(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 June 2008 (26.06.2008)

PCT

(10) International Publication Number
WO 2008/075916 A1

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(54) Title: A METHOD OF PREPARING FLAME-RETARDANT POLYESTER FIBER AND FLAME-RETARDANT POLYESTER FIBER
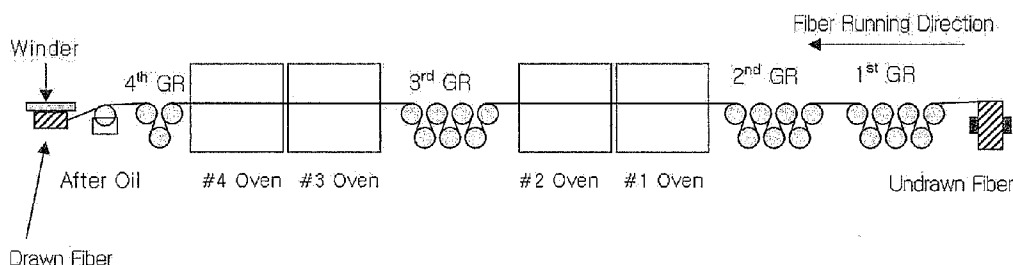
(57) Abstract: The present invention provides a method of preparing a flame retardant polyester fiber that makes it possible to prepare a flame retardant polyester fiber having excellent shape stability while preventing a lumping phenomonon and reducing powder generation and discoloration during the preparing process of the flame retardant polyester fiber, and a flame retardant polyester fiber prepared therefrom.

TITLE OF THE INVENTION

A METHOD OF PREPARING FLAME-RETARDANT POLYESTER FIBER
AND FLAME-RETARDANT POLYESTER FIBER

BACKGROUND OF THE INVENTION

5   **(a) Field of the Invention**

The present invention relates to a method of preparing a flame retardant
polyester fiber, and a flame retardant polyester fiber.

(b) Description of the Related Art

Polyester resins are generally available in many fields such as fibers, films,

10   plastic moldings, and so on because of their superior mechanical strength, heat-
resistance, and chemical resistance.   However, the polyester resins have a
disadvantage of rapid burning after being ignited, and many studies for granting flame
retardancy to the resin are actively ongoing.

As a method for granting the flame retardancy to the polyester fiber, a method

15   for coating flame retardants on the fiber surface after spinning and a method for blend-
spinning of the polyester fiber wherein un-reactive flame retardants are added before
spinning and after the polymerization thereof have been suggested.

As the flame retardants, compounds containing a halogen, mixtures of metal
oxides, compounds containing nitrogen, compounds containing phosphorus, and the

20   like have been utilized, and a method of drawing and heat-treating the fiber after
spinning the spinning composition was used according to the general direct spinning
drawing so as to promote the properties of the fiber.

However, in the case of coating the flame retardants on the fiber surface, there
are some disadvantages such as incurring expense caused by the separate post-process

25   for coating the flame retardants, the deterioration of the fiber properties caused by the
mechanical abrasion during the post-process, and the deterioration of the efficacy as it
is used repeatedly, because the flame retardants are merely coated on the fiber.

Furthermore, the blend spinning method of adding the non-reactive flame
retardants before spinning and after polymerization thereof has some disadvantages of

deterioration of the flame retardancy and the spinability of the fiber, when the non-reactive flame retardants are not uniformly mixed therein.

Furthermore, a method of making a polyester resin flame retardant by copolymerizing or blending polyester with the flame retardants during the polymerization process and preparing a polyester fiber from the resin was suggested. However, the method has a disadvantage that the properties of the fiber deteriorate according to the kinds of the flame retardants, although such method may improve the durability and the flame retardancy of the fiber in comparison with the prior method. For example, when the method uses a halogen-based flame retardant, the flame retardancy may be improved, but the polyester resin copolymerized with the flame retardant discolors and the light-resistance thereof deteriorates, and the use of flame retardant is limited because it is regarded as an environmentally harmful material. Furthermore, when the phosphorus-based flame retardant is used, there are some problems such as decreasing of thermal stability, discoloration, and deterioration of the quality of the final product.

To overcome these problems, Japan patent publication Sho 57-202251 and Sho 59-191716 suggested a method of preparing a flame retardant polyester fiber with a flame retardant polyester resin, wherein the flame retardant polyester resin is prepared by introducing a flame retardant and a polycondensation catalyst after the polycondensation is started and proceeded to some degree during the copolymerization of the polyester resin. But the method did not resolve the prior problems.

Also, when a fiber is prepared by using a general flame retardant copolymer, the drawing property and the thermal stability and so on deteriorate and it is difficult to obtain the properties required to the flame retardant polyester fiber, because the copolymer is in a heterogeneous state owing to the flame retardants copolymerized in the main chain of the resin.

Furthermore, when a flame retardant is copolymerized or blended with the polyester resin in order to obtain the flame retardancy, the maintaining time of the softening state during the solid state polymerization process becomes longer in comparison with the pure polyester resin because the melting temperature gets lower

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and the cold crystallization temperature gets higher than a pure polyester resin. Accordingly, there is a problem of a lumping phenomenon in which the polyester chips are coagulated in the solid state polymerization device owing to the high temperature during the solid state polymerization.

5   To resolve the problem, a method that slowly polymerizes the polyester while elevating the temperature stepwise from low to high during the solid state polymerization process was generally used.   However, there are some problems that much powder is generated by the abrasion between the polyester chips and discoloration (dark yellowish) of the chips occurs as the time of the solid state

10   polymerization increases, and consequently the productivity of the fiber is decreased owing to the reduction of the properties thereof.

Additionally, the flame retardant polyester fiber prepared by the prior method generally shows high thermal stress and has a disadvantage of low shape stability to heat.

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SUMMARY OF THE INVENTION

Hence, the present invention provides a method of preparing a flame retardant polyester fiber that may prevent a lumping phenomenon during the preparing process of the flame retardant polyester fiber, and also reduce the powder generation and the

20   discoloration.

Further, the present invention provides a method of preparing a flame retardant polyester fiber that enables preparation of a flame retardant polyester fiber having much better shape stability.

Such method of preparing the flame retardant polyester fiber of the present

25   invention comprises the steps of: i) preparing flame retardant polyester chips by polymerizing a composition including a primary ester compound obtained by esterification of a dicarboxylic acid compound and a diol compound, and a phosphorous-based flame retardant represented by the following Chemical Formula 1, ii) pre-crystallizing the surface of the flame retardant polyester chips, iii) solid state

polymerizing the pre-crystallized polyester chips, and iv) melting and spinning the solid state polymerized polyester chips:

[Chemical Formula 1]

$$R^1O—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R^3}{|}}{P}}—CH_2CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—OR^2$$

5   wherein R^1 and R^2 are respectively or independently hydrogen, hydroxy ethyl, or hydroxy propyl, and

R^3 is hydrogen, a C_1-C_{10} alkyl, or a phenyl.

