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(71) Applicant: **Kolon Industries, Inc.**
Gangseo-gu
Seoul
07793 (KR)

(72) Inventors:
- **PARK, Jong-ho**
  Yongin-si
  Gyeonggi-do 16910 (KR)
- **PIAO, Zhequan**
  Yongin-si
  Gyeonggi-do 16910 (KR)
- **JUNG, Dae-young**
  Yongin-si
  Gyeonggi-do 16910 (KR)

(74) Representative: **Ter Meer Steinmeister & Partner Patentanwälte mbB**
Nymphenburger Straße 4
80335 München (DE)

(54) **ARTIFICIAL LEATHER MADE OF DOPE-DYED POLYESTER FIBER AND METHOD FOR PRODUCING SAME**

(57) The present invention relates to an artificial leather composed of a dope-dyed polyester fiber, which comprises carbon black in island component of a sea-island composite fiber and polyurethane polymer elastomer during producing an artificial leather.

According to the present invention, it is possible to improve the fastness to light and the fastness to rubbing at medium and deeper color, and at the same time, to have a luxuriously high quality and to reduce the amount of dye used in the production of artificial leather.

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Description

[Technical Field]

[0001] The present invention relates to artificial leather having improved fastness and dyeing productivity by using a dope-dyed polyester sea-island type composite yarn.

[Background Art]

[0002] Artificial leather is prepared by impregnating a polymer elastomer in a nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers, followed by napping and dyeing. The artificial leather has a smooth texture and unique appearance which is similar to natural leather and is widely used in various fields such as shoes, clothes, gloves, miscellaneous goods, furniture and automobile interior materials, etc.

[0003] Conventional ultrafine yarn nonwoven artificial leather has difficulty in uniform dyeing and deep shade development of ultrafine yarns and because fibers and polyurethane elastomer are dyed differently to each other due to non-dyeability of the polyurethane elastomer, two-tone or unlevel dyeing occurs, and the dyeing cost increases by introducing an excessive amount of dye for the development of deep shade, and it is difficult to realize a high quality due to a decrease in fastness.

[0004] In order to solve the above problem, technologies using a dope-dyed fiber have been developed.

[0005] As an example thereof, Korean Patent Publication No. 1996-0023482 discloses a method for producing artificial leather having excellent fastness and touch feeling.

[0006] According to this document, it is described that the dyeing fastness of artificial leather is improved by a method of impregnating a urethane resin into a nonwoven fabric made of polyamide dope-dyed ultrafine yarns and dyeing with a vat dye. However, according to this method, the use of a vat dye results in a lower light resistance than that of a dispersion dye and it is difficult to apply it to automobile interior materials due to the low weatherability of the polyamide fiber.

[0007] As another example, Korean Patent Publication No. 2012-0021665 discloses artificial leather using a black dope-dyed sea-island type composite yarn or a black dope-dyed split type composite yarn and a method of preparing the same.

[0008] According to this document, it is described that the fastness of artificial leather is improved by using a circular knitted fabric produced by plaiting a high-shrinkage polyester with a black dope-dyed polyester ultrafine textured yarn and fabricating the textured yarn.

[0009] However, according to this method, since polyester dope-dyed yarn is limited to produce circular knitted fabric and it exhibits inferior product quality compared to suede type artificial leather made of nonwoven fabric, there is a problem that usage is limited to high value added products such as furniture, automobile interior materials or luxury goods.

[0010] In the case of using a polyamide fiber in the production of ultrafine yarn nonwoven artificial leather using a dope-dyed yarn, a metal complex salt dye or a vat dye has to be used, which causes a problem that the light resistance of the artificial leather is lowered with compared to the dispersion dye.

[0011] In addition, in the case of using a polyamide fiber in the production of ultrafine yarn nonwoven artificial leather using a dope-dyed yarn, a warp knitted fabric or a circular knitted fabric is produced, which causes a problem that the product quality is inferior with compared to the nonwoven artificial leather.

