# 

# (11) **EP 2 740 838 A2**

(12)

# EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication: 11.06.2014 Bulletin 2014/24

(21) Application number: 12819383.6

(22) Date of filing: 03.08.2012

(51) Int Cl.: **D06M** 15/564 (2006.01) **D06M** 11/38 (2006.01)

D06M 15/263 (2006.01)

(86) International application number: PCT/KR2012/006195

(87) International publication number: WO 2013/019087 (07.02.2013 Gazette 2013/06)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: 04.08.2011 KR 20110077556

(71) Applicant: Kolon Industries, Inc.
Gwacheon-si, Gyeonggi-do 427-709 (KR)

(72) Inventors:
• HAN, In Sik

Daegu 702-756 (KR)

 LEE, Hyo Jin Chilgok-gun Gyeongsangbuk-do 718-841 (KR)

 RHO, Kyeoung Hwan Daegu 706-750 (KR)

 LEE, Bum Hoon Daegu 706-040 (KR)

(74) Representative: Ter Meer Steinmeister & Partner Patentanwälte

> Mauerkircherstrasse 45 81679 München (DE)

#### (54) SUPER ABSORBENT YARN AND METHOD FOR MANUFACTURING SAME

(57) Disclosed are to a superabsorbent yarn capable of minimizing the degradation of strength and elongation thereof after coated with a superabsorbent material and minimizing white powders which might be caused and impose processing difficulties during an optical cable

manufacturing process and a method for manufacturing the same. The superabsorbent yarn of the invention comprises a yarn and a superabsorbent material coated on the yarn, wherein the superabsorbent material comprises crosslinked polyurethane.

#### Description

[Technical Field]

- [0001] The present invention relates to a superabsorbent yarn and a method for manufacturing the same, and more particularly, to a superabsorbent yarn capable of minimizing the degradation of strength and elongation thereof after coated with a superabsorbent material and minimizing white powders which might be caused and impose processing difficulties during an optical cable manufacturing process and a method for manufacturing the same.
- 10 [Background Art]

20

25

30

35

45

50

[0002] A superabsorbent yarn can be used as a reinforcing member and an water blocking member for an optical cable. [0003] Among the methods for manufacturing a superabsorbent yarn is a method comprising impregnating a yarn with an water-insoluble superabsorbent material dispersed in water, and then drying it. According to this method, however, a yarn of satisfactory absorbency cannot be prepared because the impregnation of the yarn with the superabsorbent material is inhibited by the macromolecular structure thereof.

**[0004]** A method to improve the impregnation is disclosed in US Patent 5,635,569. According to the method, a yarn coated with a superabsorbent material is manufactured by impregnating a yarn with water-in-oil emulsion comprising the superabsorbent material in the aqueous phase and then drying it. This method, however, has significant disadvantage, too. Materials causing environmental problem, such as isohexadecane, are produced during the drying process, which requires additional equipments and costs to treat such hazardous materials.

**[0005]** To solve such problems, US Patent 5,100,397, US Patent 6,319,558, and US Patent 6,284,367 respectively suggest the methods comprising coating or impregnating a substrate with an aqueous solution comprising water-soluble and crosslinkable polymer, and then performing heat treatment to crosslink the water-soluble polymer thereby converting it to an water-insoluble superabsorbent material.

[0006] The aforementioned methods require the yarn to be heat-treated at high temperature for a long time to crosslink the water-soluble polymer, which was not crosslinked at all, in such a degree that an water-insoluble material having absorbency of high level can be formed. However, the heat-treatment at high temperature for a long time causes the yarn to be damaged, thereby degrading the strength and elongation of the yarn. The degradation of the strength and elongation is a fatal flaw of the yarn which is supposed to be used as a reinforcing member for an optical cable. Furthermore, the methods have disadvantages from the economic viewpoint since the heat-treatment at high temperature for a long time lowers the productivity and requires significant energy consumption.

**[0007]** Further, since the conventional superabsorbent material has brittleness, when the superabsorbent yarn passes through a guide during an optical cable manufacturing process, the polymer layer coated on the yarn is fractured to generate white powders. The white powders generated during the optical cable manufacturing process may cause defective products.

[Disclosure]

40 [Technical Problem]

**[0008]** Therefore, the present invention is directed a superabsorbent yarn and a method for manufacturing the same capable of preventing these limitations and drawbacks of the related art.