According to such method of preparing the flame retardant polyester fiber, the lumping phenomenon in which the flame retardant polyester chips are coagulated

10   during the solid state polymerization may be prevented by pre-crystallizing the flame retardant polyester chips before the solid state polymerization, and also the powder generation and the discoloration caused by abrasion between the polyester chips may be reduced by reducing the time of the solid state polymerization.

On the other hand, the method of preparing the flame retardant polyester fiber

15   may further comprise the step of v) preparing a drawn fiber by drawing and heat-treating the undrawn fiber obtained by melting and spinning the polyester chips. Furthermore, the step v) may comprise the step of heat-treating the undrawn fiber while warper-drawing it in a drawing device that is separate from a spinning device in which melting and spinning of the polyester chips is carried out.

20   It is possible to draw an undrawn fiber with a high drawing ratio at a low speed and to apply a high relaxation ratio by heat-treating the undrawn fiber while warper-drawing it in the separate drawing device. Accordingly, the prepared fiber shows low thermal stress and has good shape stability to heat because it is possible to heat-treat the undrawn fiber under the high temperature for a long time.

25   The present invention also provides a flame retardant polyester fiber, including the unit structure represented by the following Chemical Formula 2 in the main chain thereof, wherein the orientation factor of a crystal region (F_c) is from 0.85 to 0.97, the

orientation factor of an amorphous region (F_a) is from 0.15 to 0.50, the birefringence

index ($\triangle n$) is from 0.1 to 0.2, and the crystallinity (X_c) is from 40 to 55%:

[Chemical Formula 2]

$$\left[O-\underset{\underset{O}{\parallel}}{C}-CH_2CH_2-\underset{\underset{R^3}{|}}{\overset{\overset{O}{\parallel}}{P}}-O \right]$$
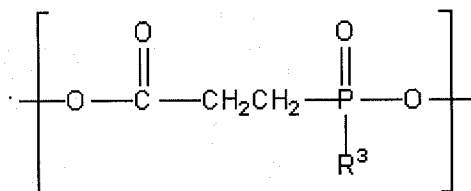
5   wherein R^3 is hydrogen, a C_1-C_{10} alkyl, or a phenyl.

Furthermore, the present invention provides an industrial fabric including such

flame retardant polyester fibers.

BRIEF DESCRIPTION OF THE DRAWINGS

10   A more complete appreciation of the invention, and many of the attendant

advantages thereof, will be readily apparent as the same becomes better understood by

reference to the following detailed description when considered in conjunction with

the accompanying drawings, wherein:

Fig. 1 is a schematic drawing showing a process of preparing a polyester fiber

15   by a direct spinning drawing method; and

Fig. 2 is a schematic drawing showing a process of preparing a polyester fiber

by a warper-drawing method according to a embodiment of the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

20   Hereinafter, referring to the attached drawings, the embodiments of the present

invention will be described in more detail.

Through repeating studies for a method of preparing a flame retardant

polyester fiber, the present inventors found that the coagulation of the chips during the

solid state polymerization, namely a lumping phenomenon, may be restrained and the

25   discoloration of the chips and the powder generation caused by abrasion may be

decreased by carrying out the step of pre-crystallizing the surface of the polyester

chips containing a phosphorus-based flame retardant before the solid state

polymerization, and accomplished the present invention. Furthermore, the present inventors confirmed that the fiber prepared by drawing and heat-treating the undrawn fiber by a warper-drawing method with a separate drawing device has superior quality and shape stability to heat than the fiber prepared by the previous direct spinning

5   drawing method.

Therefore, the method of preparing the flame retardant polyester fiber according to one embodiment of the present invention comprises the steps of: i) preparing flame retardant polyester chips by polymerizing a composition including a primary ester compound obtained by esterification of a dicarboxylic acid compound

10   and a diol compound, and a phosphorous-based flame retardant represented by the following Chemical Formula 1, ii) pre-crystallizing the surface of the flame retardant polyester chips, iii) solid state polymerizing the pre-crystallized polyester chips, and iv) melting and spinning the solid state polymerized polyester chips:

[Chemical Formula 1]

$$R^1O\text{---}\overset{\displaystyle O}{\overset{\|}{\underset{\underset{R^3}{|}}{P}}}\text{---}CH_2CH_2\text{---}\overset{\displaystyle O}{\overset{\|}{C}}\text{---}OR^2$$

15
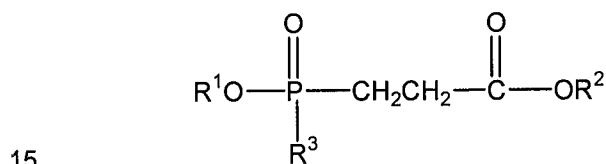
wherein R^1 and R^2 are respectively or independently hydrogen, hydroxy ethyl, or hydroxy propyl, and

R^3 is hydrogen, a C_1-C_{10} alkyl, or a phenyl.

According to such method of preparing the flame retardant polyester fiber, the

20   step i) of preparing the flame retardant polyester chips is carried out by polymerizing a composition including a primary ester compound obtained by esterification of a dicarboxylic acid compound and a diol compound, and the phosphorous-based flame retardant represented by Chemical Formula 1.

The step i) can be carried out according to the general method in the related art

25   of the present invention, and the method is not limited.

For example, the esterification may be carried out by elevating the temperature to the range of from 200°C to 300°C for 1 to 12 hours under the pressure of from 0.5 to

2 atm, after introducing 30 to 80 parts by weight of a diol compound per 100 parts by weight of a dicarboxylic acid compound.

The dicarboxylic acid compound available to the esterification may be at least one selected from the group consisting of terephthalic acid and ester derivatives thereof, and the diol compound may be at least one selected from the group consisting of ethylene glycol, diethylene glycol, neopentyl glycol, 1,4-cyclohexane dimethanol, and derivatives of bisphenol-A containing ethylene glycols at both ends thereof.

After the esterification, the phosphorous-based flame retardant is introduced therein and the polymerization is carried out for 1 to 15 hours at 200℃ to 300℃.

At this time, the phosphorous-based flame retardant represented by Chemical Formula 1 may be used, and the content of the phosphorous-based flame retardant is preferably about from 3500 to 10,000 ppm based on the phosphorous atoms. Namely, the content of the phosphorous-based flame retardant is preferably 3500 ppm or more so as to exhibit the flame retardancy at the minimum, and the content is preferably 10,000 ppm or less so as to prevent the deterioration of the properties caused by excessive use of the same.

Furthermore, the composition of the step i) may further include a color-improving agent.

The color improving agent is added for preventing the discoloration caused by the low thermal stability of the phosphorous-based flame retardant during the solid state polymerization and spinning process, and a well-known material in the related art of the present invention may be used as the color improving agent and more preferably a cobalt-based compound, for example cobalt acetate [Co(CH$_3$COO)$_2$· 4H$_2$O], can be used.