[Disclosure]

[Technical Problem]

[0012] In order to solve the above problems, the present invention provides artificial leather having improved fastness and luxurious appearance quality by using a dope-dyed polyester sea-island type composite yarn and improving the manufacturing process of the dope-dyed component and the artificial leather.

[Technical Solution]

[0013] In order to solve the above problems, the present invention provides an artificial leather composed of dope-dyed polyester fiber, in which a black polymer elastomer is impregnated and a dispersion dye is dyed in a nonwoven fabric comprising sea-island type composite fiber of which an island component is black dope-dyed polyester.

[0014] Also, the present invention provides a method of preparing artificial leather composed of dope-dyed polyester fiber comprising: preparing staple fiber from sea-island type composite fiber filament composed of black dope-dyed polyester comprising 0.08 to 3.00 % by weight of a carbon black, as an island component; preparing a nonwoven fabric

by needle punching with the staple fiber; Impregnating a polymer elastomer comprising 1 to 6 % by weight of a carbon black in the nonwoven fabric; forming napping by eluting a sea component of the sea-island type composite fiber from the nonwoven fabric to produce ultrafine fiber and grinding surface of the nonwoven fabric; and dyeing nonwoven fabric using a dispersion dye.

[Advantageous Effects]

[0015] According to the present invention, the artificial leather is prepared by impregnating a black polyurethane elastomer into a nonwoven fabric made of a black dope-dyed polyester sea-island type composite fiber and dyeing with a dispersion dye, and therefore the light fastness and fastness to rubbing of the artificial leather is improved at medium or deep shade and luxurious quality is expressed and it can be applied to advanced applications such as automobile interior materials.

[0016] In addition, the reduced amount of the dye in the process of manufacturing the artificial leather decreases the cost.

[Best Mode]

[0017] The present invention relates to a method of preparing artificial leather having improved fastness properties by preparing staple fiber from sea-island type composite fiber filament; preparing staple fiber from sea-island type composite fiber; preparing a nonwoven fabric by opening, carding, crosslapping and needle punching with the staple fiber; Impregnating a polymer elastomer comprising a carbon black in the nonwoven fabric; forming ultrafine fiber by eluting alkali soluble component of the sea-island type composite fiber from the impregnated nonwoven fabric; forming napping by grinding surface of the nonwoven fabric; and dyeing nonwoven fabric using a dispersion dye.

[0018] The step of producing the sea-island type composite fiber comprises a step of composite spinning by using a first polymer of a sea component dissolved in a solvent and eluted and a second polymer of an island component remaining unresolved in a solvent.

[0019] The first polymer of the sea component may be a copolymerized polyester, polystyrene or polyethylene, etc. and preferably a copolymerized polyester having excellent alkali solubility.

[0020] The second polymer of the island component may be nylon or polyester, etc. which are not dissolved in an alkali solvent but can be dyed by a dispersion dye and specific examples thereof include polyethylene terephthalate, polyoxyethylene benzoate, polybutylene terephthalate polytrimethylene terephthalate, polyamide, polyacrylic, polyvinyl alcohol, polytriethylene terephthalate, acetate and the like.

[0021] In the composite spinning, the island component and the sea component are introduced into respective extruders and melted and extruded. When the island component is melted and extruded, carbon black master batch is side-fed into the island component. Thereafter, the island component and the sea component are discharged and spun through a composite spinning nozzle. Hereby, a sea-island type filament comprising the island component, a black second polymer can be produced.

[0022] At this time, carbon black having a better light resistance than that of organic pigment is preferable to comprise in amount of 0.08 - 3.00 % by weight in the island component of the second polymer. If the content is less than 0.08 % by weight, pale color is dyed and the color become too light color after the exposure of light in evaluation of the fastness to light and the decrease in the amount of dye used cannot be expected. When the amount exceeds 3.00 % by weight, the degree of blackness becomes too high, and thus dyeing in a specific color is not easy.