**[0009]** An aspect of the present invention is to provide a superabsorbent yarn capable of minimizing the degradation of strength and elongation thereof after coated with a superabsorbent material and minimizing white powders which might be caused and impose processing difficulties during an optical cable manufacturing process.

**[0010]** Another aspect of the present invention is to provide a method for manufacturing a superabsorbent yarn capable of minimizing the degradation of strength and elongation thereof after coated with a superabsorbent material and minimizing white powders which might be caused and impose processing difficulties during an optical cable manufacturing process.

**[0011]** Additional advantages, objects, and features of the present invention will be set forth in part in the description which follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from practice of the invention. The objectives and other advantages of the invention may be realized and attained by the structure particularly pointed out in the written description and claims hereof.

[Technical Solution]

[0012] According to one aspect of the invention, there is provided a superabsorbent yarn comprising: a yarn; and a

2

55

superabsorbent material coated on the yarn, wherein the superabsorbent material comprises crosslinked polyurethane. **[0013]** According to another aspect of the invention, there is provided a method for manufacturing a superabsorbent yarn, the method comprising: preparing a polyurethane dispersion; adding a first crosslinking agent to the polyurethane dispersion to produce a coating solution; applying the coating solution to a yarn; then, heat-treating the yarn at 50°C to 90°C; and removing remaining moisture from the heat-treated yarn.

**[0014]** The general description provided above and the detailed description provided below are only for illustration of the present invention and should be construed as providing a more detailed description of the inventions defined in claims.

#### [Advantageous Effects]

10

30

35

40

45

50

55

**[0015]** According to the present invention, a superabsorbent material is provided to a yarn sufficiently and uniformly so that the yarn can have satisfactory absorbency, and a superabsorbent yarn can be manufactured without producing any hazardous material which may cause environmental problems. Furthermore, since the yarn is heat-treated at relatively low temperature, the degradation of the strength and elongation of the yarn can be minimized.

**[0016]** Additionally, since the superabsorbent material of the invention provided to the yarn has relatively high flexibility, when used for manufacturing an optical cable, the superabsorbent yarn of the invention can remarkably minimize the probability that the polymer layer will be broken into the white powders. Consequently, the superabsorbent yarn of the invention makes it possible to manufacture an optical cable more easily and reduce the fraction defective as well.

#### 20 [Mode for Invention]

**[0017]** Hereinafter, the superabsorbent yarn and method for manufacturing the same according to the present invention will be described in detail only for illustrative purposes.

**[0018]** Those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention. Accordingly, the present invention includes all alternations and modifications that fall within the scope of inventions described in claims and equivalents thereto.

[0019] The superabsorbent yarn of the invention comprises a yarn and a superabsorbent material coated thereon.

**[0020]** The yarn may be a continuous multifilament. Particularly, when the function as a reinforcing member being taken into account, the yarn is preferably a multifilament of high strength. Accordingly, the yarn of the invention may be formed of aramid, ultra high molecular weight polyethylene, or polybenzoxazole.

**[0021]** Optionally, the yarn may comprise a continuous aramid multifilament comprising 1 to 20,000 monofilament(s) and having linear density of 50 to 1,500 denier. While a yarn may consist of single multifilament, a plurality of multifilaments can be combined to form a yarn.

**[0022]** The superabsorbent material of the invention coated on the yarn comprises crosslinked polyurethane. Thus, the superabsorbent material of the invention has relatively high flexibility compared to the conventional superabsorbent materials consisting of ionic polymer having carboxylic acid group and/or sulfonic acid group. Owing to the improved flexibility, if an optical cable is manufactured with the superabsorbent yarn of the present invention, the probability that the polymer layer will be broken into the white powders during the manufacturing process can be minimized.

**[0023]** According to the first embodiment of the present invention, the superabsorbent material comprises polyurethane having a network structure formed through crosslinking and does not have any ionic polymer.

**[0024]** According to the second embodiment of the present invention, the superabsorbent material comprises polyurethane crosslinked with ionic polymer such as polyacrylic acid, polyacrylamide, polymethacrylamide, copolymer of acrylic acid and acrylamide, and so on. In this case, the ionic polymer and polyurethane are crosslinked with each other to form a network structure.