The color improving agent is preferably included in an amount of from 50 to 250 ppm. Namely, the content of the color improving agent is preferably 50 ppm or more so as to exhibit the color improving effect at the minimum, and the content is preferably from 250 ppm or less so as to prevent the side-reaction caused by excessive use of the same. Furthermore, when the cobalt-based compound is used as the color

improving agent, the cobalt-based compound is preferably included in an amount of from 12 to 59 ppm in the prepared fiber based on the cobalt atoms.

Furthermore, it is possible to polymerize the composition in the presence of a polycondensation catalyst in the step i). As such a polycondensation catalyst, antimony trioxide, titanium trioxide, and the like, which are commonly used in the polycondensation of polyester, may be used, but the kinds of the catalysts are not limited.

The polyester resin prepared by polymerizing the composition can be made into the flame retardant polyester chips of pellet form with uniform size, after cooling them with water.

On the other hand, the step ii) of pre-crystallizing the surface of the flame retardant polyester chips is carried out after the step i).

In the method of preparing the polyester fiber according to the embodiment of the present invention, the coagulation between the flame retardant polyester chips, namely a lumping phenomenon, may be restrained by pre-crystallizing the surface of the polyester chips prepared by the step i), according to the step ii). Particularly, the lumping phenomenon can be restrained even though the solid state polymerization is carried out at a high temperature for a short time. Therefore, the present method can give a high strength property to the polyester fiber while it restrains the lumping phenomenon, and also the powder generation caused by abrasion between the flame retardant polyester chips and the discoloration (dark yellowish) of the chips may be decreased. Therefore, the properties and the productivity of the polyester fiber can be raised, according to the method of preparing the polyester fiber.

For the method of pre-crystallizing the surface of the flame retardant polyester chips, a method of rubbing the chips together may be used. For example, the method of rubbing the chips together with a rotary force of a screw by using a pre-crystallizing device having a chip inlet, a cylinder equipped with the screw therein, and a chip outlet may be used.

Herein, the crystallinity resulting from the pre-crystallization is preferably from 0.1 to 5%. That is, the crystallinity of the surface of the chips is preferably

0.1% or more in order to sufficiently exhibit the surface pre-crystallization effect, and the crystallinity of the surface of the chip is preferably 5% or less in order to prevent a decrease of workability, because when the surface crystallizes excessively, the materials having low boiling point cannot be discharged easily from the chips and thus the polymerization proceeds heterogeneously.

After carrying out the step ii), the step iii) of solid state polymerizing the surface crystallized polyester chips is carried out.

The step iii) may be carried out according to a general method in the related art of the present invention. For example, the solid state polymerization may be proceeded by introducing the polyester chips, of which the surface is pre-crystallized in the step ii), into the solid state polymerizing device, and elevating the temperature in a stepwise manner. Furthermore, with regard to the conditions of the solid state polymerization, the solid state polymerization temperature may be from 200 to 260°C, and the solid state polymerization time may be from 15 to 50 hours. Herein, the solid state polymerization time means the time from the first onset point of elevating the temperature (room temperature, the starting point of the device operation after introducing the chips) to the starting point of cooling, and the solid state polymerization temperature means the maximum temperature applied to the solid state polymerization.

The polyester that is solid state polymerized through the process may be made into chips of a pellet form having uniform size, as in the step i).

Herein, the intrinsic viscosity of the solid state polymerized polyester chips is preferably from 0.85 to 1.35. Namely, the intrinsic viscosity of the chips is preferably 0.85 or more in order to exhibit the high strength property when they are spun into fiber, and the intrinsic viscosity of the chips is preferably 1.35 or less in order to prevent the thermal degradation during spinning at the high temperature.

On the other hand, after proceeding the step iii), the step iv) of melting and spinning the solid state polymerized polyester chips is carried out so as to prepare an undrawn fiber.

In the step iv), the undrawn fiber can be made by melting and spinning the solid state polymerized polyester chips obtained by the step iii), and subsequently cooling it with quenching air by passing it through a delayed quenching zone.

Herein, the spinning speed is preferably from 450 to 750 m/min based on a first godet-roller. Namely, the spinning speed is preferably 450 m/min or more in order to maintain the spinning tension at the minimum for winding, and the spinning speed is preferably 750 m/min or less in order to prevent the deterioration of the fiber properties caused by the decrease of drawability, because the orientation of the undrawn fiber is raised by the excessive spinning speed.

Furthermore, the spinning temperature is preferably from 265 to 315℃. Namely, the spinning temperature is preferably 265℃ or more in order to prevent the deterioration of the spinning properties caused by heterogeneous melt viscosity of the polyester chips, and the spinning temperature is preferably 315℃ or less in order to prevent the deterioration of the fiber properties caused by thermal degradation.

It is preferable that the delayed quenching zone has a heating hood (or an annealing heater) and a heat insulating plate. The temperature of the heating hood (or annealing heater) and the length of the heating hood or the heat insulating plate may be determined by considering the spinning tension and drawability, and preferably the temperature of the heating hood may be from 200 to 380℃, the length of the heating hood may be from 100 to 300 mm, and the length of the heat insulating plate may be from 60 to 200 mm. Furthermore, the temperature and the speed of the quenching air may be determined by considering the quenching efficiency and the uniformity of cooling, and preferably the temperature of the air may be from 15 to 30℃ and the speed of the air may be from 0.2 to 1.5 m/sec.

Furthermore, in the present method of preparing the flame retardant polyester fiber may further include the step of v) preparing a drawn fiber by drawing and heat-treating an undrawn fiber. More specifically, in the step v), it is preferable to prepare a drawn fiber by heat-treating the undrawn fiber while warper-drawing it in a drawing device that is separate from the spinning device in which melting and spinning of the polyester chips proceeds.

Namely, it is possible to produce the drawn fiber and the polyester fiber in the step v) by carrying out spinning and drawing at the same time in the drawing device connected with the spinning device, according to a conventional direct spinning drawing method (refer to Fig. 1), but it is also possible to obtain the advantages described hereinafter by producing the drawn fiber and the polyester fiber by heat-treating the undrawn fiber while warper-drawing it in the separate drawing device (refer to Fig. 2).

The conventional direct spinning drawing method executes direct heat-treating by a touch process, and thus there are some disadvantages that the application temperature is limited in the case of the polymers having low melting temperature (Tm), and the productivity is decreased because the method damages the fiber and deteriorates the quality and the strength of the fiber.

Furthermore, the direct spinning drawing method has disadvantages that the drawing ratio control and the relaxation ratio are restrictive because the method is carried out at a relatively high speed in comparison with the warper-drawing method. On the other hand, the warper-drawing method has some advantages that the high ratio drawing at low speed and the high relaxation ratio are possible and the quality and the strength of the fiber are superior, because the method uses heating air of an oven and the damage of the fiber is small. Particularly, the fiber can exhibit low thermal stress in the thermal aspect and the fiber may have superior thermal shape stability, because the heat-treating for a long time at a high temperature is possible.