[0023] The step of producing the nonwoven fabric according to the present invention comprises a step of forming the sea-island type filament to a staple fiber, a step of forming a web by carding and crosslapping of the staple fiber and a step of needle punching the formed web.

[0024] The step of impregnating the polymer elastomer in the nonwoven fabric is characterized in that, in case that the polymer elastomer is dissolved in an organic solvent such as dimethylformamide (DMF) to prepare an impregnation solution, carbon black is added to be 1 to 6 % by weight of the content of carbon black in the solid content of the impregnation solution and homogenized with stirring, the viscosity is adjusted with the organic solvent after the homogenization to obtain an impregnation solution, and the nonwoven fabric is impregnated in the obtained impregnation solution.

[0025] If the content of the carbon black in the solid content of the impregnating solution is less than 1 % by weight, the color density of the polymer elastomer may be lower than that of the fiber in the artificial leather and if it is more than 6 % by weight, the degree of occurrence of the effect of increasing the blackness becomes slight.

[0026] The amount of impregnation of the polymer elastomer comprising carbon black in the nonwoven fabric is preferably 20 to 40 % by weight for application to an automobile interior material. If the content is less than 20 % by weight, the specific elasticity of the polymer elastomer is difficult to develop and its ability to grasp the fibers constituting the nonwoven fabric is decreased and the appearance of the surface is deteriorated due to the occurrence of dropping

on final artificial leather product and if the content exceeds 40 % by weight, soft feeling is undesirably disappeared.

[0027] As described above, since the carbon black is directly contained in the polymer elastomer so that the carbon black is prevented from coming out again in reduction cleaning and rinsing after dyeing and the carbon black is retained in the artificial leather together with the polymer elastomer, it is possible to exhibit an excellent fastness property compared with a general artificial leather production method.

[0028] After immersing the nonwoven fabric in the impregnation solution, the polymer elastomer impregnated in the nonwoven fabric is solidified in the solidification bath and then washed in a cleaning bath.

[0029] Subsequently, the sea components of the sea-island type composite fibers are removed from the nonwoven fabric to produce a nonwoven fabric with ultrafine staple fibers.

[0030] This process produces ultrafine staple fibers by leaving the second polymer as an island component only by eluting the first polymer as a sea component by using an alkali solvent such as caustic soda aqueous solution.

[0031] In this case, it is preferable to be ultrafine so that the fineness of single yarn is 0.04 to 0.30 denier after eluting the sea component. If it exceeds 0.30 denier, soft touch specific to ultrafine fibers is not exhibited and if it is less than 0.04 denier, the dye amount to be added is large and the fastness properties may be lowered.

[0032] And then, the nonwoven fabric is napped. The napping treatment is to rub the surface of the ultrafine nonwoven fabric by means such as a sandpaper so that a large amount of hairness is formed on the surface of the nonwoven fabric.

[0033] The dyeing process can be performed after napping.

[0034] The dyes used in the dyeing process include azo-based dispersion dyes, heterocyclic azo-based dispersion dyes, anthraquinone-based dispersion dyes, condensed dispersion dyes, quinoline-based dispersion dyes, coumarin-based dispersion dyes, aminoketone-based dispersion dyes and diester dispersion dyes, etc.

[0035] In addition, dyeing may be performed for 20 to 60 minutes with maintaining the temperature of the dye solution at 100 to 135 °C.

[0036] A reduction cleaning process for removing unfixed dyes or impurities on the surface of the dyed artificial leather can be further performed. The reduction cleaning process may be performed at 40 to 100 °C for 10 to 30 minutes. Through the reduction cleaning process, the color of the artificial leather can be clearer.

[0037] The reduction cleaning liquid may be sodium hydroxide or sodium hydrosulfite.

[0038] After the reduction cleaning step, a rinsing process using water may be further performed for cleaning.

[0039] Hereinafter, the present invention will be described in more detail with reference to the following Examples and Comparative Examples. It should be noted, however, these embodiments of the present invention have been described for illustrative purposes, and therefore, the present invention is not limited thereto, and it will be apparent to those skilled in the art that modifications and variations could be made without departing from the scope and the spirit of the present invention as defined by the appended claims.