[0025] Hereinafter, the method of the invention for manufacturing a superabsorbent yarn will be described in detail.

**[0026]** The method of the invention comprises preparing a polyurethane dispersion, adding a first crosslinking agent to the polyurethane dispersion to produce a coating solution, applying the coating solution to a yarn, heat-treating the yarn at 50°C to 90°C, and removing remaining moisture from the heat-treated yarn.

**[0027]** The polyurethane dispersion comprises water as a dispersion medium, and may further comprise a second crosslinking agent. The polyurethane dispersion may be either purchased or manufactured.

**[0028]** Hereinafter, a method according to one embodiment of the present invention for manufacturing a polyurethane dispersion will be explained.

**[0029]** First, diol and diisocianate react with each other to form a polyurethane precursor. According to one embodiment of the present invention, the diol is polyethylene glycol (PEG) and the diisocianate is 1,8-octanediisocianate or hexylmethanediisocianate. More particularly, the polyurethane precursor is obtained by mixing the diol and diisocianate at the molar ratio of 1:1 to 1:2 and then heating the mixture at 70 to 90 °C.

**[0030]** A polyurethane precursor dispersion is prepared by adding water to the polyurethane precursor thus obtained and stirring it at 500 to 1,500 rpm.

**[0031]** Optionally, before the polyurethane precursor dispersion is manufactured, the viscosity of the polyurethane precursor may be decreased. For example, the step for decreasing the viscosity of the polyurethane precursor can be performed by adding dibutyltin dilaurate and acetone to the polyurethane precursor so that the proportion of the solid components thereof can be 20 to 40%. Optionally, the polyurethane precursor whose viscosity has been decreased may be cooled to about 10°C.

**[0032]** Subsequently, a mixture is produced by adding an aqueous solution including a second crosslinking agent dissolved therein to the polyurethane precursor dispersion while stirring it at 100 to 300 rpm. According to one embodiment of the present invention, diethylenetriamine is used as the second crosslinking agent.

**[0033]** Then, the mixture is heated at 40°C to 80°C for 1 to 3 hours to complete the polyurethane dispersion. The polyurethane in the dispersion has mean particle diameter of 1 to 1,000 nm. The mean particle diameter can be obtained by measuring the particle diameters 10 times by means of a laser particle size analyzer (LS230, Culter, USA) and then calculating the average thereof.

[0034] Subsequently, the first crosslinking agent is added to the polyurethane dispersion thus obtained to produce a coating solution.

**[0035]** According to the first embodiment of the present invention, the coating solution is produced by adding the first crosslinking agent for crosslinking the polyurethanes with themselves to the polyurethane dispersion. The first crosslinking agent may be methylenebisacrylamide.

**[0036]** According to the second embodiment of the present invention, the coating solution is produced by adding a monomer for an ionic polymer, an initiator for the polymerization of the monomer, and the first crosslinking agent for crosslinking the ionic polymer with the polyurethane to the polyurethane dispersion.

**[0037]** The monomer for an ionic polymer may be acrylic acid, acrylamide, methacrylamide, and so on, the initiator may be a photopolymerization initiator such as potassium persulfate, and the first crosslinking agent may be methylenebisacrylamide.

**[0038]** For example, the coating solution may be produced by adding acrylamide of 70 to 90 % by total weight of the polyurethane solid components in the polyurethane dispersion, methylenebisacrylamide of 0.5 to 2 % by total weight of the acrylamide, and a predetermined amount of potassium persulfate to the polyurethane dispersion.

**[0039]** Then, the coating solution thus produced is applied to a yarn. That is, to impregnate the yarn with the coating solution, the yarn is coated with the coating solution. A variety of coating methods such as painting, rolling, printing (i.e., dot printing), spraying, brushing, swabbing, or dip coating can be used.

**[0040]** Subsequently, the coating solution-impregnated yarn is heat-treated so that the polyurethane in the coating solution can be crosslinked. Through such heat treatment, the polyurethanes are crosslinked with themselves in the first embodiment of the invention and the polyurethane is crosslinked with the ionic polymer in the second embodiment of the invention, to finally form the superabsorbent material on the multifilament.