Namely, the damage to the polyester fiber can be inhibited and the properties thereof can be improved by producing the drawn fiber and the polyester fiber by heat-treating the undrawn fiber while warper-drawing it in the separate drawing device (see Fig. 2), and it is possible to impart superior heat shape stability to the fiber by granting low thermal stress to the polyester fiber.

On the other hand, in the case of producing the drawn fiber according to the direct spinning drawing method as shown in Fig. 1 in the step v), it is possible to draw and heat-treat the undrawn spun fiber by contacting with the high temperature godet-roller (hereinafter "G/R") continuously.

At this time, there is a limit to elevate the heat-treating temperature because the flame retardant copolymer having a low melting temperature melts and sticks easily to the G/R, and there is a disadvantage that this causes deterioration of the productivity and the quality. Furthermore, it is required to raise the relaxation ratio in order to lower the dry heat shrinkage that represents the degree of the shape stability of the fiber, but when the relaxation ratio is raised in the direct spinning drawing method, the productivity is decreased because the fiber deviates on the G/R heavily.

In comparison, as shown in Fig. 2, it is possible to produce the drawn fiber by heat-treating the undrawn fiber while warper-drawing it in the separate drawing device, wherein the drawing device includes at least three groups of godet-rollers and at least two hot air ovens, and each godet-roller group preferably includes at least three godet-rollers.

Furthermore, it is preferable that the heat-treating and the warper-drawing are carried out under the conditions of the godet-roller temperature being from 90 to 150 ℃, the hot air oven temperature being from 210 to 275 ℃, the total drawing ratio being from 5.5 to 6.7, the relaxation ratio being from 5 to 20 %, and the winding speed being from 150 to 300 m/min.

Namely, when the temperature of the godet-roller is below 90 ℃, hairiness may be formed and the drawing property may be decreased owing to the excessive drawing tension, and when the temperature is over 150℃, the polyester is crystallized and the drawing property may be deteriorated.

Furthermore, when the temperature of the hot air oven is below 210℃, the drawing property may be decreased because of the excessive drawing tension and it is difficult to lower the shrinkage ratio of the fiber because of the low heat-treating efficiency, and when the temperature is over 275℃, the fiber breaks easily because of the low melting point of the flame retardant polyester. Herein, the number of hot air ovens may be 2 or more, and the temperature of each hot air oven can be determined and combined with each other in the temperature range.

In addition, when the total drawing ratio is over 6.7 times, the hairiness is heavily formed and the quality of the fiber is decreased, and when the ratio is below 5.5 times, it is difficult to exhibit the strength.

When the relaxation ratio is below 5%, it is difficult to exhibit the low shrinkage property, and when the ratio is over 20%, it is difficult to exhibit the strength as well as to work because of the excessive fiber deviation.

Further, when the winding speed is below 150 m/min, the productivity decreases, and when the speed is over 300 m/min, it is difficult to remove a wrap, which may be formed on the godet-roller, as well as the string-up is difficult during the working process.

After proceeding the step v), the method may further include the step vi) of after-oiling the fiber so as to pick up the liquefied phosphorus-based flame retardant onto the drawn fiber, and the flame retardancy of the polyester fiber may be increased with this step.

Furthermore, according to another embodiment of the present invention, a flame retardant polyester fiber prepared by the method is provided.

This flame retardant polyester fiber comprises the unit structure represented by the following Chemical Formula 2 in the main chain thereof, wherein the orientation factor of a crystal region (F_c) is from 0.85 to 0.97, the orientation factor of an amorphous region (F_a) is from 0.15 to 0.50, the birefringence index ($\triangle n$) is from 0.1 to 0.2, and the crystallinity (X_c) is from 40 to 55%:

[Chemical Formula 2]
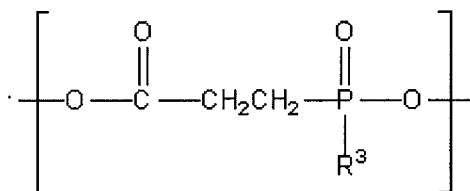
wherein R^3 is hydrogen, a C_1-C_{10} alkyl, or a phenyl.

Namely, the crystallinity of the flame retardant polyester fiber is increased by the pre-crystallization during the preparing process and the fiber becomes to have the orientation factor of the crystal region (F_c) that is from 0.85 to 0.97, the orientation

factor of the amorphous region (F_a) that is from 0.15 to 0.50, the birefringence index ($\triangle n$) that is from 0.1 to 0.2, and the crystallinity (X_c) that is from 40 to 55%. With this, the powder generation may be remarkably decreased while the lumping phenomenon is restrained during the preparing process of the flame retardant polyester

5   fiber.

Furthermore, by controlling the orientation factor of the crystal region and the amorphous region, the birefringence index, and the crystallinity to be in the above ranges, the flame retardant polyester fiber of the present invention may have a melting temperature (T_m) of 235 °C or more and an intrinsic viscosity of from 0.75 to 1.05, even

10 as it satisfies the limit oxygen index of from 27 to 37, and particularly the b value of color tone is 7.0 or less and the discoloration may be improved. Furthermore, the flame retardant polyester fiber of the present invention has superior properties such as the strength of 6.0 g/d or more and the shrinking ratio (measured by Testrite under the conditions of 190 °C, 15 min, 0.01 g/d) of 8.0 % or less, when the fineness of the single

15 fiber is from 4.0 to 5.5 denier (De).

In addition, the flame retardant polyester fiber may have the thermal stress (180 °C, Load=0.025-0.100g/d) of from 0.002 to 0.030 g/d. Namely, the flame retardant polyester fiber can exhibit more low thermal stress and thus it may have better shape stability to the heat, because the flame retardant polyester fiber is heat-

20 treated at a high temperature for a long time during the preparing process, particularly the drawing process.

On the other hand, the flame retardant polyester fiber may comprise a phosphorus-based flame retardant in an amount of from 3000 to 9000 ppm based on phosphorus atoms. Namely, the content of the phosphorus-based flame retardant in

25 the fiber may be equal to or less than the content of the phosphorus-based flame retardant in the chips, because some of the phosphorus-based flame retardant may be decomposed in the process of preparing the flame retardant polyester fiber.

According to the other embodiment of the present invention, an industrial fabric including the flame retardant polyester fiber is provided. The industrial fabric

30 may be prepared by the general method according to kinds of the fabrics or the

application field or the use thereof. However, the present industrial fabric includes the flame retardant polyester fiber having good flame retardancy and more superior properties, and thus the present fabric shows more superior properties and it can be applied to various fields.

5   Hereinafter, preferable examples and comparative examples are presented for understanding the present invention. However, the following examples are only for illustrating the present invention and the present invention is not limited to or by them.

