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(71) Applicant: **Xinxiang Chemical Fibre Co., Ltd.**
Xinxiang, Henan 453000 (CN)

(72) Inventors:
- **XIE, Yueting**
  Xinxiang, Henan 453000 (CN)
- **LI, Ming**
  Xinxiang, Henan 453000 (CN)
- **SHAO, Changjin**
  Xinxiang, Henan 453000 (CN)
- **YAO, Yongxin**
  Xinxiang, Henan 453000 (CN)
- **CHEN, Xian**
  Xinxiang, Henan 453000 (CN)
- **XING, Shanjing**
  Xinxiang, Henan 453000 (CN)
- **ZHU, Shengtao**
  Xinxiang, Henan 453000 (CN)
- **ZHANG, Zhengfeng**
  Xinxiang, Henan 453000 (CN)
- **YAO, Faquan**
  Xinxiang, Henan 453000 (CN)
- **XIAO, Junjiang**
  Xinxiang, Henan 453000 (CN)

(74) Representative: **Gunzelmann, Rainer**
Wuesthoff & Wuesthoff
Patentanwälte und Rechtsanwalt PartG mbB
Schweigerstraße 2
81541 München (DE)

(54) CELLULOSE FIBER REGENERATED FROM JUNCAO BY MEANS OF NMMO SOLVENT METHOD AND PREPARATION METHOD THEREFOR

(57) Provided in the present invention are a cellulose fiber regenerated from Juncao by means of an NMMO solvent method and a preparation method therefor. The preparation method comprises the steps of (1) adding a DMSO/NMMO mixed solvent to Juncao pulp, simultaneously adding an antioxidant and cobalt chloride thereto, and mixing same until uniform, so as to obtain a mixed system; and (2) swelling and dissolving the mixed system to obtain a Juncao viscose solution, and filtering, defoaming and spinning the Juncao viscose solution to obtain a cellulose fiber regenerated from Juncao. In the present invention, Juncao pulp is used to replace traditional cotton pulp and wood pulp, and the existing dissolution conditions for regenerated cellulose fibers are innovated, such that the problem of insufficient raw materials for the production of cellulose fibers at present is effectively relieved, and the prepared cellulose fiber regenerated from Juncao can reach the standard of first-class products.

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Description

[0001] The present application claims the priority to Chinese Patent Application No. CN202211181794.7, titled "N-METHYLMORPHOLINE-N-OXIDE (NMMO) SOLVENT METHOD-BASED JUNCAO REGENERATED CELLULOSE FIBER AND PREPARATION METHOD THEREOF", filed with China National Intellectual Property Administration (CNIPA) on September 27, 2022, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The present disclosure belongs to the field of novel chemical textile materials, and specifically relates to an *N*-methylmorpholine-N-oxide (NMMO) solvent method-based Juncao regenerated cellulose fiber and a preparation method thereof.

BACKGROUND

[0003] Lyocell fiber, one of the green fibers in the 21st century, is mainly prepared by subjecting wood raw materials to refining to obtain a wood pulp, directly dissolving the wood pulp in a solvent *N*-methylmorpholine-*N*-oxide (NMMO) to obtain a cellulose solution without a chemical reaction, and then subjecting the cellulose solution to spinning. In recent years, the Lyocell fiber has developed rapidly. There has been research and development of bamboo-based Lyocell fiber, but there are few reports on Juncao-based Lyocell fiber. At present, it has become a technical problem in the research and development of textile field to make high-value use of Juncao and prepare a Juncao regenerated cellulose fiber with an excellent performance.

[0004] A solubility degree of cellulose in the NMMO has a great influence on the spinnability of the solution and the fiber properties. Generally speaking, NMMO has a high melting point, and cellulose and NMMO are easily degraded during co-dissolving/melting. As a water content in NMMO increases, the melting point of the solution decreases, but an ability of the water-containing NMMO to dissolve cellulose also decreases. Accordingly, it is of great significance for the preparation of an NMMO solvent method-based Juncao regenerated cellulose fiber with an excellent performance to solve the dissolution problem of Juncao fiber in NMMO.

SUMMARY

[0005] Aiming at the problems and deficiencies in the prior art, an objective of the present disclosure is to provide an NMMO solvent method-based Juncao regenerated cellulose fiber and a preparation method thereof.

