



⑪ Publication number : **0 570 227 A2**

⑫ **EUROPEAN PATENT APPLICATION**

⑳ Application number : **93303718.6**

⑤① Int. Cl.⁵ : **D01F 6/92**

㉔ Date of filing : **13.05.93**

③① Priority : **14.05.92 JP 121961/92**
15.04.93 JP 88602/93

④③ Date of publication of application :
18.11.93 Bulletin 93/46

⑥④ Designated Contracting States :
DE FR GB IT

⑦① Applicant : **TEIJIN LIMITED**
6-7, Minamihommachi 1-chome Chuo-ku
Osaka-shi, Osaka 541 (JP)

⑦② Inventor : **Yamada, Hironori**
3-16, Befu-cho

Matsuyama-shi, Ehime (JP)

Inventor : **Fujita, Hiroshi**

3-7-16, Sonenishi-machi

Toyonaka-shi, Osaka (JP)

Inventor : **Tamura, Atsuo**

3-9-1, Minohara

Ibaraki-shi, Osaka (JP)

Inventor : **Kuroda, Toshimasa**

1-10-33, Nanpeidai

Takatsuki-shi, Osaka (JP)

⑦④ Representative : **Votier, Sidney David et al**
CARPMAELS & RANSFORD 43, Bloomsbury
Square
London WC1A 2RA (GB)

⑤④ **Polyester fiber having excellent deep dyeability and process for producing the same.**

⑤⑦ A polyester fiber having an excellent deep dyeability, comprising a polyester consisting essentially of recurring units of ethylene terephthalate, and incorporated therein, a polyoxyalkylene glycol derivative represented by the following general formula (I), pores defined by traces of removal of said polyoxyalkylene glycol derivative being present on the surface of said fiber :



wherein Z represents a residue of at least one dihydroxy compound selected from the group consisting of an aliphatic diol having 5 to 10 carbon atoms, an alicyclic diol having 3 to 15 carbon atoms, a bisphenol compound and a dihydric phenol, A represents an alkylene group having 2 to 4 carbon atoms, X represents a residue of a monohydroxy compound and m is a positive integer.

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a polyester fiber having an excellent deep dyeability and a process for producing the same. More particularly, it is concerned with a polyester fiber which has on its surface pores having a unique morphology, exhibits improved deepness and brilliance of color upon being dyed and is excellent in the frictional fading resistance; and a process for producing the same.

10 2. Description of the Related Art

Polyesters have been widely used as a synthetic fiber by virtue of their excellent properties. Since, however, the polyester fibers are inferior in the deepness of color upon being dyed compared to natural fibers, such as wool and silk, cellulosic fibers, such as rayon and acetate, acrylic fibers, etc., they are disadvantageously poor in the color developing property and brilliance.

In order to eliminate this drawback, attempts have been made to make an improvement in dyes, chemical modification of polyesters, etc. However, none of the attempts have provided satisfactory results. Further, a proposal has been made of a method wherein a transparent thin film is formed on the surface of a polyester fiber (see Japanese Unexamined Patent Publication (Kokai) No. 53-111192), a method wherein the surface of a textile fabric is subjected to plasma irradiation at 80 to 500 mA·sec/cm² to form fine uneven portions on the surface of the fiber, (see Japanese Examined Patent Publication (Kokoku) No. 59-11709), and other methods. Even these methods provide no satisfactory effect of improving the deepness of color. Further, the transparent thin film formed on the surface of the fiber easily falls off in washing, that is, is unsatisfactory in durability. In the method wherein use is made of plasma irradiation, since no uneven portion occurs on the surface of the fiber at its portion which is shaded from the irradiation, a smooth fiber face is unfavorably exposed on the surface due to rolling of yarns within the fiber structure to form color spots.

On the other hand, examples of proposals of a method for imparting uneven portions to the surface of polyester fibers include a method for producing a hygroscopic fiber wherein a fiber comprising a polyester and, incorporated therein, polyoxyethylene glycol or polyoxyethylene glycol and a sulfonic acid compound is treated with an aqueous alkali solution to form, on the surface of the fiber, crimped pores arranged in the direction of the fiber axis; and a method for producing a hygroscopic fiber wherein a polyester fiber produced by adding and incorporating fine particles of an inert inorganic material, such as zinc oxide or calcium phosphate, into a polyester reaction system is treated with an aqueous alkali solution to elute the inorganic fine particles, thereby forming pores. Far from an improvement in the deepness of color, the fibers produced by the above-described methods unfavorably give rise to a lowering in the visually appreciated deepness of color. Specifically, in these methods, when the treatment with the aqueous alkali solution is unsatisfactory, the effect of improving the deepness of color is not recognized at all. On the other hand, when the treatment with the aqueous alkali solution is satisfactory, far from an improvement in the deepness of color, a lowering in the visually appreciated deepness of color occurs probably attributable to irregular reflection of light due to the pores, so that the color looks whitish even when the fiber is deeply dyed. Moreover, the strength of the resultant fiber remarkably lowers, and the fiber is easily fibrillated, which renders the above-described methods unsuitable for practical use.