[Examples]

Example 1

10   Bis-(β-oxyethyl)terephthalate was prepared by the esterification reaction, wherein 50 parts by weight of ethylene glycol per 100 parts by weight of terephthalic acid was introduced into an esterification reactor, and then the reactor was heated at 240 ℃ for 4 hours while extracting water from the reactor by pressurizing at the pressure of 1.0 kg/cm².

15   4.5 parts by weight (6519 ppm based on the content of phosphorus) of 3-(hydroxyphenyl phosphinyl) propanoic acid, which is a phosphorus-based flame retardant, and 0.015 parts by weight (36 ppm based on the content of cobalt) of cobalt acetate that is a color improving agent were introduced therein, they were polymerized at 286 ℃ under a pressure of 755 mmHg for 4.5 hours in the presence of the antimony

20   trioxide, which is a polycondensation catalyst, and they were made into the flame retardant polyester chips of a pellet form.

The flame retardant polyester chips were introduced into a surface crystallization device of an abrasion type, which is a device for rubbing the chips on each other by using a rotary force of a screw, and then the surface of the chips was pre-

25   crystallized at room temperature for 1 minute.

Subsequently, the surface-crystallized polyester chips were solid state polymerized at the temperature of 230℃ for 31 hours by using a solid state polymerizing device of a vacuum dryer type, so as to produce the solid state polymerized chips having the intrinsic viscosity of 1.0 g/dl. Herein, the solid state

30   polymerization time was estimated by the time from the first onset point of elevating

the temperature (room temperature, the starting point of the device operation after introducing the chips) to the starting point of cooling, and the solid state polymerization temperature means the maximum temperature applied to the solid state polymerization.

5   The solid state polymerized chips were spun at a temperature of 290 ℃ (based on the set point of the spinning block) and passed through the delayed quenching zone composed of the heating hood (or annealing heater), of which the temperature was 300 ℃ and the length was 200 mm, and the heat insulating plate, of which the length was 70 mm, and then the undrawn fibers were prepared by cooling them with a

10   quenching-air at 20 ℃ and the undrawn fibers were wound with a speed of 650 m/min.

The undrawn fibers were drawn in a warper-drawing device (or draw-warper) under the conditions of the drawing ratio being 5.8 times, the G/R temperature being 115 ℃, the hot air oven temperature being 250 ℃, the relaxation ratio being 15%, and the winding speed being 230 m/min, so as to produce the polyester fibers having 1000

15   denier, wherein the fineness of the single fiber was 5.2 DPF (denier per filament).

Examples 2-3 and Comparative Examples 1-2

As disclosed in Table 1 below, the flame retardant polyester fibers were prepared substantially according to the same method as in Example 1, except that the

20   content of the phosphorus-based flame retardant and cobalt acetate, the pre-crystallizing of the surface of the chip, and the conditions of the solid state polymerization were varied.

[Table 1]

Classification	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
Content of the phosphorus (P) of the flame retardant (ppm)	6519	3620	9100	6519	-
Content of the color improving agent (ppm)	150	60	240	-	-

Pre-crystallizing of the surface of chips		○	○	○	×	×
Conditions of the solid state polymerization	Time (h)	31	27	40	185	20
	Temperature (℃)	230	233	225	230	235
Color tone of chips (b value)		2.2	2.0	4.3	9.0	0.9
Amount of the powder generation (g/7ton)		540	450	830	2670	270
Intrinsic viscosity of the chips (g/dl)		1.0	1.2	0.9	1.3	1.0
Spinning temperature (℃)		290	305	273	310	290

Referring to the above Table 1, it should be noted that the powder generation of Examples 1 to 3, wherein the surface of the chips was pre-crystallized, was apparently decreased in comparison with Comparative Example 1, wherein the chips were not pre-crystallized.

Examples 4-8 and Comparative Example 3

As disclosed in Table 2 below, the flame retardant polyester fibers were prepared substantially according to the same method as in Example 1, except that the conditions of the spinning part and the drawing part were varied.

In addition, the flame retardant polyester fiber of Comparative Example 3 was prepared according to the direct spinning drawing method by using the chips of Example 1.

[Table 2]

Classification		Example 4	Example 5	Example 6	Example 7	Example 8	Comparative Example 3
Heating Hood	Temperature (℃)	380	230	340	350	300	320
	Length	300	300	200	300	300	200

	(mm)						
Length of the heat insulating plate (mm)		180	180	100	200	200	100
Quenching -air	Temperature (℃)	24	22	22	17	29	22
	Speed (m/s)	1.0	0.5	0.5	0.4	1.4	0.7
Spinning speed (m/min)		520	620	700	800	950	550
Drawing ratio (times)		6.6	6.3	6.1	5.8	5.6	5.7
G/R temperature (℃)		95	115	125	132	145	240
Temperature of the hot air oven (℃)		215	240	260	270	255	-
Relaxation ratio (%)		19.0	15.5	9.0	6.0	12.0	13.0
Winding speed of the drawn fiber (m/min)		165	220	235	260	285	2800
Fineness of the single fiber (De)		5.2	4.4	4.8	5.0	5.2	5.2

[Experimental Examples]

According to the standards below, the properties of the polyester fibers prepared by the Examples and the Comparative Examples were measured, and the results are disclosed in the below Tables 3 and 4.

1) Melting Temperature (Tm; ℃)

The melting temperature of the fiber was measured by using a differential scanning calorimeter (DSC, Perkin-Elmer 7 series thermal analysis system), with a scanning speed of 20 ℃/min.

2) Birefringence Index (Δn)

The birefringence index was measured by using an interference microscope (a product by Cal Zeiss Co. German, Model Name: JENAPOLUINTERPHAKO) and calculated according to the following Calculation Formula 1:

[Calculation Formula 1]

$$Birefringence\ Index\ (\Delta n) = \frac{R+S}{1,000 \times D}$$

wherein R is a compensator retardation value (nm), S is a retardation of quartz shim (nm), and D is a fiber diameter (μm).

3) Crystallinity (X_c: %): Density Gradient Method

After introducing the islands in the sea fibers into a density meter (a product by Shibayama Co. Japan, Model Name: Model SS) including a mixed solvent of normal heptane and carbon tetrachloride and leaving them at 23℃ for 1 day, the bulk density (ρ) of the islands in the sea fibers in which the sea component and the island component are combined together was measured.