[0006] In order to achieve the above objective of the present disclosure, the present disclosure adopts the following technical solutions:

[0007] A first aspect of the present disclosure provides a preparation method of an NMMO solvent method-based Juncao regenerated cellulose fiber, including the following steps:

(1) adding a dimethyl sulfoxide (DMSO)/NMMO mixed solvent into a Juncao pulp, and then adding an antioxidant and cobalt chloride to allow mixing uniformly to obtain a mixed system; and

(2) subjecting the mixed system to swelling and dissolving to obtain a Juncao fiber gel solution, and then subjecting the Juncao fiber gel solution to filtration, defoaming, and spinning to obtain the Juncao regenerated cellulose fiber.

[0008] Further, the cobalt chloride in the mixed system has a content of 0.01 ppm to 0.5 ppm.

[0009] Further, the Juncao pulp in the mixed system has a concentration of 3 wt% to 5 wt%.

[0010] Further, the DMSO/NMMO mixed solvent is obtained by mixing a DMSO solution and an NMMO solution at a mass ratio of (2-20):(80-98).

[0011] Furthermore, the DMSO/NMMO mixed solvent is obtained by mixing a DMSO solution and an NMMO solution at a mass ratio of (10-20):(80-90).

[0012] Further, the DMSO solution has a concentration of 85 wt% to 99 wt%, and the NMMO solution has a concentration of 50 wt% to 98 wt%.

[0013] Furthermore, the DMSO solution has a concentration of 90 wt% to 95 wt%, and the NMMO solution has a concentration of 75 wt% to 98 wt%.

[0014] Further, the swelling in step (2) is conducted at 35°C to 50°C for 30 min to 120 min.

[0015] Furthermore, the swelling in step (2) is conducted at 35°C to 45°C for 50 min to 120 min.

[0016] Further, the dissolving in step (2) is conducted at 80°C to 120°C for 2 h to 5 h.

[0017] Furthermore, the dissolving in step (2) is conducted at 90°C to 115°C for 3.5 h to 5 h.

[0018] Further, the spinning in step (2) is conducted in an NMMO solution with a concentration of 1 wt% to 8 wt% as a

coagulation bath.

[0019] Further, the antioxidant in step (1) is propyl gallate.

[0020] Further, the propyl gallate is added at 0.01 wt% to 0.05 wt%, preferably 0.01 wt% to 0.025 wt% of the Juncao pulp.

[0021] Furthermore, the spinning in step (2) is conducted in an NMMO solution with a concentration of 1 wt% to 6 wt% as a coagulation bath.

[0022] Further, the coagulation bath is at 15°C to 30°C, preferably 18°C to 25°C.

[0023] Further, the spinning in step (2) is conducted at a spinning speed of 60 m/min to 180 m/min, preferably 70 m/min to 150 m/min.

[0024] Further, the spinning in step (2) is conducted at a sizing amount of 0.1% to 3.5%, preferably 0.5% to 3.0%.

[0025] Further, the spinning in step (2) is conducted at a spinning metering pump flow rate of 0.54 mL/r to 0.835 mL/r.

[0026] A second aspect of the present disclosure provides a Juncao regenerated cellulose fiber prepared by the preparation method in the first aspect.

[0027] Compared with the prior art, the present disclosure has the following beneficial effects:

1. In the present disclosure, a DMSO/NMMO mixed solvent is used to replace a traditional solvent system of the regenerated cellulose fiber, and an antioxidant (preferably propyl gallate) and cobalt chloride are added to promote the swelling and dissolving of cellulose. A quality of the obtained regenerated cellulose fiber can reach a first-class standard, where a filament fiber has a dry breaking strength of (3.80-4.70) CN/dtex and a dry elongation at break of 15.87%; a staple fiber has a dry breaking strength of 2.03 CN/dtex and a dry elongation at break of not less than 16.0%.
2. In the present disclosure, the Juncao pulp used can be made from Juncao through pulping process. The Juncao has high yield and low price, and can effectively alleviate the problem of insufficient raw materials for the existing regenerated cellulose fiber production. In addition, the NMMO solvent method-based Juncao regenerated cellulose fiber can be directly prepared using existing production equipment, thereby greatly reducing a production cost of the cellulose fiber and improving the economic benefits of enterprises.
3. In the present disclosure, the dissolving has mild conditions, is environmental-friendly, and shows non-toxic, thus meeting requirements of the national efficient development strategy.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0028] The present disclosure will be further illustrated below with reference to examples. It should be noted that, unless otherwise specified, all technical and scientific terms used in the present disclosure have the same meanings as in the technical field to which the present disclosure belongs. The experimental methods in the following examples without specifying specific conditions all adopt conventional techniques in the art or follow the conditions recommended by the manufacturers. All of the used reagents or instruments which are not specified with manufacturers are conventional commercially-available products.