A proposal has been made of a method wherein a fiber comprising a polyester and, incorporated therein, an inorganic fine particle, such as silica having a particle diameter of 80 m μ or less, is subjected to a weight reduction treatment with an alkali to impart irregular uneven portions having a size of 0.2 to 0.7 μ m to the surface of the fiber and, at the same time, to allow fine uneven portions having a size of 50 to 200 m μ to exist within the uneven portions, thereby improving the deepness of color (see Japanese Examined Patent Publication (Kokoku) No. 59-24233). Even in this method, the effect of improving the deepness of color is unsatisfactory. Moreover, probably because of very complicated morphology of the uneven portions, the uneven portions are broken due to the external physical action, such as friction, which unfavorably causes the broken portion to be remarkably faded as compared with the unbroken portions or to have a gloss different from that of the unbroken portions (this phenomenon being usually called "friction mark") and further causes the fiber to be easily fibrillated.

A further proposal has been made of a method wherein a fiber comprising a polyester and, incorporated therein, a low-molecular weight organic compound composed mainly of an imide compound having a molecular weight of 1000 or less is subjected to a weight reduction treatment with an alkali to improve the color. Since, however, the imide compound is finely dispersed in a polyester due to its good compatibility with the polyester, uneven portions formed on the surface of the fiber are so fine that the deep dyeability is poor. Moreover, the even portions are unfavorably susceptible to being broken by an external physical action, such as friction.

SUMMARY OF THE INVENTION

The present invention has been made with a view to eliminating the above-described problems of the prior art, and an object of the present invention is to provide a polyester fiber having not only an excellent deep dyeability and no significant effect on fading by friction and gloss, but also a good fibrillation resistance; and a process for producing the same.

The present inventors have conducted extensive and intensive studies with a view to attaining the above-described object and, as a result, have found that a fiber comprising a polyester and, incorporated therein, a particular polyalkylene oxide glycol derivative less likely to be eluted and removed from a polyester fiber during a weight reduction treatment with an alkali, has improved deepness and brilliance of color by virtue of the formation of fine uneven portions on the surface of the fiber during the weight reduction treatment with an alkali and, at the same time, is less likely to give rise to fading by friction and fibrillation since substantially no pores are formed within the fiber even when the polyalkylene oxide glycol derivative as a modifier is eluted during dyeing, and that in such a polyester fiber, since the formation of uneven portions caused by friction is less liable to occur, a change in the gloss (friction mark) becomes less liable to occur, which has led to the completion of the present invention.

Accordingly, the present invention provides:

1. a polyester fiber having an excellent deep dyeability, comprising a polyester consisting essentially of recurring units of ethylene terephthalate, and incorporated therein, a polyoxyalkylene glycol derivative represented by the following general formula (I), pores defined by traces of removal of said polyoxyalkylene glycol derivative being present on the surface of said fiber:



wherein Z represents a residue of at least one dihydroxy compound selected from the group consisting of an aliphatic diol having 5 to 10 carbon atoms, an alicyclic diol having 3 to 15 carbon atoms, a bisphenol compound and a dihydric phenol, A represents an alkylene group having 2 to 4 carbon atoms, X represents a residue of a monohydroxy compound and m is a positive integer;

2. a polyester fiber having an excellent deep dyeability according to the above item 1, which has a surface density of 1.380 g/cm³ or more as determined by a laser Raman microprobe analysis;

3. a polyester fiber having an excellent deep dyeability according to the above item 1, wherein the polyoxyalkylene glycol derivative has an average molecular weight of 1000 to 5000; and

4. a process for producing a polyester fiber having an excellent deep dyeability, comprising subjecting a polyester fiber comprised of a polyester consisting essentially of recurring units of ethylene terephthalate, and incorporated therein, 0.1 to 10% by weight of a polyoxyalkylene glycol derivative represented by the following general formula (I), to a weight reduction treatment with an aqueous solution of an alkali compound to form pores on the surface of the fiber:



wherein Z represents a residue of at least one dihydroxy compound selected from the group consisting of an aliphatic diol having 5 to 10 carbon atoms, an alicyclic diol having 3 to 15 carbon atoms, a bisphenol compound and a dihydric phenol, A represents an alkylene group having 2 to 4 carbon atoms, X represents a residue of a monohydroxy compound and m is a positive integer.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a scanning electron photomicrograph showing the surface morphology of a polyester fiber after dyeing in Example 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polyester contemplated in the present invention is mainly a polyester consisting essentially of recurring units of ethylene terephthalate. The term "essentially" used herein is intended to mean 90% by mole or more of the recurring units, preferably 95% by mole or more of the recurring units. That is, the polyester may have a third copolymerized moiety so far as the amount of the comonomer is 10% by mole or less. Preferred ex-