[Example 1]

1) Production of sea-island type staple fiber

[0040] Polyethylene terephthalate was prepared as an island component and an alkali soluble copolymer polyester was prepared as a sea component and the island component and the sea component were introduced into respective extruders to melt and extrude the when the island component was melt and extruded, carbon black master batch was side-fed to the island component and discharged through a spinning nozzle to prepare a sea-island type filament having a carbon black of 1.5 % by weight in the island component of black polyethylene terephthalate.

[0041] Then, the sea-island type filament was stretched, crimped so that the crimp number became 10 /inch, fixed by heating and then cut into 51 mm to prepare a sea-island type staple fiber.

2) Production of nonwoven fabric

[0042] A multi-layered web was formed through the carding and the crosslapping of the sea-island type staple fiber followed by needle punching to prepare a nonwoven fabric.

3) Production of nonwoven fabric in which elastomer is impregnated

[0043] The nonwoven fabric was immersed in an impregnation solution containing polyurethane and carbon black, the polyurethane was coagulated in an aqueous solution of dimethylformamide, washed with water to prepare a black polyurethane-impregnated nonwoven fabric in which 30 % by weight of a polyurethane elastomer containing 5 % by weight of carbon black is impregnated.

4) Production of artificial leather

[0044] A sea component was eluted by treating the nonwoven fabric in which the black polyurethane was impregnated, with a caustic soda aqueous solution having a concentration of 5 % by weight. By the above, a nonwoven fabric of black polyethylene terephthalate fibers having a number of fibers divided per filament of 16 and a single yarn fineness of 0.15 denier was prepared.

[0045] The surface of the nonwoven was ground with sandpaper having a roughness of # 150 to form the napped, and then was dyed under the following dyeing conditions.

<Dyeing condition>

[0046]

A) Dye:

Black dispersion dye (anthraquinone-based) 0.8% o.w.f. (on the weight of fiber)
Red dispersion dye (anthraquinone-based) 0.5% o.w.f.
Blue dispersion dye (anthraquinone-based) 1.5% o.w.f.
Yellow dispersion dye (anthraquinone-based) 0.5% o.w.f.

B) UV-absorber: triazine derivative 4.0% o.w.f.
C) Dispersant: nonionic fatty acid ester 1 g / L
D) Acid: acetic acid 1 g / L
E) Bath ratio (additive weight: solvent weight): 1:20
F) Dyeing temperature and time: 125 °C, 50 min

[0047] After completion of the dyeing, the dyeing residue was discharged from the dyeing machine and water was again added to the dyeing machine and then reduction cleaned under reduction cleaning condition (sodium hypochlorite: 8 g/L, sodium hydroxide 4 g/L, bath ratio 1:20) and dried to prepare an artificial leather having a deep black color.

[Examples 2 and 3]

[0048] These Examples were performed in the same manner as the Example 1, except that the content of carbon black in the island component of the sea-island type filament, the content of carbon black in the polyurethane, and the dye amount in dyeing were as shown in Table 1. Artificial leather having black or dark gray with medium shades was prepared in the Example 2 and artificial leather having pale gray was prepared in Example 3.

[Comparative Examples 1 to 6]

[0049] The artificial leathers were prepared by performing the same manner as the Example 1, except that the content of carbon black in the island component of the sea-island type filament, the content of carbon black in the polyurethane, and the dye amount in dyeing were as shown in Table 1.