**[0041]** The heat treatment may be performed by passing the continuous multifilament through a heating unit. According to one embodiment of the present invention, the temperature of the heating unit, i.e., the heating temperature, is 50 to  $90\,^{\circ}$ C, and the time taken for the continuous multifilament to pass through the heating unit, i.e., the heat time, is 2 to 5 hours.

**[0042]** Then, the remaining moisture, if any, is removed from the heat-treated yarn. The remaining moisture may be removed by heating the heat-treated yarn at 100°C or higher under the atmospheric pressure or by heating it at 80°C or more under the reduced.

**[0043]** According to the present invention, the heat treatment can be performed at the temperature lower than such heat treatment temperature (not lower than 150°C) as required to crosslink the water-soluble polymer in a degree enough to transform it into an water-insoluble material. Consequently, the present invention has advantages in that the degradation of the strength and elongation of the yarn which would have been serious if the heat treatment were performed at the high temperature can be minimized and the superabsorbent material can also be provided to various kinds of substrates which are vulnerable to the heat treatment at the high temperature.

**[0044]** Hereinafter, the advantageous effects of the present invention will be described in more detail with reference to Examples and Comparative Examples. The present invention is not limited to the Examples below which are illustrated only for the easy understanding of the invention.

# 50 <u>Example 1</u>

10

20

30

35

40

45

55

[0045] Polyurethane precursor was prepared by mixing polyethylene glycol and 1,8-octanediisocianate at the molar ratio of 3:4 and heating it at about 80°C. The viscosity of the polyurethane precursor was decreased by adding dibutyltin dilaurate and acetone to the polyurethane precursor so that the proportion of the solid components thereof becomes 30%. Then, polyurethane precursor dispersion was prepared by adding distilled water to the polyurethane precursor while stirring it at 1,000 rpm. Diethylenetriamine aqueous solution was added thereto to produce a mixture, and the mixture was stirred at about 60°C for 2 hours to complete the polyurethane dispersion. Then, coating solution was prepared by adding methylenebisacrylamide to the polyurethane dispersion.

[0046] A yarn including continuous aramid multifilaments was dipped into the coating solution thus obtained to impregnate the yarn with the coating solution.

**[0047]** Subsequently, the coating solution-impregnated yarn was heat-treated at about 70°C for 3 hours so that the superabsorbent material having a network structure formed through the crosslinking of the polyurethanes with themselves could be formed on the yarn. The yarn was heated at about 120°C to remove any remaining moisture therefrom to complete a superabsorbent material-coated yarn.

#### Example 2

15

25

30

40

45

55

[0048] A coating solution was prepared by adding acrylamide, methylenebisacrylamide, and potassium persulfate to a polyurethane dispersion made in the same manner as that of the Example 1.

**[0049]** A yarn including continuous aramid multifilaments was impregnated with the coating solution by dipping the yarn into the coating solution, and then the coating solution-impregnated multifilaments were heat treated at about 70°C for 3 hours so that a superabsorbent material having a network structure formed through the crosslinking of the polyurethane with polyacrylamide could be formed on the yarn. The yarn was heated at about 120°C to remove any remaining moisture therefrom to complete a superabsorbent material-coated yarn.

#### Comparative Example 1

[0050] Distilled water was added to 30 wt.% sodium polyacrylate aqueous solution (SUBLOC-1000, SUSAN POLYMER Co., Ltd.) to produce aqueous solution including 10% by weight of sodium polyacrylate. Then, continuous aramid multifilament was impregnated with the aqueous solution by dipping the multifilament into the aqueous solution. Then, the aqueous solution-impregnated multifilament was heat-treated at about 70°C for 3 hours to complete a superabsorbent material-coated yarn.

#### Comparative Example 2

**[0051]** Aramid multifilament was impregnated with sodium polyacrylate aqueous solution which was made in the same manner as that of the Comparative Example 1. Then, the aqueous solution-impregnated multifilament was heat-treated at about 200°C for 30 seconds to complete a superabsorbent material-coated yarn.

**[0052]** The absorbency, strength, elongation, and brittleness of the yarns produced in the Examples 1 and 2 and the Comparative Examples 1 and 2 were respectively measured in accordance with the following methods, and the results thereof are shown in Table 1 below.