amples of the comonomer include aromatic dicarboxylic acids, such as isophthalic acid, 5-sodiumsulfoisophthalic acid, naphthalenedicarboxylic acid, diphenyldicarboxylic acid, diphenoxyethanedicarboxylic acid and methylterephthalic acid, aliphatic dicarboxylic acids, such as adipic acid and sebacic acid, aliphatic glycols, such as trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, octamethylene glycol and decamethylene glycol, alicyclic glycols, such as 1,4-cyclohexanedimethanol, aromatic diols, such as hydroquinone and bisphenol A, and other comonomers, for example, oxycarboxylic acids, such as oxybenzoic acid, oxynaphthoic acid and β -hydroxyethoxybenzoic acid. A minor amount (usually 10% by weight or less based on the polyester) of a polyoxyalkylene glycol may be copolymerized. Further, a polycarboxylic acid, such as trimellitic acid or pyromellitic acid, or a polyol, such as glycerin, trimethylolpropane or pentaerythritol, may be copolymerized in such an amount that the polyester remains substantially linear (usually in an amount of 1% by mole or less).

It is important that the polyoxyalkylene glycol derivative (hereinafter often referred to as "modifier PAG agent") incorporated in the above-described polyester is a poly(oxyalkylene) glycol derivative having a terminal hydroxyl group blocked with a residue of a monohydroxy compound as represented by the following general formula (I):



wherein Z represents a residue of at least one dihydroxy compound selected from the group consisting of an aliphatic diol having 5 to 10 carbon atoms, an alicyclic diol having 3 to 15 carbon atoms, a bisphenol compound and a dihydric phenol, A represents an alkylene group having 2 to 4 carbon atoms, m is a positive integer and X represents a residue of a monohydroxy compound.

In the general formula (I), the expression "Z represents a residue of at least one dihydroxy compound selected from the group consisting of an aliphatic diol having 5 to 10 carbon atoms, an alicyclic diol having 3 to 15 carbon atoms, a bisphenol compound and a dihydric phenol" is intended to mean a residue formed by removing a dihydroxyl group from the above-described dihydroxy compound. Specific examples of the dihydroxy compound constituting this residue are as follows. Examples of the aliphatic diol having 5 to 10 carbon atoms include pentane-1,5-diol and hexane-1,6-diol, examples of the alicyclic diol having 3 to 15 carbon atoms include cyclohexane-1,4-dimethanol, examples of the bisphenol compound include bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane [bisphenol A], bis(4-hydroxyphenyl) sulfone [bisphenol S], 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, and examples of the dihydric phenol include hydroquinone, catechol and resorcin.

Among the above-described dihydroxy compounds, bisphenol compounds are preferred, and 2,2-bis(4-hydroxyphenyl) propane is particularly preferred because it can prevent the occurrence of the friction mark.

In the general formula (I), examples of the alkylene group A include alkylene groups having 2 to 4 carbon atoms, for example, ethylene, propylene and butylene; and mixed groups comprising the above-described alkylene groups, for example, a mixed group comprising ethylene and propylene.

The alkylene group A combines with oxygen atom O to form an oxyalkylene group (AO). A plurality of oxyalkylene groups (AO) present in one molecule may be the same or different. The form of addition may be of a block addition type, a random addition type and a type comprising a combination of both types.

The average molecular weight of the polyoxyalkylene glycol derivative is preferably 1,000 to 5,000, particularly preferably 2,000 to 4,000. Since a hot water treatment is usually effected at 100°C or above prior to a weight reduction treatment with an alkali, for example, in the case of hard twist woven fabrics, when the average molecular weight is less than 1,000, a considerable amount of the polyoxyalkylene glycol derivative is unfavorably eluted, so that it becomes difficult to effectively form pores on the surface of the fiber in the subsequent weight reduction treatment with an alkali. On the other hand, when the average molecular weight exceeds 5,000, pores on the surface of the fiber provided by the weight reduction with an alkali are liable to become substantially streaked, so that not only is the effect of improving the deep dyeability lowered, but also a tendency to lower the fibrillation resistance, etc., is observed.

The expression "residue of a monohydroxy compound" is intended to mean a residue formed by eliminating a hydroxyl group from the monohydroxy compound. Specific examples of the hydroxy compound constituting the residue include alcohols, such as methanol and ethanol, and phenol compounds, such as phenol and cresol.

