Title: SPANDEX FIBERS CONTAINING PARTIALLY DEHYDROXYLATED HYDROTALCITE

Abstract: This invention provides a spandex fiber comprising a partially dehydroxylated hydrotalcite in an amount of 0.1 to 10% by weight, which has excellent discoloration-resistance and chlorine-resistance as well as the intrinsic properties of spandex fiber, and thus it can be advantageously used in the manufacture of underwears, socks, and sports apparel.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
SPANDEX FIBERS CONTAINING PARTIALLY DEHYDROXYLATED HYDROTALCITE

FIELD OF THE INVENTION

The present invention relates to a spandex fiber containing a partially dehydroxylated hydrotalcite which has excellent discoloration-resistance and chlorine-resistance as well as the intrinsic properties of spandex fiber.

DESCRIPTION OF THE PRIOR ART

Spandex fibers have high rubber-like elasticity and excellent physical properties such as high tensile force and restoration force suitable for use in, e.g., underwears, socks and sports wears. Spandex fibers consist predominantly of polyurethane, whose physical properties deteriorate when exposed to chlorinated water, e.g., if a swimming wear manufactured by warp-knitting spandex and polyamide is exposed to swimming-pool water containing from 0.5 to 3 ppm of active chlorine.

Accordingly, many attempts have been made to improve the chlorine-resistance of spandex fibers by adding an additive thereto. For example, US Patent No. 4,340,527 suggests the use of zinc oxide; US Patent No. 5,626,960, a mixture of huntite and hydromagnesite; Korean Patent Publication No. 92-3250, a combination of calcium carbonate and barium carbonate; JP Application Laid-Open No. H6-81215, an MgO/ZnO solid solution; JP Application Laid-Open No. S59-133248, magnesium oxide, magnesium hydroxide or hydrotalcite; and JP Application Laid-Open No. H3-292364, hydrotalcite treated with a higher fatty acid and a silane coupling agent.

US Patent No. 5,447,969, in particular, discloses the use of hydrotalcite having crystallized water and being coated with a Cio-30 fatty
acid, to improve the dispersability of the hydrotalcite and thus prevent the hydrotalcite aggregation during the course of preparing spandex, thereby reducing the rise of discharge pressure and the frequency of yarn breakage while spinning, the discoloration during tannin solution-treatment, and the swelling when immersed in chlorinated water. More specifically, in such patent, the dry spinning process of a polyurethane solution is conducted at a high temperature condition of 330 °C to obtain spandex yarn. However, the use of hydrotalcite having crystallized water and being coated with a C_{10-30} fatty acid causes the spandex yarn discoloration to yellow-brown during the dry spinning process conducted at a temperature of 250 °C or higher.

US Patent No. 6,692,828 discloses the use of hydrotalcite coated with a melamin-based compound having good heat-resistance as an additive to improve the chlorine-resistance of spandex fibers. However, the spandex yarn still undergoes discoloration during dry spinning conducted at 250 °C or higher.

EP Application Publication No. 1 262 499 A1 discloses the use of partially decarbonated hydrotalcite milled to an average grain size of \( \mu m \) or less for improving the chlorine-resistance of polyurethane spandex. The partially decarbonated hydrotalcite is obtained by decomposing a part of carbonic ion moieties of hydrotalcite into carbon dioxide and oxygen. The carbonic ion of hydrotalcite is important for imparting the chlorine-resistance to a spandex fiber. Accordingly, the resultant spandex has the hydrotalcite containing a low carbonic ion content, thereby having unsatisfactory chlorine-resistance.

Korean Patent Application Publication No. 2006-5814 discloses a method for preparing a spandex fiber having good discoloration-resistance and chlorine-resistance by using hydrotalcite which is coated with a melamine-based compound and free of crystallized water, without dehydroxylation- or decarbonation-treatment. However, said hydrotalcite only dehydrated should be carefully handled since it is high hygroscopic and tends to convert to the original form having crystallized water, during making
its slurry or a mixture of the slurry and a polymer in spandex production. Also, such a high hygroscopicity still leads to the discoloration of the spandex yarn during dry spinning at 250 °C or higher.

Such a discolored spandex deteriorates a product quality and it can be impossible to dye the spandex white, although having good chlorine-resistance. Accordingly, it is necessary to improve both discoloration and chlorine-resistance of a spandex fiber.

SUMMARY OF THE INVENTION

It is a primary object of the present invention to provide a spandex fiber having excellent chlorine-resistance without discoloration during spinning at a temperature of 200 °C or higher.

In accordance with one aspect of the present invention, there is provided a spandex fiber comprising a partially dehydroxylated hydrotalcite in an amount of 0.1 to 10 % by weight.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects and features of the present invention will become apparent from the following description of the invention taken in conjunction with the accompanying drawings, which respectively show:

FIG. 1: a diagram showing the structure of hydrotalcite;

FIG. 2: an $^{27}$Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum of the hydrotalcite (Mg$_8$Al$_4$(OH)$_{24}$(CO$_3$)$_2$·6H$_2$O) used in Preparation 2;

FIG. 3: an $^{27}$Al MAS NMR spectrum of the partially dehydroxylated hydrotalcite (Mg$_8$Al$_4$(OH)$_{16}$O$_4$(CO$_3$)$_2$) obtained in Preparation 2;

FIG. 4: an $^{27}$Al MAS NMR spectrum of the spandex yarn obtained in Example 2;

FIG. 5: an $^{27}$Al MAS NMR spectrum of the hydrotalcite extracted from
the spandex yarn of Example 2;

FIG. 6: an infrared (IR) absorption spectrum of the hydrotalcite 
(Mg₈Al₄(OH)₂₄(CO₃)₂·6H₂O) used in Preparation 2;

FIG. 7: an IR absorption spectrum of the partially dehydroxylated 
hydrotalcite (Mg₈Al₄(OH)β₄(CO₃)₂) obtained in Preparation 2;

FIG. 8: an IR absorption spectrum of the hydrotalcite extracted from the 
spandex yarn of Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The spandex fiber of the present invention has excellent 
chlorine-resistance and does not undergo discoloration during spinning process 
conducted at 200 °C or higher, which may be prepared by heat-treating a 
ydrotalcite having crystallized water at a temperature of 200 to 390 °C to 
induce dehydration and partial dehydroxylation and then adding a partially 
dehydroxylated hydrotalcite thus obtained to a polyurethane solution.