Based on the density, the crystallinity was calculated according to the following Calculation Formula 2 by using the theoretical densities of the perfect crystal region (ρ_c=1.457g/cm³) and the perfect amorphous region (ρ_a = 1.336g/cm³) of the polyester:

[Calculation Formula 2]

$$Crystallinity[X_c(\%)] = \frac{\rho - \rho_a}{\rho_c - \rho_a} \times 100 .$$

4) Orientation Factor of the Crystal (F_c)

The full width at half-maximum intensity (FWHM) of the peak representing the characteristics of the crystal orientation was measured by carrying out azimuthal scanning to the (010) face and the (100) face of the crystal with an X-ray diffractometer, and the orientation factor of the crystal of the island component was calculated. The following Calculation Formulae 3 and 4 were used for calculating the orientation factor of the crystal (F_c) from FWHM:

[Calculation Formula 3]

$$Density(\rho) = \sin^{-1}(\cos\frac{2\theta}{2} \times \sin\frac{FWHM}{2})$$

[Calculation Formula 4]

$$Orientation\ Factor\ of\ the\ Crystal\ (F_c) = \frac{90 - density(\rho)}{90}.$$

5

5) Orientation Factor of the Amorphous (Fₐ)

The orientation factor of the amorphous (Fₐ) was calculated by substituting the crystallinity (Xc), the orientation factor of the crystal (Fc) and the birefringence index (△n) into the following Calculation Formula 5:

10   [Calculation Formula 5]

$$Orientation\ Factor\ of\ the\ Amorphous\ (F_a) = \frac{\Delta n - X_c \times F_c \times \Delta n_c}{(1 - X_c) \times \Delta n_a}$$

wherein △nc is an intrinsic birefringence index of the crystal (0.29), and △nₐ is an intrinsic birefringence index of the amorphous (0.20).

15   ### 6) Strength and Intermediate Elongation

The strength and the intermediate elongation were measured 10 times by using a tension tester (the length of specimen: 250mm, the tension speed: 300 mm/min.), and the average thereof was obtained.

20   ### 7) Shrinking Ratio (%)

The shrinking ratio of the fiber was measured by Testrite MK-V (a product by Testrite Co.) at the temperature of 190℃ under the tension of 0.01g/d for 15 min.

8) Intrinsic Viscosity of the fiber

25   After extracting the spinning oil from the specimen with carbon tetrachloride and dissolving the specimen in ortho chlorophenol at 160±2℃, the viscosity of the specimen in a capillary was measured by using an automatic viscometer (Skyvis-4000)

at the temperature of 25℃, and the intrinsic viscosity (IV) of the fiber was calculated according to the following Calculation Formula 6:

[Calculation Formula 6]

Intrinsic Viscosity (IV) = $\{(0.0242 \times Rel) + 0.2634\} \times F$

Rel = (seconds of solution × specific gravity of solution × viscosity coefficient) / (OCP viscosity)

F= (IV of the standard chip) / (average of three IV measured from the standard chip with standard action)

9) The Fineness of the Single Fiber

The fineness of the single fiber (or denier per filament) was obtained according to the following Calculation Formula 7 by dividing the total fineness of the fibers (or total denier of the filaments) with the number of the fibers (or filaments):

[Calculation Formula 7]

Denier per Filament (DPF) = Total denier of the filaments / the number of filaments.

10) Color Tone of the Fiber (b value)

In the case of the solid state polymerized chips, the b value was measured by using a spectrophotometer (a product by Nippon Denshoku Co., Model No.: SE-2000). In the case of the fibers, after winding the fiber on a creel with 80 cycles, the b value was measured to the two folds thereof by using computer color matching (CCM, Model No.: Datacolor SF-600).

11) Limit Oxygen Index (LOI)

After tube-knitting the fibers, the surface of the specimen was exposed to flame of a torch in an oxygen index combustibility tester (Fire Testing Technology), and whether the combustion continues and expands or not was observed with bare eyes 5 times at intervals of 5 seconds. When the specimen did not catch fire or self-extinguished a fire, the portion of oxygen in the air(V_{O2}) was raised, and the flame

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retardancy test was carried out again with a new specimen set on the tester. The portion of oxygen in the air was raised and the same test was carried out until the specimen caught fire and the combustion continued and expanded. When the specimen caught fire and the combustion continued or expanded, the portion of oxygen

5   in the total air was measured and the limited oxygen index was calculated according to the following Calculation Formula 8:

[Calculation Formula 8]

$$LOI = \frac{V_{O2}}{V_{O2} + V_{N2}} \times 100 .$$

10   **12) Workability (F/D)**

As an index representing the productivity of the fiber, the portion of the full-cheese doffing number to the total doffing number was calculated according to the following Calculation Formula 9:

[Calculation Formula 9]

15    $$F/D(\%) = \frac{Number\ of\ Full\ Cheese\ Doffing}{Number\ of\ Full\ Cheease\ Doffing + Number\ of\ Cheese\ Doffing} \times 100$$

13) Thermal Stress (g/d)

The thermal stress according to temperature was measured by using a thermal stress tester (Kanebo Co.) under the conditions of the first load of 0.025 g/d and 0.100

20   g/d with a scan speed of 2.5℃/sec, and the thermal stress at 180℃ under the first load condition was calculated according to the following Calculation Formula 10:

[Calculation Formula 10]

$$Thermal\ stress(g/d) = \frac{Measured\ Thermal\ Stress\ (g, @180°C)}{Fineness\ of\ the\ Fiber\ (d) \times 2} .$$

25   **14) The Number of Hairiness (ea/10⁶m)**

The number of hairiness was measured by using a Fluff-Detector.

[Table 3]

Classification		Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
Melting temperature (℃)		241	247	236	238	255
Birefringence index ($\triangle n$)		0.146	0.173	0.137	0.144	0.196
Orientation factor of the crystal (F_c)		0.922	0.930	0.903	0.919	0.936
Orientation factor of the amorphous (F_a)		0.272	0.480	0.242	0.271	0.676
Crystallinity (X_c)		43.0	44.3	41.5	42.3	44.6
Intrinsic viscosity of the fiber (g/dl)		0.89	0.98	0.78	0.84	0.92
Content of the phosphorus (P) (ppm)		6450	3520	9000	6180	100
Limit oxygen index (%)		32	27	36	31	22
Color tone of the fiber (b value)		4.3	2.7	6.6	9.5	1.4
Strength (g/d)		7.0	7.3	6.6	6.0	7.6
Shrinking ratio (%)		3.0	2.1	5.8	3.7	0.6
Thermal stress (@ 180℃)	@ 0.025g/d	0.010	0.002	0.015	0.011	0.001
	@ 0.100g/d	0.018	0.015	0.029	0.020	0.005
Fineness of the single fiber (De)		5.2	5.2	5.2	5.2	5.2
Number of hairiness (ea/10^6m)		1.0	0.7	1.2	3.5	0.5
Workability (%)		99.1	99.3	98.3	83.7	99.8

[Table 4]

Classification	Example 4	Example 5	Example 6	Example 7	Example 8	Comparative Example 3
Melting temperature (℃)	239	244	243	242	241	236
Birefringence index ($\triangle n$)	0.158	0.148	0.178	0.188	0.133	0.141
Orientation factor of the crystal (F_c)	0.943	0.928	0.920	0.931	0.889	0.909
Orientation factor of the amorphous (F_a)	0.384	0.287	0.467	0.474	0.173	0.229