The polyester fiber of the present invention should comprise a polyester containing the above-described modifier PAG agent. In order to incorporate the modifier PAG agent in the polyester, the modifier PAG agent may be added, for example, to a starting compound of the polyester or a polymerization reaction mixture in

any stage until the synthesis of the above-described polyester is completed, followed by the completion of the synthesis of the polyester. Alternatively, a chip of the polyester and the modifier PAG agent may be simply dry-blended with each other, or they may be previously melt-mixed with each other in a melt extruder. A modifier-PAG-agent-containing polyester produced by mixing a modifier PAG agent heat-melted at the melting point or a higher temperature with a polyester chip and cooling the mixture to a temperature below the melting point to adhere the modifier PAG agent to the surface of the chip of the polyester is also preferably used in the present invention. Moreover, it is also possible to use a method which comprises dispersing a modifier PAG agent in a liquid or a melt, pouring and mixing the dispersion into a polyester and, immediately after the mixing, subjecting the mixture to spinning.

The composition thus produced may contain, as other components, optional additives, for example, catalysts, antioxidants, ultraviolet absorbers, flame retardants, optical brighteners, dulling agents and colorants. Further, it is also favorable to incorporate chain extenders such as 2,2'-bis(2-oxazoline) and 2,2'-bis(3,1-benzoxazin-4-one) from the viewpoint of preventing an increase in the degree of polymerization and a lowering in the degree of polymerization at the time of melt spinning.

There is no particular limitation on the method of melt-spinning the polyester composition thus produced, and any conventional melt-spinning methods for forming a polyester fiber may be adopted. The fiber to be spun herein may be any of a solid fiber having no hollow portion and a hollow fiber having a hollow portion. Further, the external shape and hollow portion in the cross section of the spun fiber may be any of circular and non-circular shapes.

Pores defined by traces of removal of the above-described polyoxyalkylene glycol derivative should be present on the surface of the polyester fiber according to the present invention. For this reason, in the polyester fiber of the present invention, it is preferred for pores defined by traces of elution of an amorphous portion of the polyester to be present in addition to the pores defined by traces of removal of the modifier PAG agent. Such pores defined by traces of elution of an amorphous portion of the polyester can be formed by optionally subjecting the fiber produced by the above-described method to twisting or crimping and/or effecting weaving, followed by a treatment, for example, with an aqueous solution of an alkali compound to remove the PAG agent together with the polyester. In this case, the amount of incorporation of the modifier PAG agent is preferably in the range of from 0.1 to 10% by weight, particularly preferably in the range of from 0.5 to 5% by weight. When the amount of incorporation is less than 0.1% by weight, it becomes difficult to form pores on the surface of the polyester fiber, which renders the deep dyeability unsatisfactory. On the other hand, when the amount of incorporation exceeds 10% by weight, a remarkable improvement in the deep dyeability and sharpness can no longer be attained. On the contrary, not only is the frictional durability lowered, but also the lowering in the melt viscosity is so large that it becomes difficult to effect the melt spinning.

Preferred examples of the alkali compound include sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, sodium carbonate and potassium carbonate. Among them, sodium hydroxide and potassium hydroxide are particularly preferred.

Although the concentration of the aqueous solution of the alkali compound varies depending upon the kind of the alkali compound, treatment conditions, etc., it is usually preferably in the range of from 0.01 to 40% by weight, particularly preferably in the range of from 0.1 to 30% by weight. The treatment temperature is preferably in the range of from room temperature to 100°C, and the treatment time is usually in the range of from 1 min to 4 hr. The amount of removal through elution in the treatment with an aqueous solution of an alkali compound should be 2% by weight based on the weight of the fiber. The treatment with the aqueous solution of an alkali compound enables a number of unique elliptical pores comprising traces of removal of the modifier PAG agent to be formed on the surface of the fiber or in the vicinity of the surface of the fiber.

The polyester fiber of the present invention preferably has a surface density of 1.380 g/cm³ or more as determined by a laser Raman microprobe analysis (see A.J. Helveger, J. Polym. Sci., 10, 317 (1972)) in addition to the satisfaction of the above-described requirements. When the surface density of the fiber is less than 1.380 g/cm³, since the crystallization is unsatisfactory, there is a tendency that properties, such as frictional fading resistance or fibrillation resistance, deteriorate.

In the laser Raman microprobe analysis used herein, a novel method developed by A.J. Helveger for determining the degree of crystallization of polyesters comprising polyethylene terephthalate is applied. In this method, the density is determined by the following equation from a half band width of a Raman band attributable to the stretching vibration of a carbon-oxygen double bond at a wave number of 1730 cm⁻¹ of a Raman spectrum observed when the polyester is irradiated with a laser beam having a position resolution on the order of 1 μm:

$$D = -0.004785H + 1.45995$$

wherein D represents the density and H represents the half band width of a Raman band at a wave number of about 1730 cm⁻¹.