Thus, in accordance with the present invention, hydrotalcite is 
partially dehydroxylated by heat-treatment conducted at a high temperature 
for a long period beyond those disclosed in Korean Patent Application 
Publication No. 2006-5814, and it is not decarbonated to give sufficient 
chlorine-resistance, other than that used in EP Application Publication No. 1 
262 499 Al.

Although US patent No. 5,447,969 discloses that the use of 
ydrotacite having crystallized water is effective for preventing the problems 
of the discoloration during tannin solution-treatment and the swelling when 
immersed in chlorinated water, such problems is found to be overcome by 
using the partially dehydroxylated hydrotalcite having no crystallized water 
according to the present invention.

The spandex fiber according to the present invention is described in 
detail as follows.
It should be understood that the terms used herein is defined considering the function of the present invention and the meaning will be modified according to the intent of the skill in the art, without limiting the constitution of the present invention.

The term "spinning" or "spinning process" used herein means either melt-spinning or dry-spinning. The term "spinning temperature" used herein means the maximum temperature to which a spandex polymer is subjected during a spinning process, e.g., the melting temperature of a polymer chip in a melt-spinning process, or the spinning chamber temperature of a dry-spinning process. The term "discoloration" means that a white fiber gets colored as yellow or brown.

The hydrotalcite used in the present invention is a type of metal hydroxide whose structure consist of two octahedral units having metal cation of 2 or 3 valences (M$^{+2}$ or M$^{+3}$) surrounded by six hydroxide ions (OH$^-$) in the form of double layers, anions (A$^-$) and H$_2$O molecules for balancing the charged capacity between the double layers, as shown in FIG. 1. Such a hydrotalcite can be heat-treated at a high temperature to remove H$_2$O molecules from between the double layers and further heat-treated at a higher temperature to induce dehydroxylation. If the hydrotalcite is heat-treated at a higher temperature than the dehydroxylation temperature, decarbonation may be induced (see Stanimirova et al., Clay Minerals, 39: 177-191, 2004).

The term "partially dehydroxylated hydrotalcite" used herein means a hydrotalcite obtained by heat-treating a hydrotalcite having crystallized water at a high temperature to induce dehydration and dehydroxylation which may be represented by 2OH$^- \rightarrow$ H$_2$O + O$^2^-$. The partially dehydroxylated hydrotalcite has both octahedral and tetrahedral sites, the latter containing a metal cation surrounded by four hydroxyl groups within the double-layered structure (see Stanimirova et al., Clay Minerals, 39: 177-191, 2004).

In the present invention, the partially dehydroxylated hydrotalcite
may be represented by formula (I):

\[ M^{2+}_{12}yAl_{y}(OH)_{24-2z}A(CO_3)_{y/2}mH_2O \]  

(I)

wherein, \( M \) is Mg or Ca or Zn, \( y \) is a value in the range of \( 2.4 < y \leq 4 \), \( z \) is a value in the range of \( 0 < z \leq 8 \), and \( m \) is zero or a positive number.

It is preferred that the partially dehydroxylated hydrotalcite is selected from the group consisting of compounds of \( \text{Mg}_8\text{Al}_4(\text{OH})_6\text{O}_4(\text{CO}_3)_2 \), \( \text{Mg}_8\text{Al}_4(\text{OH})_8\text{O}_8(\text{CO}_3)_2 \), \( \text{Mg}_9\text{Al}_3(\text{OH})_{18}\text{O}_3(\text{CO}_3)_{1.5} \), \( \text{Mg}_9\text{Al}_3(\text{OH})_{12}\text{O}_6(\text{CO}_3)_{1.5} \), \( \text{Mg}_{9.6}\text{Al}_{2.4}(\text{OH})_{i_2}\text{O}_{24}(\text{CO}_3)_{1.2} \), \( \text{Mg}_{9.6}\text{Al}_{2.4}(\text{OH})_{i_4}\text{O}_{48}(\text{CO}_3)_{1.2} \), \( \text{Mg}_8\text{Al}_4(\text{OH})_{i_6}\text{O}_4(\text{CO}_3)_{1.2}\text{O}_6\text{O}_5 \), \( \text{Mg}_8\text{Al}_4(\text{OH})_{i_8}\text{O}_8(\text{CO}_3)_{2}\text{O}_7\text{H}_2\text{O}_5 \), \( \text{Mg}_9\text{Al}_3(\text{OH})_{i_{18}}\text{O}_3(\text{CO}_3)_{1.5}\text{O}_7\text{H}_2\text{O}_5 \), \( \text{Mg}_9\text{Al}_3(\text{OH})_{i_{12}}\text{O}_6(\text{CO}_3)_{1.5}\text{O}_8\text{H}_2\text{O}_5 \), and a mixture thereof.

