(s) Vernon C. Smith, James B. Hobgood, Frederick E. Barwick III and Robert W. McCullough

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Page following the sheet of drawings under the listed inventors, add the name of ---Robert W. McCullough, Riverside, Conn.---.

Column 7, line 74, change "90°-100°C" to ---99°-100°C---.

Signed and sealed this 12th day of September 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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