Dyeing of the polyester of the present invention requires no special dyeing conditions, and the polyester may be dyed under conditions commonly adopted in the dyeing of polyester fibers, that is, at 130°C under high pressure. In this dyeing treatment, although part of the modifier PAG agent remaining within the fiber is removed, since it is removed without the formation of pores within the fiber, the fibrillation resistance is not lowered.

In the present invention, a further improvement in the deep dyeability and brilliance can be attained by coating the polyester fiber thus obtained with a polymer having a lower index of refraction than the polyester fiber. Examples of the polymer having a lower index of refraction include, but not limited to, fluoropolymers, such as polytetrafluoroethylene, tetrafluoroethylene/propylene copolymer, tetrafluoroethylene/hexafluoropropylene copolymer, tetrafluoroethylene/ethylene copolymer, tetrafluoroethylene/tetrafluoropropylene copolymer, polyfluorovinylidene, polypentadecafluorooctyl acrylate, polyfluoroethyl acrylate, polytrifluoroisopropyl methacrylate and polytrifluoroethyl methacrylate, silicon compounds, such as polydimethylsilane, polymethylhydrogensiloxane and polydimethylsiloxane, acrylic esters, such as ethylene/vinyl acetate copolymer, polyethyl acrylate and polyethyl methacrylate, and polyurethane polymers. A proper polymer having a lower index of refraction than the substrate fiber constituting fiber products may be selected from the above-described polymers. In this case, it is preferred to select polymers in such a manner that the difference in the index of refraction from that of the substrate fiber becomes as large as possible.

The polymer having a low index of refraction for coating the surface portion of the polyester fiber is commercially available usually in the form of an organic solvent solution or a water-based emulsion. It is preferably in the form of a water-based emulsion since the surface portion is coated after dyeing.

The surface portion of the polyester fiber of the present invention, preferably textile fabrics comprising polyester fibers, may be coated with the emulsion of a polymer having a lower index of refraction by any method, such as padding, spraying, kiss roll application, knife coating, in-bath adsorption, etc. It is a matter of course that these methods can be applied to fiber products in any form, such as tows, filaments, yarn textile fabrics and nonwoven fabrics.

Since the above-described modifier PAG agent used in the present invention has suitable compatibility with polyester, the moveability of the molecular chain of the polyester is improved, which contributes to an improvement in the crystallization rate. As a result, the crystallization of the fiber at its surface portion can be enhanced particularly by heat setting during stretching. When the polyester fiber thus produced is subjected to a weight reduction treatment, for example, with an aqueous solution of an alkali compound, a partially precipitated PAG agent is mainly dissolved and removed together with amorphous polyester in an effective manner with a high crystalline polymer portion remaining unremoved. This enables fine uneven portions having a shorter length in the direction of the fiber axis to be formed and, at the same time, a fiber surface having a high degree of crystallization (a high density) to be formed.

The reason why the modifier PAG agent remaining unextracted in the step of the above-described weight reduction treatment is removed in the subsequent step of dyeing resides in the state of distribution of the modifier PAG agent, and even after the modifier PAG agent is removed, the fiber diameter remains unchanged and substantially no void is formed within the fiber. In the prior art, when use is made of polyethylene glycol or other substance with both terminals being in an unblocked state is used, since the compatibility is so low that longitudinal uneven portions are formed on the surface of the fiber and, at the same time, the agent present within the fiber is eluted to form a number of voids. By contrast, in the present invention, uneven portions having a short length in the direction of the fiber axis are formed, and the formation of voids within the fiber is reduced.

Thus, the polyester fiber according to the present invention exhibits very significant effects, that is, is excellent in the deep dyeability and brilliance and has good frictional fading resistance and fibrillation resistance. Further, when the residual amount of the modifier PAG agent is large, the effect of improving the antistatic property can also be attained.

The present invention will now be described in more detail with reference to the following Examples. In Examples, "parts" and "%" are "parts by weight" and "% by weight", respectively, and the amount of the modifier PAG agent remaining unremoved in polyester fibers after the weight reduction with an alkali and the dyeing of the resultant polyester fibers, and the deepness of color and frictional fading of dyed fabrics were determined by the following methods.

① Residual Amount of Modifier PAG

A sample fabric was treated with chloroform to determine the amount of extraction. Separately, this treatment was effected in the same manner as that described above, except that no modifier PAG agent was added. The residual amount of the modifier PAG agent was determined from the difference in the amount of extraction.