In accordance with the present invention, the starting hydrotalcite having crystallized water is preferably heat-treated at a temperature of 200 to 390 °C, more preferably 250 to 300 °C under a moisture-free atmosphere of nitrogen, helium, oxygen, hydrogen or carbon dioxide.

If the hydrotalcite having crystallized water is heat-treated at a temperature less than 200 °C, the hydrotalcite may not be dehydroxylated.

If the hydrotalcite having crystallized water is heat-treated at a temperature higher than 390 °C, the hydrotalcite may undergo dehydroxylation and further decarbonation, leading to deteriorated chlorine-resistance. Accordingly, the partially dehydroxylated hydrotalcite obtained from the heat-treatment at about 250 to 300 °C is useful for the improvement of chlorine-resistance.

The partially dehydroxylated hydrotalcite of the present invention may adsorb moisture in air, but most of the moisture adsorbed is vaporized at about 100 °C, and thus such adsorbed moisture is different from crystallized water which is present in the hydrotalcite before heat-treatment and vaporizes at about 170 to 220 °C. Accordingly, the partially dehydroxylated hydrotalcite is believed to give no affection on the
discoloration of the spandex yarn during a spinning process at 200 °C or higher since the moisture adsorbed therein is already removed at about 100 °C while the hydrotalcite having crystallized water may induce the discoloration of the spandex yarn as the initial crystallized water thereof vaporizes during a spinning process at 200 °C or higher.

Also, the inventive spandex fiber prepared by adding the partially dehydroxylated hydrotalcite has superior chlorine-resistance than that prepared by adding hydrotalcite having crystallized water, which is considered as a result that the layered double hydroxide system of the partially dehydroxylated hydrotalcite is changed to enhance its capacity for water absorption and ion-exchange.

The polyurethane used in the preparation of the spandex fiber according to the present invention may be prepared by a conventional method known in the art, e.g., by reacting an organic diisocyanate and a diol polymer to produce a polyurethane precursor, dissolving the precursor in an organic solvent and allowing the resulting solution to react with a diamine and monoamine. The organic diisocyanate which may be used in the present invention includes diphenylmethane-4,4'-diisocyanate, hexamethylenediisocyanate, toluenediisocyanate, butylenediisocyanate and hydrogenated diphenylmethane-4,4'-diisocyanate. Also, examples of the diol polymer which may be used in the present invention include polytetramethylene ether glycol, polypropylene glycol, polycarbonate diol, etc. The diamine is used as a chain extender and examples thereof are ethylenediamine, propylenediamine and hydrazine. The monoamine is used as a chain terminator and it may be diethyldiamine, monoethanolamine or dimethylamine.

In the present invention, the polyurethane for preparing the spandex fiber may further comprise organic additives including hindered phenol-based compounds, benzofuranons, semicarbazides, benzotriazoles, hindered amine-based compounds, and polymeric tertiary amine stabilizers such as a tertiary nitrogen atom-containing polyurethane and polydialkyl...
aminoalkyl methacrylate, so as to prevent the spandex fiber from
discoloration and deterioration in physical properties.

Furthermore, the spandex fiber of the present invention may further
comprise inorganic additives such as titanium dioxide and magnesium stearate. The titanium dioxide may be used in an amount of 0.1 to 5 % by weight according to the whiteness of the spandex fiber desired. The magnesium stearate may be used in an amount of 0.1 to 2 % by weight to enhance the unwinding property of the spandex fiber.

In accordance with the present invention, the partially dehydroxylated
hydrotalcite is used in an amount of 0.1 to 10 % by weight based on the
weight of the polyurethane used. When the amount is less than 0.1 % by weight, the chlorine-resistance of the spandex fiber may be insufficient, and when the amount is higher than 10 % by weight, the strength, elongation and modulus of the spandex fiber deteriorate.

In the preparation of the spandex fiber according to the present
invention, the partially dehydroxylated hydrotalcite may be added to the
polyurethane at any convenient time, e.g., after mixing with an additive followed by a sand-grinding or milling process, or after a sand-grinding or milling process in the absence of an additive.

In the present invention, the partially dehydroxylated hydrotalcite may be further coated or not coated with a coating agent conventionally used in
the art, which does not affect the chlorine-resistance and discoloration of the spandex yarn. Examples of the coating agent include aliphatic alcohols, fatty acids, fatty acid salts, fatty acid esters, phosphoric acid esters, styrene/maleic acid anhydride copolymers and derivatives thereof, silane-based coupling agents, titanate-based coupling agents, polyorganosiloxanes, polyorganohydrogensiloxanes and melamine-based
compounds. Among these, fatty acids, fatty acid salts and/or melamine-based compounds are preferred since said two formers exhibit
excellent coating efficiency and the latter can minimize discoloration upon
the dehydroxylation of hydrotalcite by heat-treatment.
The coating process for hydrotalcite may be conducted by adding a coating agent to a solvent such as water, alcohol, ether or dioxane in an amount of 0.1 to 10 % by weight based on the weight of hydrotalcite to obtain a coating agent solution, adding hydrotalcite thereto and stirring the resulting solution at an elevated temperature of 50 to 170 °C (if necessary, using a high-pressure reactor) for 10 minutes to 2 hours, followed by filtering and drying. Alternatively, the coating process may be conducted by heat-melting a coating agent without solvent and mixing the melted coating agent with hydrotalcite in a high-speed mixer.

Particularly, the coating process using the melamine-based compounds in water should be conducted at a temperature of 150 °C or higher under pressure, due to a high melting point of the melamine-based compound.