Crystallinity (X_c)		41.3	42.8	48.8	53.2	44.1	43.7
Intrinsic viscosity of the fiber (g/dl)		0.87	0.89	0.90	0.91	0.91	0.85
Content of the phosphorus (P) (ppm)		6390	6430	6450	6460	6470	6150
Limit oxygen index (%)		31	32	32	32	32	30
Color tone of the fiber (b value)		6.5	6.0	5.3	4.9	4.2	9.6
Strength (g/d)		6.7	7.5	7.8	7.8	7.0	5.1
Shrinking ratio (%)		5.7	4.5	5.5	5.8	3.3	4.7
Thermal stress (@ 180 ℃)	@ 0.025g/d	0.015	0.014	0.017	0.016	0.013	0.021
	@ 0.100g/d	0.029	0.025	0.028	0.030	0.022	0.039
Fineness of the single fiber (De)		5.2	4.4	4.8	5.0	5.2	5.2
Number of hairiness (ea/10^6m)		1.8	1.6	0.8	2.0	1.2	5.8
Workability (%)		96.5	98.4	97.7	98.3	96.1	67.5

As shown Tables 3 and 4, it is identified that Examples 1 to 8, in which the surface of the polyester chips was pre-crystallized, show better flame retardancy in comparison with Comparative Examples 1 to 2 (particularly, Comparative Example 2),

5   in which the pre-crystallization was not applied, and also the workability thereof is good and the properties of the fiber such as strength and the like is uniformly maintained as good (particularly, in comparison with Comparative Example 1; at least one of the workability and the several properties thereof may be equivalent or better and they exhibit remarkably superior flame retardancy in comparison with

10   Comparative Example 2), because the lumping phenomonon, the powder generation, and the discoloration are prevented during the preparing process.

Furthermore, in comparison with Comparative Example 3, in which a direct spinning drawing was applied and the pre-crystallization step was not carried out as in Comparative Example 1, it can be known that the workability, the quality, and the shape stability of the fiber of Examples 1 to 8 are excellent.

5   Although the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A method of preparing a flame retardant polyester fiber comprising the steps of:

     i) preparing flame retardant polyester chips by polymerizing a composition including a primary ester compound obtained by esterification of a dicarboxylic acid compound and a diol compound, and a phosphorous-based flame retardant represented by the following Chemical Formula 1;

     ii) pre-crystallizing the surface of the flame retardant polyester chips;

     iii) solid state polymerizing the pre-crystallized polyester chips; and

     iv) melting and spinning the solid state polymerized polyester chips,

     [Chemical Formula 1]

$$R^1O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R^3}{|}}{P}}-CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OR^2$$
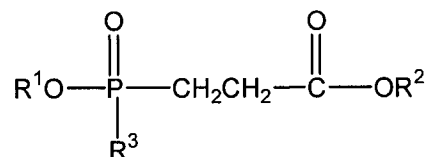
wherein R^1 and R^2 are independently hydrogen, hydroxy ethyl, or hydroxy propyl, and

     R^3 is hydrogen, a C_1-C_{10} alkyl, or a phenyl.

2. The method according to Claim 1, further comprising the step of

     v) preparing a drawn fiber by drawing and heat-treating an undrawn fiber obtained by melting and spinning the polyester chips.

3. The method according to Claim 2, wherein the step v) comprises the step of

     heat-treating the undrawn fiber while warper-drawing it in a drawing device separated from a spinning device in which melting and spinning of the polyester chips proceeds.

4. The method according to Claim 1, wherein the phosphorus-based flame retardant of the step i) is included in the composition in an amount of from 3500 to 10,000 ppm based on the phosphorus atoms.

5.   The method according to Claim 1, wherein the composition of the step i) further includes a cobalt-based compound as a color improving agent in an amount of from 50 to 250 ppm, and the cobalt-based compound is included in the prepared fiber in an amount of from 12 to 59 ppm based on the cobalt atoms.

5

6.   The method according to Claim 1, wherein the composition of the step i) is polymerized in the presence of a polycondensation catalyst.

7.   The method according to Claim 1, wherein the pre-crystallization of the step ii) is

10   carried out by rubbing the flame retardant polyester chips on each other.

8.   The method according to Claim 7, wherein the pre-crystallization of the step ii) is carried out so that the crystallinity of the flame retardant polyester chips is from 0.1 to 5%.

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9.   The method according to Claim 1, wherein the solid state polymerization of the step iii) is carried out at a temperature of from 200 to 260℃ for 15 to 50 hours so that the intrinsic viscosity of the polyester is from 0.85 to 1.35.

20   10.   The method according to Claim 1, wherein the step iv) comprises the steps of melting the solid state polymerized polyester chips at a temperature of from 265 to 315 ℃ and spinning the same at a spinning speed of from 450 to 750 m/min.

11.   The method according to Claim 10, further comprising the steps of:

25   passing the fiber through an annealing heater having a heating hood, of which the temperature is from 200 to 380℃ and the length is from 100 to 300 mm, and a delayed quenching zone having a heat insulating plate, of which the length is from 60 to 200 mm, after the melting and spinning step; and

quenching the fiber with quenching air so as to produce an undrawn fiber, wherein the air speed is from 0.2 to 1.5 m/sec and the temperature thereof is from 15 to 30℃.

12.   The method according to Claim 3, wherein the drawing device includes at least three groups of godet-rollers and at least two hot air ovens, and each godet-roller group includes at least three godet-rollers.

13.   The method according to Claim 12, wherein the step v) is carried out by heat-treating the undrawn fiber while warper-drawing it under the conditions of the godet-roller temperature being from 90 to 150 ℃, the hot air oven temperature being from 210 to 275 ℃, the total drawing ratio being from 5.5 to 6.7, the relaxation ratio being from 5 to 20 %, and the winding speed being from 150 to 300 m/min.

14.   The method according to Claim 2, further comprising the step of
        vi) after-oiling the fiber so as to pick-up the liquefied phosphorus-based flame retardant onto the drawn fiber.

15.   A flame retardant polyester fiber, comprising the unit structure represented by the following Chemical Formula 2 in the main chain thereof, wherein the orientation factor of a crystal region (F_c) is from 0.85 to 0.97, the orientation factor of an amorphous region (F_a) is from 0.15 to 0.50, the birefringence index ($\triangle n$) is from 0.1 to 0.2, and the crystallinity (X_c) is from 40 to 55%:

[Chemical Formula 2]

$$\left[-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R^3}{|}}{P}}-O- \right]$$
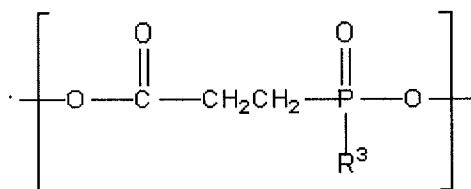
wherein R^3 is hydrogen, a C_1-C_{10} alkyl, or a phenyl.