[Table 1]

	Content of carbon black in island component (wt%)	Content of carbon black in polyurethane (wt%)	Black dispersion Dye (% o.w.f.)	Red dispersion dye (% o.w.f.)	Blue dispersion dye (% o.w.f.)	Yellow dispersion dye (% o.w.f.)
Example 1	1.5	5	0.8	0.5	1.5	0.5
Comparative Example 1	0	5	10.55	2.49	5.17	10.51
Comparative Example 2	0	1	11.02	2.41	5.23	10.8
Comparative Example 3	0	0	11.5	2.3	5.3	11

(continued)

	Content of carbon black in island component (wt%)	Content of carbon black in polyurethane (wt%)	Black dispersion Dye (% o.w.f.)	Red dispersion dye (% o.w.f.)	Blue dispersion dye (% o.w.f.)	Yellow dispersion dye (% o.w.f.)
Example 2	0.45	1	0	0.8	0	5
Comparative Example 4	0	1	1.45	1.06	0	7.06
Comparative Example 5	0	0	2.2	1.15	0	7.5
Example 3	0.1	1	0	0.1	0.12	0.12
Comparative Example 6	0	0	0	1.55	1.47	1.22

[0050] Table 2 shows the colorimetric values measured using CCM for the dyed materials in the above Examples and Comparative Examples.

[Table 2]

	L	a	b	DE
Example 1	20.19	0.18	0.05	
Comparative Example 1	20.66	0.04	0.24	0.53
Comparative Example 2	19.97	0.34	-0.12	0.32
Comparative Example 3	20.42	-0.18	0.12	0.43
Example 2	36.12	9.58	13.01	
Comparative Example 4	36.56	9.32	13.26	0.57
Comparative Example 5	35.84	9.36	12.88	0.38
Example 3	52.14	0.73	3.6	
Comparative Example 6	52.6	0.61	3.79	0.51

[0051] From the above Tables 1 and 2, it is confirmed that the amounts of the dyes used for the same color density in Examples was smaller than that in Comparative Examples.

[0052] Evaluation results using the following evaluation methods for the above Examples and Comparative Examples are shown in Table 3 below.

<Evaluation method>

1. Fastness to light

[0053] The artificial leather prepared in the above Examples and Comparative Examples was irradiated with a light quantity of 338.6 KJ/m^2 according to the method specified in the ISO 105-B06: 1998 condition 5, and the grade of fastness to light was determined using the gray scale (ISO 105 A02).

2. Fastness to rubbing

[0054] The Fastness to rubbing was measured according to ISO 105 X12 method.

[0055] In the evaluation of the fastness to dry rubbing, two specimens of 50 mm width and 130 mm length parallel to the longitudinal direction are fixed to the test stand of the rubbing tester and the rubbers of the test rollers are covered with white cotton cloth of 50 mm length and 50 mm length and fixed. After applying a load of 9 $\pm$ 0.2 N to the rubber, the surface of the specimen was reciprocated 10 times at a reciprocating speed of 10 times/min and the passing distance

of 100 mm. The white cotton cloth was peeled off and the contamination degree of the white cotton cloth was judged according to gray scale.

[0056] The fastness to wet rubbing is evaluation in the same manner as the fastness to dry rubbing and the water is picked up at 98 to 100% in the white cotton cloth.

3. Dye amount (unit: times)

[0057] It is calculated by dividing total used amount of dye in the Comparative Example (% O.w.f.) by total used amount of dye in the Example (% o.w.f.).

4. Surface color uniformity

[0058] If artificial leather does not show coloration of polyurethane to exhibit dichroism, it marks as bad and if not, it marks as good.

<Evaluation result>

[0059]

[Table 3]

	Fastness to light (grade)	Fastness to dry rubbing (grade)	Fastness to wet rubbing (grade)	Dye amount* (times)	Surface color uniformity
Example 1	4	4~5	4	-	Good
Comparative Example 1	2~3	4	3~4	8.7	Good
Comparative Example 2	2~3	4	3~4	8.9	Bad
Comparative Example 3	2~3	4	3~4	9.1	Bad
Example 2	3	4~5	4	-	Good
Comparative Example 4	2	4	4	1.7	Good
Comparative Example 5	2	4	4	2.2	Bad
Example 3	4	4~5	4~5	-	Good
Comparative Example 6	3	4~5	4~5	12.5	Good
*) The respective amount of dye used in Comparative Examples 1, 2 and 3 is a multiple of Example 1 and those in Comparative Examples 4, 5 is a multiple of Example 2, and that in Comparative Example 6 is a multiple of Example 3.					