The coating process using the fatty acids or fatty acid salts in water is preferably carried out at a temperature of 100 °C or higher. When the coating temperature is less than 100 °C, it is difficult to achieve uniform coating and non-discoloration, and the amount of the coating agent required increases. For example, the fatty acids or fatty acid salts is used in an amount of about 3 % by weight based on the hydrotalcite in the coating process at less than 100 °C, while its amount may be reduced to 1.5 % by weight based on the hydrotalcite in the coating process at 100 °C or higher. Such a reduced amount of the coating agent can reduce its discoloration during heat-treating of the hydrotalcite.

The fatty acids which may be used as a coating agent in the present invention are preferably selected from mono- or poly-hydroxy fatty acids having linear or branched hydrocarbon chains of 3 to 40 carbon atoms, e.g., lauric acid, carproic acid, palmitic acid and stearic acid.

The fatty acid salts which may be used as a coating agent in the present invention are formed from mono- or di-functional and saturated or unsaturated fatty acid having 6 to 30 carbon atoms, and a metal selected from metals of Groups I to III of Elementary Periodic Table and zinc. Examples
of the fatty acid salts include lithium, magnesium, calcium, aluminum or zinc salts of oleic acid, palmitic acid or stearic acid, preferably magnesium stearate, calcium stearate and aluminum stearate, more preferably magnesium stearate.

The melamine-based compounds which may be used as a coating agent in the present invention include melamine compounds, phosphor-containing melamine compounds and melamine cyanurate compounds, optionally substituted with an organic compound having a carboxyl group, which may be used alone or in combination.

Examples of the melamine compounds include methylene dimelamine, ethylene dimelamine, trimethylene dimelamine, tetramethylene dimelamine, hexamethylene dimelamine, decamethylene dimelamine, dodecamethylene dimelamine, 1,3-cyclohexylene dimelamine, p-phenylene dimelamine, 1/7-xylene dimelamine, diethylene trimelamine, triethylene tetramelamine, tetraethylene pentamelamine, hexaethylene heptamelamine and melamine formaldehyde.

Examples of phosphor-containing melamine compounds include any of the above-mentioned melamine compounds coupled with phosphoric acid or a phosphate, e.g., dimelamine pyrophosphate, melamine primary phosphate, melamine secondary phosphate, melamine polyphosphate and melamine salt of bis-(pentaerythritol phosphate) phosphoric acid, etc.

Examples of the melamine cyanurate compounds include melamine cyanurates substituted with at least one substituent selected from methyl, phenyl, carboxymethyl, 2-carboxyethyl, cyanomethyl and 2-cyanoethyl.

It is preferred that the above melamine-based compounds are reacted with an organic compound having a carboxyl group. Examples of the organic compound having a carboxyl group include aliphatic monocarboxylic acids (e.g., caprylic acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, eicosanoic acid and behenic acid); aliphatic dicarboxylic acids (e.g., malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebasic
acid, 1,9-nonanedicarboxylic acid, 1,10-decanedicarboxylic acid, 1,11-undecanedicarboxylic acid, 1,12-dodecanedicarboxylic acid, 1,13-tridecanedicarboxylic acid and 1,14-tetradecanedicarboxylic acid); aromatic monocarboxylic acids (e.g., benzoic acid, phenylacetic acid, α-naphthoic acid, β-naphthoic acid, cinnamic acid, /?-amino hippuric acid and 4-(2-thiazoylsulfamyl)-phthalaninoic acid); aromatic dicarboxylic acids (e.g., terephthalic acid, isophthalic acid and phthalic acid); aromatic tricarboxylic acids (e.g., trimellitic acid, 1,3,5-benzenetricarboxylic acid and tris(2-carboxyethyl) isocyanurate), aromatic tetracarboxylic acids (e.g., pyromellitic acid and biphenyltetracarboxylic acid); aliphatic cyclic monocarboxylic acids (e.g., cyclohexane carboxylic acid); and aliphatic cyclic dicarboxylic acids (e.g., 1,2-cyclohexane dicarboxylic acid).

A coating agent enhances the dispersibility of the hydrotalcite in a spandex polymer solution and maintain the spinnability of the spandex.

However, although the hydrotalcite is not coated, it can exhibit excellent spinnability substantially equivalent to that of the coated hydrotalcite when sand-grinded or milled.

The sand-grinding or milling process may be conducted by milling a mixture or slurry of the hydrotalcite, a small amount of polyurethane and a solvent using a conventional bead mill. The small amount of polyurethane used can enhance the dispersibility of the hydrotalcite. Examples of the solvent which may be used in the sand-grinding or milling process include dimethylacetamide, dimethylformamide, dimethylsulfoxide and a mixture thereof.

Particularly, when the hydrotalcite is sand-grinded or milled to have secondary particles of an average size of about 15 µm or less, it can exhibit functions substantially equivalent to those of the hydrotalcite coated and sand-grinded or milled, during the preparation of the spandex fiber.

Also, in the present invention, the heat-treatment for dehydroxylation of the hydrotalcite may be conducted using various types of dryers to give heat of about 200 to 390 °C, e.g., those operated in a convection, conduction,
radiation, microwaves or vacuum heating process.

The present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is not restricted by the specific Examples.

Example

Preparation of partially dehydroxylated hydrotalcite

Preparation 1

Stearic acid and hydrotalcite of formula \( \text{Mg}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)_2\cdot\text{OH}_2\text{O} \) were successively added to water. The amount of stearic acid was 2 wt% based on the weight of the hydrotalcite. The resulting mixture was stirred at 150 °C for 20 minutes, filtered and dried, to obtain hydrotalcite coated with stearic acid. The coated hydrotalcite was heat-treated at 250 °C for 4 hours, to obtain hydrotalcite of formula \( \text{Mg}_8\text{Al}_4(\text{OH})_i\Theta_4(\text{CO}_3)_2 \) coated with stearic acid.