## 35 Measurement of Absorbency of Yarn

[0053] 2g of the yarn was obtained and cut into the samples of uniform length. Then, the samples were dipped into 500mL of 20°C distilled water for 2 minutes respectively. Centrifugation (2000 rpm, 1 min.) was used to remove the excess of water from the samples which were completely wet. The weights of the excessive water-removed samples were measured respectively, and then they were dried with hot air in the oven of 110°C for 24 hours. The weights of the dried samples were measured respectively, and then the absorbency of the yarn was calculated in accordance with the following formula:

## Absorbency of Yarn (%) = $[(A-B)/B] \times 100$

wherein A is the mean weight of the excessive water-removed samples and B is the mean weight of the samples dried with hot air.

# Measurement of Strength and Elongation of Yarn

**[0054]** Tensile force was applied to a sample having a length of 25cm with Instron Tester (Instron Engineering Corp., Canton, Mass) in accordance with ASTM D885 until it was broken, and the strength and elongation at the breaking moment were obtained. The tensile rate was 300mm/min and the initial load was fineness x 1/30 g. The test was repeated 5 times, and then the mean values thereof were calculated.

#### Measurement of Brittleness of Yarn

**[0055]** The brittleness of the yarn is a property causing white powders during an optical cable manufacturing process. The higher the stiffness of the yarn is, the higher the brittleness thereof is. Thus, the brittleness of the yarn was indirectly figured out by measuring the stiffness thereof. The stiffness of the yarn was measured 10 times in accordance with the method regulated in ASTM D885 38, and the mean value thereof was calculated.

<Table 1>

	Absorbency (%)	Strength (gf/d)	Elongation (%)	Stiffness (gf)
Ex.1	200	22	2.91	20
Ex.2	256	22	2.80	22
Comp. Ex.1	72	22	2.85	29
Comp. Ex.2	285	21	2.56	31

## Claims

1. A superabsorbent yarn comprising:

a yarn; and

a superabsorbent material coated on the yarn,

wherein the superabsorbent material comprises crosslinked polyurethane.

- 2. The superabsorbent yarn of claim 1, wherein the superabsorbent material comprises polyurethane having a network structure formed through crosslinking.
- 3. The superabsorbent yarn of claim 1, wherein the polyurethane is crosslinked with polyacrylic acid, polyacrylamide, or polymethacrylamide.
  - 4. The superabsorbent yarn of claim 1, wherein the yarn is a continuous aramid multifilament.
  - **5.** A method for manufacturing a superabsorbent yarn, the method comprising:

preparing a polyurethane dispersion;

adding a first crosslinking agent to the polyurethane dispersion to produce a coating solution;

applying the coating solution to a yarn;

then, heat-treating the yarn at 50°C to 90°C; and

removing remaining moisture from the heat-treated yarn.

- **6.** The method of claim 5, wherein the preparing the polyurethane dispersion comprises:
- making diol and diisocianate react with each other to produce a polyurethane precursor;

adding water to the polyurethane precursor to produce a polyurethane precursor dispersion; adding an aqueous solution including a second crosslinking agent dissolved therein to the polyurethane precursor

dispersion to produce a mixture; and

- heating the mixture at 40°C to 80°C.
- 7. The method of claim 6, wherein the preparing the polyurethane dispersion further comprises, before producing the polyurethane precursor dispersion, decreasing viscosity of the polyurethane precursor.
  - **8.** The method of claim 7, wherein the decreasing the viscosity of the polyurethane precursor is performed by adding dibutyltin dilaurate and acetone to the polyurethane precursor.
  - **9.** The method of claim 6, wherein the diol is polyethylene glycol, and the diisocianate is hexylmethanediisocianate or 1,8-octanediisocianate.

6

10

5

15

25

20

35

45

40

50

55

	10.	The method of claim 6, wherein the second crosslinking agent is diethylenetriamine.
	11.	The method of claim 5, wherein the first crosslinking agent is methylenebisacrylamide.
5	12.	The method of claim 11, wherein acrylamide is further added to the polyurethane dispersion to produce the coating solution.
10	13.	The method of claim 12, wherein potassium persulfate is further added to the polyurethane dispersion to produce the coating solution.
15		
20		
25		
30		
35		
40		
45		
50		
55		

#### REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

## Patent documents cited in the description

- US 5635569 A [0004]
- US 5100397 A [0005]

- US 6319558 B **[0005]**
- US 6284367 B [0005]