② Deepness of Color

The degree of deep dyeing (K/S) was used as a measure of the deepness of color. The spectral re-

flectance (R) of a sample fabric was measured with a Shimadzu RC-330 spectrophotometer, and the degree of deep dyeability was determined according to the following Kubelka-Munk's equation. The larger this value, the larger the deep dyeing effect (measurement wavelength: 500 mμ).

$$K/S = (1 - R)^2/2R$$

wherein K represents an absorption coefficient and S represents a scattering coefficient.

③ Frictional Fading Resistance

In this test, a surface abrasion tester, of the type recommended by the Japan Society for the Promotion of Science, for a test on color fastness to rubbing was used as a tester, and a georgette consisting of 100% of polyethylene terephthalate was used as a friction fabric. A test fabric was subjected to surface abrasion 200 times under a load of 500 g, and the degree of fading was judged by using a grey scale for a change in color. When the abrasion resistance was very low, the frictional fading resistance was evaluated as the 1st grade, while when the abrasion resistance was very high, the frictional fading resistance was evaluated as the 5th grade. A frictional fading resistance of the 4th grade or higher is required for practical use.

④ Surface Density of Fiber

A Raman spectrum for the surface of the fiber (in some samples, the center portion of the cross section of the fiber) was measured with a laser beam having a position resolution on the order of 1μm by using a laser Raman microprobe manufactured by Jobin-Yvon. The half band width of the resultant Raman band at a wave number of about 1730 cm⁻¹ was determined, and the density was calculated according to the following equation:

$$D = -0.004785H + 1.45995$$

wherein D represents the density (g/cm³) and H represents the half band width of a Raman band at a wave number of about 1730 cm⁻¹.

⑤ Crystallization Rate of Polymer

A differential scanning calorimeter (Model 1090 manufactured by Du Pont (E.I.) de Nemours & Co.) was used to determine a crystallization peak temperature, T_{ci}, during temperature rise at a rate of 20°C/min and a crystallization peak temperature, T_{cd}, when the temperature was raised to 300°C, maintained at that temperature for 3 min and then spontaneously lowered. The value determined by the equation ΔT = T_{cd} - T_{ci} was used as a parameter of the crystallization rate. The larger the value, the higher the crystallization rate.

⑥ Friction Mark Resistance

An about 0.1 mm-thick polyethylene terephthalate film was sandwiched between woven fabrics subjected to weight reduction with an alkali, and the assembly was passed through a calender roll of 130°C (linear pressure: 10 kg/cm), dyed and subjected to final setting to provide a dyed woven fabric (A) subjected to weight reduction. The above-described procedure was repeated, except that the assembly was not passed through the calender roll, thereby providing a dyed woven fabric (B) subjected to weight reduction. The dyed woven fabrics (A) and (B) were subjected to measurement of L* value (contrast index) with Macbeth MS-2020 (manufactured by Instrumental Color System Limited), and the friction mark resistance was evaluated based on the difference in the L* value (ΔL*) between both dyed woven fabrics.

$$\Delta L^* = L^* (\text{net A}) - L^* (\text{net B})$$

The friction mark resistance should be 1.7 or less in terms of the ΔL* value from the practical viewpoint. Examples 1 to 12 and Comparative Examples 1 to 6

A transesterification still was charged with 100 parts of dimethyl terephthalate, 60 parts of ethylene glycol, 0.063 part (0.069% by mole based on dimethyl terephthalate) of calcium acetate monohydrate and 0.009 part (0.007% by mole based on dimethyl terephthalate) of cobalt acetate tetrahydrate as an orthochromatic agent, and the temperature of the system was raised from 140 to 220°C in a nitrogen atmosphere over a period of 3 hr to effect a transesterification reaction while distilling off the formed methanol. Thereafter, the system was stirred at 220°C for 20 min, and 0.058 part (0.080% by mole based on dimethyl terephthalate) of trimethyl phosphate as a stabilizer was added. At the same time, purging of excess ethylene glycol with heating was initiated. 10 min after the initiation of the purging, 0.04 part (0.027% by mole based on dimethyl terephthalate) of antimony trioxide was added as a polycondensation catalyst. Subsequently, polyoxyalkylene glycol derivatives listed in Table 2 were added thereto in an amount specified in Table 1. When the temperature of the contents reached 240°C, the purging of ethylene glycol was terminated. The reaction product was transferred to a polymerizer. Then, a reaction was allowed to react with heating under atmospheric pressure until the temperature of the contents reached 260°C. Thereafter, the system was evacuated from 760 mmHg to 1 mmHg over a period of one hr. At the same time, the temperature of the contents was raised to 280°C over a period of 1.5 hr. The reaction was continued under a reduced pressure of 1 mmHg or less at a polymerization temperature of 280°C until the intrinsic viscosity [IV] reached about 0.64.