Preparation 2

Stearic acid, melamine polyphosphate and hydrotalcite of formula \( \text{Mg}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)_2\cdot6\text{H}_2\text{O} \) were successively added to water. The amounts of stearic acid and melamine polyphosphate were 2 wt% and 1 wt%, respectively, based on the weight of the hydrotalcite. The resulting mixture was stirred at 160 °C for 30 minutes, filtered and dried, to obtain the hydrotalcite coated with stearic acid and melamine polyphosphate. The coated hydrotalcite was heat-treated at 250 °C for 4 hours, to obtain hydrotalcite of formula \( \text{Mg}_8\text{Al}_4(\text{OH})_{16}\text{O}_4(\text{CO}_3)_2 \) coated with stearic acid and melamine polyphosphate.

Preparation 3

The procedure of Preparation 2 was repeated except that the
hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_2(\text{CO}_3)_2\cdot\text{OH}_2\text{O}$ was coated with 3 wt% of melamine polyphosphate, to obtain hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_{16}\text{O}_4(\text{CO}_3)_2$ coated with melamine polyphosphate. Then, the resultant was exposed to moist air for 7 days, to obtain hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_{16}\text{O}_4(\text{CO}_3)_2\cdot\text{OH}_2\text{O}$ coated with melamine polyphosphate.

**Preparation 4**

Hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$ was heat-treated at 250°C for 4 hours, to obtain hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_{16}\text{O}_4(\text{CO}_3)_2$. The resultant was immersed in water at room temperature for 5 hours and dried at 60°C for 48 hours, to obtain hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_{16}\text{O}_4(\text{CO}_3)_2\cdot\text{H}_2\text{O}$.

**Preparation 5**

The procedure of Preparation 1 was repeated except that hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{24}(\text{CO}_3)_{1.5}\cdot\text{H}_2\text{O}$ was coated with 1.5 wt% of stearic acid, to obtain hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{18}\text{O}_3(\text{CO}_3)_{1.5}$ coated with stearic acid.

**Preparation 6**

The procedure of Preparation 2 was repeated except that hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{24}(\text{CO}_3)_{1.5}\cdot\text{H}_2\text{O}$ was coated with 1.5 wt% of stearic acid and 1 wt% of melamine polyphosphate, to obtain hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{18}\text{O}_3(\text{CO}_3)_{1.5}$ coated with stearic acid and melamine polyphosphate.

**Preparation 7**

The procedure of Preparation 2 was repeated except that hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{24}(\text{CO}_3)_{1.5}\cdot\text{H}_2\text{O}$ was coated with 3 wt% of melamine polyphosphate, to obtain hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{18}\text{O}_3(\text{CO}_3)_{1.5}$ coated with melamine polyphosphate. Then, the
resultant was exposed to moist air for 7 days, to obtain hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{18}\text{O}_3(\text{CO}_3)_{1.5}\cdot 7.5\text{H}_2\text{O}$ coated with melamine polyphosphate.

**Preparation 8**

Hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{24}(\text{CO}_3)_{1.5}\cdot 7.5\text{H}_2\text{O}$ was heat-treated at 250 °C for 4 hours, to obtain hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{18}\text{O}_3(\text{CO}_3)_{1.5}$. The resultant was immersed in water at room temperature for 5 hours and dried at 60 °C for 48 hours, to obtain hydrotalcite of formula $\text{Mg}_9\text{Al}_3(\text{OH})_{18}\text{O}_3(\text{CO}_3)_{1.5}\cdot 8\text{H}_2\text{O}$.

**Comparative Preparation 1**

The coating procedure of Preparation 2 was repeated except that hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 5\text{H}_2\text{O}$ was coated with 3 wt% of stearic acid-substituted melamine polyphosphate. The resultant was heat-treated at 180 °C for 4 hours, to obtain hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ coated with stearic acid-substituted melamine polyphosphate.

**Comparative Preparation 2**

The coating procedure of Preparation 2 was repeated except that the hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot \text{SH}_2\text{O}$ was coated with 3 wt% of stearic acid-substituted melamine polyphosphate. The resultant was dried at 100 °C for 1 hours, to obtain hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot \text{SH}_2\text{O}$ coated with stearic acid-substituted melamine polyphosphate.

**Comparative Preparation 3**

The coating procedure of Preparation 2 was repeated except that the hydrotalcite of formula $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_3\cdot 3.5\text{H}_2\text{O}$ was coated with 3 wt% of melamine cyanurate. Then, the resultant was dried at 100 °C for 1 hours,
to obtain hydrotalcite of formula $\text{Mg}_4\text{Al}_2(\text{OH})_{13}\text{CO}_3\cdot3.5\text{H}_2\text{O}$ coated with melamine cyanurate.

**Comparative Preparation 4**

Stearic acid and hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot5\text{H}_2\text{O}$ were successively added to water. The amount of stearic acid was 3 wt% based on the weight of the hydrotalcite, and the resulting mixture was stirred at 95 °C for 30 minutes, filtered and dried, to obtain hydrotalcite coated with stearic acid. The coated hydrotalcite was heat-treated at 180 °C for 4 hours, to obtain hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ coated with stearic acid.

**Comparative Preparation 5**

Hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot\text{SH}_2\text{O}$ was heat-treated at 180 °C for 4 hours, to obtain hydrotalcite of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$.

**Experimental Example 1: $^{27}\text{Al}$ Magic angle spinning nuclear magnetic resonance (MAS NMR) analysis of hydrotalcite**

The hydrotalcite obtained was analyzed by $^{27}\text{Al}$ magic angle spinning nuclear magnetic resonance (MAS NMR) to examine the partial dehydroxylation thereof.