[0060] From Table 3, when both the ultrafine fibers composed of the artificial leather and the polyurethane contain carbon black (Examples 1, 2 and 3), the fastness to light, the fastness to dry rubbing and the fastness to wet rubbing thereof is confirmed to be excellent as grade 4 or higher and the surface color uniformity is also excellent.

[0061] Further, in the case of ultrafine yarn without carbon black (Comparative Examples 1 to 6), the fastness to light was remarkably lowered, and in particular, when the carbon black was not present in either of the ultrafine yarn and the polyurethane, it can be confirmed that the used amount of dye increases for showing the same color.

[Industrial Applicability]

[0062] As described above, the present invention can solve problems such as ununiform dyeing and difficulty in uniform and clear development of color with a deep shade in nonwoven artificial leather for fashion goods such as suede type

furniture skin material, inner skin and outer skin of bags, It is possible to improve the cost saving and the fastness property by improving the problem of excess dye to be added for color development with medium or deep shade.

Claims

1. An artificial leather composed of dope-dyed polyester fiber, in which a black polymer elastomer is impregnated and a dispersion dye is dyed in a nonwoven fabric comprising sea-island type composite fiber of which an island component is black dope-dyed polyester.

2. The artificial leather composed of dope-dyed polyester fiber of claim 1, wherein the black dope-dyed polyester comprises 0.08 to 3.00 % by weight of a carbon black.

3. The artificial leather composed of dope-dyed polyester fiber of claim 1, wherein the black polymer elastomer comprises 1 to 6 % by weight of a carbon black.

4. The artificial leather composed of dope-dyed polyester fiber of claim 1, which has fastness to light of at least grade 4, fastness to dry rubbing of at least grade 4 and fastness to wet rubbing of at least grade 4 according to ISO 105-B06: 1998 method (condition 5).

5. A method of preparing artificial leather composed of dope-dyed polyester fiber comprising:

   preparing staple fiber from sea-island type composite fiber filament composed of black dope-dyed polyester comprising 0.08 to 3.00 % by weight of a carbon black, as an island component;
   preparing a nonwoven fabric by needle punching with the staple fiber;
   Impregnating a polymer elastomer comprising 1 to 6 % by weight of a carbon black in the nonwoven fabric;
   forming napping by eluting a sea component of the sea-island type composite fiber from the nonwoven fabric to produce ultrafine fiber and grinding surface of the nonwoven fabric; and
   dyeing nonwoven fabric using a dispersion dye.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

D06N 3/12(2006.01)i, D06N 3/00(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)
D06N 3/12; D06N 3/00; D06N 3/14; D06P 1/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: sea-island, composite fiber, carbon black, spun dyed fiber, polyester, polyurethane, elastic body, needle punching, non-woven fabric, disperse dye, artificial leather

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011-523985 A (ALCANTARA S.P.A.) 25 August 2011 See claims 1, 2, 10, 12, 16; and paragraphs [0035], [0037], [0056], [0064], [0077], [0113], [0135]-[0145].	1-5
A	KR 10-1999-0031830 A (HYOSUNG CORPORATION) 06 May 1999 See the entire document.	1-5
A	JP 2003-313784 A (KURARAY CO., LTD.) 06 November 2003 See the entire document.	1-5
A	KR 10-2016-0035918 A (KOLON INDUSTRIES, INC.) 01 April 2016 See the entire document.	1-5
A	JP 2005-133256 A (KURARAY CO., LTD.) 26 May 2005 See the entire document.	1-5

☐ 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
"E" earlier application or patent but published on or after the international filing date
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"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
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 MARCH 2018 (30.03.2018)	**30 MARCH 2018 (30.03.2018)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 189 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2017/014186

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Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- KR 20120021665 **[0007]**