The resultant polymer was chipped by the conventional method, dried and melt-spun at 285°C using a spinneret provided with 36 circular bores having a diameter of 0.3 mm. Then, the resultant unstretched yarn was stretched and heat-treated with a feed roller of 84°C and a plate heater of 180°C in such a stretch ratio that the elongation of the finally produced stretched yarn was 30%, thereby providing a stretched yarn of 75 denier/36 filaments.

This flat yarn was subjected to hard twisting, that is, 2500 T/m of S twisting and 2500 T/m of Z twisting, and the hard twist yarns were subjected to a steaming treatment at 80°C for 30 min to effect twist setting. In the hard twist yarns, two S twist yarns and two Z twist yarns were alternately arranged at an end spacing of 47 yarns/cm and a pick spacing of 32 yarns/cm to weave a crepe georgette woven fabric.

The resultant raw woven fabric was subjected to relaxation at the boiling temperature for 20 min in a rotary washer, creping and presetting by a conventional method, and treated with a 3.5% aqueous sodium hydroxide solution at the boiling temperature to provide a woven fabric having a percentage weight reduction of 20%.

The woven fabric after the alkali treatment was dyed with 15% owf of Dianix Black HG-FS (a product of Mitsubishi Kasei Corp.) at 130°C for 60 min and then subjected to reduction cleaning with an aqueous solution containing 1 g/liter sodium hydroxide and 1 g/liter hydrosulfite at 70°C for 20 min to provide a fabric dyed in black.

The deepness and brilliance of color of the treated fabrics are provided in Table 1. For the fabrics dyed in black, the frictional fading resistance after subjecting the fabrics to surface abrasion 200 times are also provided in the table.

Table 1

	Modifier PAG Agent		Crystallization Rate of Polymer			Residual Amt. of Modifier PAG Agent		Fiber Surface Density	Properties of Dyed Fabric		Remarks
	Kind	Amt. of addition (wt.%)	T _{ci} (°C)	T _{cd} (°C)	ΔT (°C)	After weight reduction with alkali (wt.%)	After dyeing treatment (wt.%)		K/S	Practical fading resistance (Grade)	
Ex. 1	PAG-1	0.5	155	202	47	0.5	0.1	1.383	27.9	5	
Ex. 2	Do.	2	152	205	53	1.9	0.2	1.387	29.2	5	Density of center of fiber: 1.371 g/cm ³
Ex. 3	Do.	5	147	208	61	4.6	1.0	1.387	30.1	5	
Ex. 4	Do.	8	145	209	64	6.7	0.5	1.387	31.2	4	
Ex. 5	Do.	10	142	212	70	8.5	0.9	1.388	30.3	4	
Comp. Ex. 1	Do.	13	141	213	72	10.7	1.6	1.387	30.0	3-4	
Comp. Ex. 2	-	-	177	194	17	-	-	1.370	19.2	4-5	Density of center of fiber: 1.368 g/cm ³
Comp. Ex. 3	PAG-11	5	175	196	21	1.1	0.5	1.365	21.2	3-4	
Comp. Ex. 4	PAG-1	5	147	208	61	-	1.9	1.382	19.8	4	No weight reduction with alkali
Ex. 6	PAG-3	5	151	204	53	4.8	1.3	1.387	30.3	5	
Ex. 7	PAG-4	5	147	206	59	4.8	1.4	1.387	30.2	5	
Ex. 8	PAG-2	5	156	203	47	2.3	0.5	1.383	26.3	4	
Ex. 9	PAG-5	5	152	202	50	4.9	2.5	1.383	25.3	3-4	
Ex. 10	PAG-6	5	148	207	59	4.2	0.8	1.386	30.0	5	
Ex. 11	PAG-7	5	148	208	60	4.3	0.6	1.387	30.2	5	
Ex. 12	PAG-8	5	146	210	64	4.4	0.9	1.388	30.8	5	
Comp. Ex. 5	PAG-9	5	176	190	14	4.6*	4.2*	1.368	22.3	4-5	* Copolymerized with polyester.
Comp. Ex. 6	PAG-10	5	174	191	17	4.2*	4.2*	1.370	20.0	4-5	Do.

Table 2

Abbreviation	Chemical Structural Formula	Average Molecular Weight
PAG-1	CH₃ (OCH₂CH₂)_mO — C(CH₃)₂ — O(CH₂CH₂O)_nCH₃ $m + n = 20$	1136
PAG-2	Ditto	696
PAG-3	Ditto	1576
PAG-4	Ditto	2456
PAG-5	Ditto	4260
PAG-6	CH₃ (OCH₂CH₂)_mO — C(CH₃)₂ — O(CH₂CH₂O)_nCH₃ $m + n = 35$	1818
PAG-7	CH₃ (OCH₂CH₂)_mO — C(CH₃)₂ — O(CH₂CH₂O)_nCH₃ $m + n = 22$	1348

Table 2 (continued)