Specifically, $^{27}\text{Al}$ MAS NMR analysis was performed using a 400 MHz solid state NMR spectrometer (Varian, USA) under the conditions of: $\text{Al}_2\text{O}_3$ standard, 104.21 MHz transmitter frequency, 15 kHz spinning rate, scan numbers of times: 512 (hydrotalcite powder) or 8192 (hydrotalcite-contained yarn) and one pulse having 2.3 μs of pulse length.

The $^{27}\text{Al}$ MAS NMR result obtained can be used to determine the structure surrounding $\text{Al}^{3+}$ within the hydrotalcite. For example, the data from $^{27}\text{Al}$ MAS NMR for the initial hydrotalcite of $\text{Mg}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)_2\cdot6\text{H}_2\text{O}$ used in Preparation 2 shows a peak for octahedrally coordinated $\text{Al}^{3+}$ as shown in FIG. 2, while the data for the hydrotalcite of $\text{Mg}_8\text{Al}_4(\text{OH})_{16}\text{O}_4(\text{CO}_3)_2$ obtained in Preparation 2 shows
peaks for both octahedrally coordinated $\text{Al}^{3+}$ and tetrahedrally coordinated $\text{Al}^{3+}$ as a result of partial dehydroxylation, as shown in FIG. 3.

Thus, the hydrotalcite obtained in Preparation 2 was found to be partially dehydroxylated, as witnessed by the presence of the tetrahedral peak.

**Experimental Example 2: Infrared (IR) analysis of hydrotalcite**

The hydrotalcite obtained in Preparation 2 was also analyzed by IR spectroscopy to examine the partial dehydroxylation thereof. If the hydrotalcite is partially dehydroxylated, an IR absorption spectrum shows a distinct peak at wave numbers of about 1500 to 1600 cm$^{-1}$.

Specifically, IR analysis was performed using IFS 88 (Bruker, German) according to ATR (attenuated total reflectance) under the conditions of: 400 to 4000 cm$^{-1}$ wave number area, 4 cm$^{-1}$ resolution and scan numbers: 16.

The IR absorption spectrum of the initial hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$, used in Preparation 2 shows a significant absorption peak at wave numbers of about 1300 to 1400 cm$^{-1}$ as shown in FIG. 6, while the spectrum for the hydrotalcite of formula $\text{Mg}_8\text{Al}_4(\text{OH})_6\theta_4(\text{CO}_3)_2$ obtained in Preparation 2 shows significant absorption peaks at wave numbers of about 1300 to 1400 cm$^{-1}$ and about 1500 to 1600 cm$^{-1}$ as shown in FIG. 7.

Thus, only the hydrotalcite obtained in Preparation 2 was found to be partially dehydroxylated, as witnessed by the presence of a distinct peak at about 1500 to 1600 cm$^{-1}$.

**Examples 1 to 8 and Comparative Examples 1 to 5**

518 g of diphenylmethane-4,4'-diisocyanate and 2,328 g of polytetramethylene ether glycol (Mw 1,800) were reacted with stirring at 80 °C under a nitrogen atmosphere for 90 minutes to produce a polyurethane prepolymer having isocyanate groups at both terminals. After cooling the
prepolymer to room temperature, 4,269 g of dimethylacetamide was added to obtain a polyurethane prepolymer solution. Subsequently, 34.4 g of ethylenediamine, 10.6 g of propylenediamine and 9.1 g of diethylamine were dissolved in 1,117 g of dimethylacetamide. The resultant solution was added to the prepolymer solution at 10 °C or below to obtain a polyurethane solution.

Based on the total weight of the solid portion of the polyurethane solution, 1 wt% of ethylenebis(oxyethylene)bis-(3-(5-t-butyl-4-hydroxy-w- toyl)-propionate), 1 wt% of l,l,r,r-tetramethyl-4,4'-(methylene-di-p- phenylene)disemicarbazide, 1 wt% of poly(N,N-diethyl-2-aminoethyl methacrylate), 0.5 wt% of titanium dioxide, 0.5 wt% of magnesium stearate, 4 wt% of each hydrotalcite obtained from Preparations 1-8 and Comparative Preparations 1-5, which were dispersed and ground in dimethylacetamide by using Advantis V3 (Drais Mahnheim, Germany), were mixed with the polyurethane solution, to obtain a polyurethane spinning solution.

The polyurethane spinning solution was then defoamed and dry-spinnned at a spinning temperature of 250 °C, to obtain a 4-filament 40-denier spandex fiber.

The spandex fibers obtained were measured for the following properties, and the results are shown in Table 1.

(1) Chlorine-resistance

The spandex yarn subjected to 50% stretching was treated with water (pH 4.2, 97 to 98 °C) for 2 hours and cooled to at room temperature. The spandex yarn was dipped in 45 t of chlorinated water (pH 7.5) containing 3.5 ppm of active chlorine for 24 hours, and its strength was measured with Instron 4301 (Instron Co., USA) by applying 1 kg cell to a sample piece of 5 cm long, at 300 mm/min of cross head speed, to calculate the strength preservation rate as follows:

\[
\text{Strength preservation rate (\%)} = \left( \frac{S}{S_0} \right) \times 100
\]
(wherein, $S_0$ is strength before treatment, and $S$ is strength after treatment)