16. The flame retardant polyester fiber according to Claim 15, wherein the limited oxygen index (LOI) is from 27 to 37, the melting temperature (Tm) is 235℃ or more, the intrinsic viscosity is from 0.75 to 1.05, the b value of the color tone is 7.0 or less, the strength is 6.0 g/d or more, the shrinking ratio (measured by Testrite under the

5   conditions of 190℃, 15 min, 0.01 g/d) is 8.0 % or less, and the fineness of the single fiber is from 4.0 to 5.5 denier (De).

17. The flame retardant polyester fiber according to Claim 15, wherein the thermal stress (180℃, Load=0.025-0.100g/d) is from 0.002 to 0.030 g/d.

10

18. The flame retardant polyester fiber according to Claim 15, comprising the phosphorus-based flame retardant in an amount of from 3000 to 9000 ppm based on phosphorus atoms.

15   19. An industrial fabric, including the flame retardant polyester fiber of Claim 15.
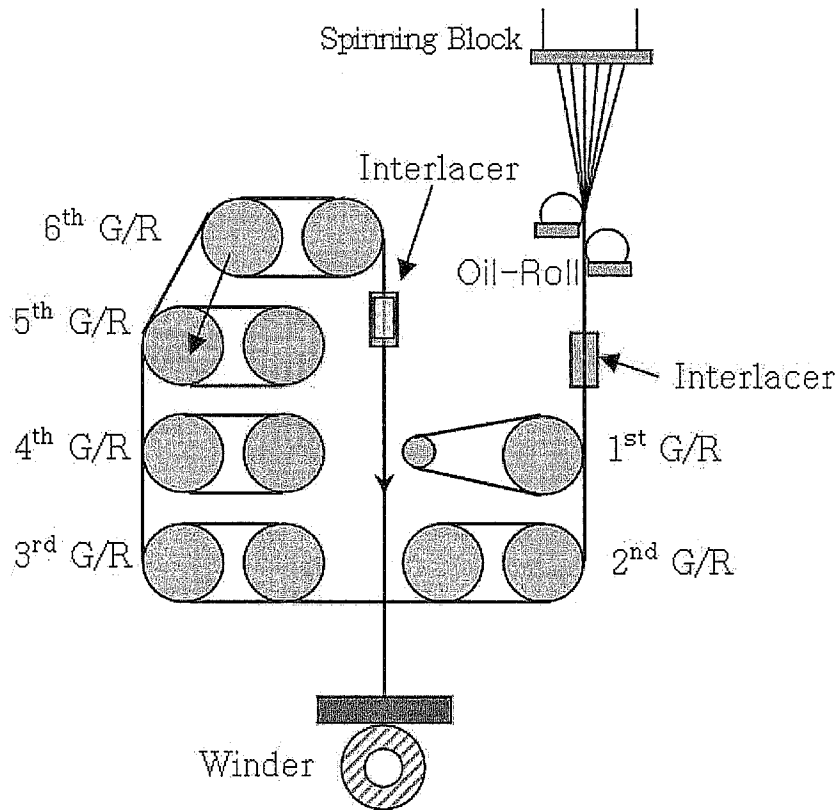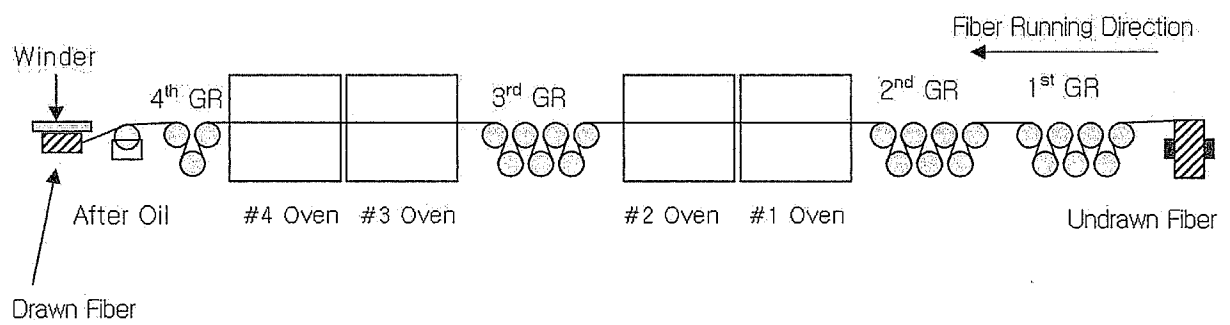
Fig. 1

Spinning Block

Interlacer

6th G/R

5th G/R

Oil-Roll

4th G/R

Interlacer

1st G/R

3rd G/R

2nd G/R

Winder

Fig. 2

Fiber Running Direction

Winder

4th GR

3rd GR

2nd GR

1st GR

After Oil

#4 Oven

#3 Oven

#2 Oven

#1 Oven

Undrawn Fiber

Drawn Fiber

INTERNATIONAL SEARCH REPORT	International application No.
	PCT/KR2007/006709

A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/62(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applictions for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS(KIPO INTERNAL), Kyeword : "polyester, flame, retadant"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 07166422 A (Kuraray Co. Ltd.) 27 June 1995 See the abstract, the claims and the chemical formula	1-19
A	KR 1019990006227 A (Huvis Corp.) 25 January 1999 See the abstract, the claims and the chemical formula	1-19
A	JP 2005076147 A (Kaneka Corp.) 24 Maarch 2005 See the abstract, the claims and the chemical formula	1-19
P, A	KR 100737977 B1 (Saehan Ind. Incorp.) 13 July 2007 See the abstract, the claims and the chemical formula	1-19

☐ Further documents are listed in the continuation of Box C.	☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 APRIL 2008 (14.04.2008)	**14 APRIL 2008 (14.04.2008)**

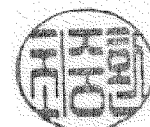| Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea	CHOI Joong Hwan
Facsimile No. 82-42-472-7140	Telephone No. 82-42-481-8408

Box No. II   Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III   Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

   The present application is found to contain two inventions as follows:
   1. Claims 1-14 are related to a method of preparing a flame retardant polyester fiber comprising the steps of i) to iv).
   2. Claims 15-19 are related to a flame retardant polyester fiber characterized by the various properties with the specific range.

   The only common technical feature between claims 1-14 and 15-19 is a flame retardant polyester comprising the unit structure represented by the following Chemical Formula 2 in the main chain. However, this feature lacks novelty and/or inventive step with respect to the following documents cited in this ISR : (a)JP 07166422 A, (b)KR 1019990006227 A. Thus, there is no technical relationship left over the prior art among the claimed inventions, leaving the claims without a single general inventive concept.
   Hence, there is a lack of unity "a posteriori"(PCT Rules 13.1 and 13.2).

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 07166422 A	27-06-1995	None	
KR 1019990006227 A	25-01-1999	None	
JP 2005076147 A	24-03-2005	None	
KR 100737977 B1	13-07-2007	None	