Abbreviation	Chemical Structural Formula	Average Molecular Weight
PAG-8	$\text{CH}_3 (\text{OCH}_2\text{CH}_2)_p \left(\begin{array}{c} \text{OCHCH}_2 \\ \\ \text{CH}_3 \end{array} \right)_m \text{O} \left(\begin{array}{c} \text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array} \right)_n \text{O} \left(\begin{array}{c} \text{CH}_2\text{CH}_2\text{O} \\ \\ \text{CH}_3 \end{array} \right)_q \text{CH}_3$ $m + n = 2, p + q = 48$	2484
PAG-9	$\text{H} (\text{OCH}_2\text{CH}_2)_m \text{O} \left(\begin{array}{c} \text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array} \right)_n \text{O} \left(\begin{array}{c} \text{CH}_2\text{CH}_2\text{O} \\ \\ \text{CH}_3 \end{array} \right)_q \text{CH}_3$ $m + n = 22$	1196
PAG-10	$\text{HO} (\text{CH}_2\text{CH}_2\text{O})_{25}\text{H}$	1118
PAG-11	$\text{HO} (\text{CH}_2\text{CH}_2\text{O})_{200}\text{H}$	8818

Example 13

A dyed fabric was provided in the same manner as that of Example 4, except that twist setting was effected by a hot water treatment in a high-pressure washer at 130°C for one hr. The friction mark resistance of this woven fabric was as good as 1.5.

Claims

1. A polyester fiber having an excellent deep dyeability, comprising a polyester consisting essentially of recurring units of ethylene terephthalate, and incorporated therein, a polyoxyalkylene glycol derivative represented by the following general formula (I), pores defined by traces of removal of said polyoxyalkylene glycol derivative being present on the surface of said fiber:



wherein Z represents a residue of at least one dihydroxy compound selected from the group consisting of an aliphatic diol having 5 to 10 carbon atoms, an alicyclic diol having 3 to 15 carbon atoms, a bisphenol compound and a dihydric phenol, A represents an alkylene group having 2 to 4 carbon atoms, X represents a residue of a monohydroxy compound and m is a positive integer.

2. A polyester fiber as set forth in claim 1, wherein the polyester comprises 90% by mole or more of the recurring units of ethylene terephthalate.
3. A polyester fiber as set forth in claim 1, wherein the polyoxyalkylene glycol derivative has an average molecular weight of 1000 to 5000.
4. A polyester fiber as set forth in claim 1, wherein the aliphatic diol having 5 to 10 carbon atoms is selected from pentane-1,5-diol and hexane-1,6-diol.
5. A polyester fiber as set forth in claim 1, wherein the alicyclic diol having 3 to 15 carbon atoms is cyclohexane-1,4-dimethanol.
6. A polyester fiber as set forth in claim 1, wherein the disphenol compound is selected from bis(4-hydroxyphenyl) methane, 2,2-bis(4-hydroxyphenyl)propane, bis(4-hydroxyphenyl)sulfone and 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane.
7. A polyester fiber as set forth in claim 1, wherein the dihydric phenol is selected from hydroquinone, catechol and resorcin.
8. A polyester fiber as set forth in claim 1, wherein the alkylene group as A is selected from alkylene groups of 2 to 4 carbon atoms and mixtures one or more thereof.
9. A polyester fiber as set forth in claim 1, wherein the monohydroxy compound is selected from methanol, ethanol, phenol and cresol.
10. A polyester fiber as set forth in claim 1, which has a surface density of 1.380 g/cm³ or more as determined by a laser Raman microprobe analysis.
11. A polyester fiber as set forth in claim 1, which has a surface coating of a polymer having a lower index of refraction than the polyester fiber.
12. A process for producing a polyester fiber having an excellent deep dyeability, comprising subjecting a polyester fiber comprised of a polyester consisting essentially of recurring units of ethylene terephthalate, and incorporated therein, 0.1 to 10% by weight of a polyoxyalkylene glycol derivative represented by the following general formula (I) to a weight reduction treatment with an aqueous solution of an alkali compound to form pores on the surface of the fiber:



5

wherein Z represents a residue of at least one dihydroxy compound selected from the group consisting of an aliphatic diol having 5 to 10 carbon atoms, an alicyclic diol having 3 to 15 carbon atoms, a bisphenol compound and a dihydric phenol, A represents an alkylene group having 2 to 4 carbon atoms, X represents a residue of a monohydroxy compound and m is a positive integer.

10

13. A process according to claim 12, wherein the content of the polyalkylene glycol derivative in the starting polyester fiber is 0.5 to 5% by weight.

15

14. A process according to claim 12, wherein the alkali compound is selected from sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, sodium carbonate and potassium carbonate.

20

25

30

35

40

45

50

55

Fig. 1