(2) Discoloration-resistance

Tubular knitted fabric was prepared using a spandex alone with a tubular knitting machine (KT-400, 4 inches of diameter, 400 needles, Nagata Seiki Company, Japan), and scoured in water whose weight was 40 times as much as the weight of the fabric using a mixture of scouring agents, 2 g/L of UNITOL CT-81 (Shinyoung Chemical, Korea), 3 g/L of UNITOL-SMS (Shinyoung Chemical, Korea) and 0.5g/L of NaOH at 90°C for 30 minutes. The scoured fabric was measured for its yellowing value "$b" with a color-view spectrophotometer (BKY-Gardener, USA) under the conditions of: instrument geometry = 45°/0°, illuminant/observer = D65/10°, 11 mm sample port aperture, and 3 repeat measurements. Lower $b$ value means less discoloration.
As shown in Table 1, the spandex fibers of Examples 1 to 8 contain the partially dehydroxylated hydrotalcite and thus they did not discolor during spinning at a temperature of 200 °C or higher and were also good resistant to

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<tr>
<th>Ex.</th>
<th>Coating agent (amounta)</th>
<th>Hydrotalcite</th>
<th>Strength preservation rate after 24 hours</th>
<th>Yarn color (&quot;b&quot; value)</th>
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<tr>
<td>1</td>
<td>Stearic acid (2 wt%)</td>
<td>Mg₈Al₆(OH)₁₆O₄ (CO₃)₂</td>
<td>94%</td>
<td>-1.5</td>
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<td>2</td>
<td>Stearic acid (2 wt%) +</td>
<td>Mg₈Al₆(OH)₁₆O₄ (CO₃)₂</td>
<td>93%</td>
<td>-1.7</td>
</tr>
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<td></td>
<td>Melamine polyphosphate</td>
<td>Mg₈Al₆(OH)₁₆O₄ (CO₃)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1 wt%)</td>
<td>(CO₃)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Melamine polyphosphate</td>
<td>Mg₈Al₆(OH)₁₆O₄</td>
<td>89%</td>
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<tr>
<td></td>
<td>(3 wt%)</td>
<td>(CO₃)₂.6H₂O</td>
<td></td>
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<td>4</td>
<td>-</td>
<td>Mg₈Al₆(OH)₁₆O₄ (CO₃)₂</td>
<td>87%</td>
<td>-1.8</td>
</tr>
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<td></td>
<td></td>
<td>(CO₃)₂.7H₂O</td>
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<td></td>
</tr>
<tr>
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<td>Stearic acid (1.5 wt%)</td>
<td>Mg₉Al₃(OH)₁₈O₃ (CO₃)₁.₅</td>
<td>97%</td>
<td>-1.7</td>
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<td></td>
<td></td>
<td>(CO₃)₁.₅</td>
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<tr>
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<td>Stearic acid (1.5 wt%) +</td>
<td>Mg₉Al₃(OH)₁₈O₃ (CO₃)₁.₅</td>
<td>95%</td>
<td>-1.8</td>
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<td>Mg₉Al₃(OH)₁₈O₃ (CO₃)₁.₅</td>
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<tr>
<td></td>
<td>(1 wt%)</td>
<td>(CO₃)₁.₅</td>
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<td>Melamine polyphosphate</td>
<td>Mg₉Al₃(OH)₁₈O₃ (CO₃)₁.₅</td>
<td>90%</td>
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<td></td>
<td>(3 wt%)</td>
<td>(CO₃)₁.₅.₇5H₂O</td>
<td></td>
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<tr>
<td>8</td>
<td>-</td>
<td>Mg₉Al₃(OH)₁₈O₃ (CO₃)₁.₅</td>
<td>87%</td>
<td>-1.9</td>
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<td>(CO₃)₁.₅.₈H₂O</td>
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<td>Com.</td>
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<tr>
<td>1</td>
<td>(3 wt%)</td>
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<tr>
<td>Com.</td>
<td>Stearic acid-substituted</td>
<td>Mg₆Al₂(OH)₁₆CO₃.₅H₂O</td>
<td>82%</td>
<td>6</td>
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<td>2</td>
<td>(3 wt%)</td>
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<td>Melamine cyanurate</td>
<td>Mg₄₅Al₂(OH)₁₅CO₃.₃5H₂O</td>
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<tr>
<td>3</td>
<td>Stearic acid (3 wt%)</td>
<td>Mg₆Al₂(OH)₁₆CO₃</td>
<td>84%</td>
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<tr>
<td>4</td>
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<td>Mg₆Al₂(OH)₁₆CO₃</td>
<td>83%</td>
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<tr>
<td>5</td>
<td>-</td>
<td>Mg₆Al₂(OH)₁₆CO₃</td>
<td>83%</td>
<td>4</td>
</tr>
</tbody>
</table>

a: The amount of the coating agent based the weight of hydrotalcite
anti-chlorine. In contrast, the spandex fibers containing hydrotalcites having crystallized water (Comparative Examples 2 and 3) exhibited poor resistant to both discoloration during spinning at a high temperature and chlorine. Also, the spandex fibers containing hydrotalcites which is not partially dehydroxylated and the absence of crystallized water (Comparative Examples 4 and 5) were more resistant to discoloration than those containing hydrotalcites having crystallized water, however, they were less resistant to discoloration and also to chlorine, as compared with the inventive spandex fibers.

Experimental Example 3: $^{27}$Al MAS NMR analysis of hydrotalcite contained in spandex fiber

The spandex yarn obtained in Example 2 was analyzed by $^{27}$Al MAS NMR by the procedure of Experimental Example 1, and the result is shown in FIG. 4.

As can be seen from FIG.4, the data for the spandex fiber of Example shows peaks for both octahedrally coordinated Al$^{3+}$ and tetrahedrally coordinated Al$^{3+}$.

Experimental Example 4: $^{27}$Al MAS NMR analysis of hydrotalcite extracted from spandex fiber

The spandex yarn obtained in Example 2 was evaluated for the presence of partially dehydroxylated hydrotalcite.

Specifically, the spandex yarn of Example 2 was de-oiled by petroleum-ether treatment, the oil-free yarn was dissolved in dimethylacetamide having 100 ppm or less of moisture to a concentration of 1.3% or less, and the solution was subjected to centrifugation twice to extract hydrotalcite. The extracted hydrotalcite was dried at 60 °C and analyzed by $^{27}$Al MAS NMR according to the procedure of Experimental Example 1.

The result confirmed that the extracted hydrotalcite has both octahedral and tetrahedral structures, as shown in FIG. 5.
Experimental Example 5: IR analysis of hydrotalcite extracted from spandex fiber

The hydrotalcite extracted from the spandex fiber obtained in Example 2 was also analyzed by IR spectroscopy according to the procedure of Experimental Example 2.

As a result, the IR absorption spectrum for the extracted hydrotalcite shows a significant absorption peak at wave numbers of about 1500 to 1600 cm\(^{-1}\) as shown in FIG. 8.

As described above, the spandex fiber of the present invention has high resistance to both chlorine and discoloration during spinning at a temperature of 200 °C or higher, and is therefore useful for underwear, socks, and particularly, sports apparel such as swimsuit.

While the invention has been described with respect to the specific embodiments, it should be recognized that various modifications and changes may be made by those skilled in the art to the invention which also fall within the scope of the invention as defined as the appended claims.
WHAT IS CLAIMED IS:

1. A spandex fiber comprising a partially dehydroxylated hydrotalcite in an amount of 0.1 to 10 % by weight.

2. The spandex fiber of claim 1, wherein the partially dehydroxylated hydrotalcite is represented by formula (I):

\[
M_{12}y\text{Al}_x(OH)_{24+2z}O_6(CO_3)_{y/2} \cdot mH_2O \tag{I}
\]

wherein,

- \(M\) is \(Mg_5Ca\) or \(Zn_5\)
- \(y\) is a value in the range of \(2.4 < y \leq 4\),
- \(z\) is a value in the range of \(0 < z \leq 8\), and
- \(m\) is zero or a positive number.

3. The spandex fiber of claim 2, wherein the partially dehydroxylated hydrotalcite is selected from the group consisting of compounds of \(Mg_8Al_4(OH)_{16}O_4(CO_3)_{25}\), \(Mg_8Al_4(OH)_{8}O_8(CO_3)_{12}\), \(Mg_9Al_3(OH)_{10}O_3(CO_3)_{1.5}\), \(Mg_5Al_2(OH)_{12}O_6(CO_3)_{1.5}\), \(Mg_9Al_2(OH)_{12}O_6(CO_3)_{1.5}\), \(Mg_9Al_2(OH)_{12}O_6(CO_3)_{1.5}\), \(Mg_8Al_4(OH)_{8}O_8(CO_3)_{2}7H_2O\), \(Mg_9Al_3(OH)_{18}O_3(CO_3)_{1.5}7.5H_2O\), and a mixture thereof.

4. The spandex fiber of any one of claims 1 to 3, wherein the partially dehydroxylated hydrotalcite is prepared by heat-treating a hydrotalcite having crystallized water at a temperature ranging from 200 to 390 °C.

5. The spandex fiber of claim 4, wherein the partially dehydroxylated hydrotalcite is prepared by heat-treating the hydrotalcite having crystallized water at a temperature ranging from 250 to 300 °C.

6. The spandex fiber of any one of claims 1 to 3, whose \(^{27}\text{Al}\) magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum shows peaks for both octahedrally coordinated \(\text{Al}^{3+}\) and tetrahedrally coordinated \(\text{Al}^{3+}\).
7. The spandex fiber of any one of claims 1 to 3, whose infrared (IR) absorption spectrum shows significant absorption peaks at wave numbers of 1300 to 1400 cm\(^{-1}\) and 1500 to 1600 cm\(^{-1}\).

8. The spandex fiber of any one of claims 1 to 3, wherein the partially dehydroxylated hydrotalcite has secondary particles having an average size of 15 \(\mu\text{m}\) or less.
**FIG. 1**

- Hydroxide layer $[M^{II+},M^{III}(OH)_2]^{x-}$
- Interlayer $A^{i-}$ anions
- Water molecules
- Hydroxide layer $[M^{II+},M^{III}(OH)_2]^{x-}$
- $M^{II}$ or $M^{III}$ metal cation
- $OH^-$ anions

**FIG. 2**

- Al$^{3+}$
- Contained Octahedral Peak
FIG. 3

$\text{Al}^{3+}$
- Contained Octahedral Peak

$\text{Al}^{3+}$
- Contained Tetrahedral Peak
FIG. 4

$\text{Al}^{3+}$
- Contained Octahedral Peak

$\text{Al}^{3+}$
- Contained Tetrahedral Peak
A. CLASSIFICATION OF SUBJECT MATTER

DOIF 6/70(2006.01)1

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)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

- Further documents are listed in the continuation of Box C
- See patent family annex

- Special categories of cited documents
  - "A" document defining the general state of the art which is not considered to be of particular relevance
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  - "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

- 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
- 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
- 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
- Document member of the same patent family

Date of the actual completion of the international search: 30 APRIL 2007 (30 04 2007)

Date of mailing of the international search report: 30 APRIL 2007 (30.04.2007)

Name and mailing address of the ISA/KR

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Facsimile No 82-42-472-7140

Authorized officer

CHOI Joong Hwan

Telephone No 82-42-481-8408

Form PCT/ISA/210 (second sheet) (April 2007)
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