[0029] To provide clearer understanding of the technical solutions of the present disclosure for those skilled in the art, the technical solutions in the present disclosure will be described in detail below in conjunction with specific examples.

[0030] In order to study an influence of the dosage of cobalt chloride on a performance of the obtained Juncao regenerated cellulose fiber, experiments of Examples 1 to 5 and Comparative Example 1 are conducted. The Juncao cellulose fibers obtained in the following Examples 1 to 5 and Comparative Example 1 are all filaments, and spinning equipment is a continuous spinning machine.

Example 1:

[0031] A preparation method of an NMMO solvent method-based Juncao regenerated cellulose fiber included the following steps:

(1) 3 kg of a Juncao pulp was sterilized and disinfected with a 1.2% ethanol solution, and dried for later use;
(2) 90 wt% of a DMSO solution and 96 wt% of an NMMO solution were mixed at a mass ratio of 15:85 to obtain a mixed solvent, and the mixed solvent was added into a dried Juncao pulp obtained in step (1), and then 0.01 wt% of propyl gallate and 0.08 ppm of cobalt chloride were added into the Juncao pulp and mixed evenly to obtain a mixed system;
(3) the mixed system obtained in step (2) was subjected to swelling fully at 35°C for 120 min, and then heated to 100°C to continue dissolving for 4.5 h to obtain a Juncao fiber gel solution; and
(4) the Juncao fiber gel solution was filtered, defoamed, and spun, and a resulting spinning solution was placed in a coagulation bath to form primary silk, which was then drawn, dried, and oiled to obtain a regenerated cellulose fiber, which was then directly wound to obtain the Juncao regenerated cellulose fiber; where
the coagulation bath was a 5 wt% NMMO aqueous solution at 23°C, and the spinning was conducted at a spinning speed of 100 m/min, a sizing amount of 1.3%, and a metering pump flow rate of 0.835 mL/r.

Example 2:

[0032] Example 2 was substantially the same as Example 1, except that 0.11 ppm of cobalt chloride was added in step (2).

Example 3:

[0033] Example 3 was substantially the same as Example 1, except that 0.13 ppm of cobalt chloride was added in step (2).

Example 4:

[0034] Example 4 was substantially the same as Example 1, except that 0.17 ppm of cobalt chloride was added in step (2).

Example 5:

[0035] Example 5 was substantially the same as Example 1, except that 0.26 ppm of cobalt chloride was added in step (2).

Comparative Example 1:

[0036] Comparative Example 1 was substantially the same as Example 1, except that no cobalt chloride was added in step (2).

Performance Test:

[0037] The dry breaking strength and dry elongation at break of the Juncao regenerated cellulose fibers obtained in Examples 1 to 5 and Comparative Example 1 were tested. The results were shown in Table 1, where a fiber variety was 120D/38F, F represented a number of spinning nozzle holes, and D represented the mass of 9 km fiber (i.e., fineness).

Table 1 Influence of cobalt chloride dosage on fiber filament properties

Item name	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1
DMSO-NMM O (solution mass ratio)	15:85	15:85	15:85	15:85	15:85	15:85
Cobalt chloride dosage (ppm)	0.08	0.11	0.13	0.17	0.26	0
Spinning speed (m/min)	100	100	100	100	100	100
Fiber variety	120D/38F	120D/38F	120D/38F	120D/38F	120D/38F	120D/38F
Dry breaking strength (CN/dtex)	2.83	3.88	4.03	4.66	3.96	3.19
Dry elongation at break (%)	14.60	14.72	14.78	15.87	14.39	13.46
Fiber quality	First-class filament	First-class filament	First-class filament	First-class filament	First-clas s filament	Qualified

[0038] As shown in Table 1, compared with Comparative Example 1 in which cobalt chloride was not added, the dry breaking strength and dry elongation at break of the filament fiber products obtained in Examples 1 to 5 in which cobalt chloride was added during the swelling and dissolving were significantly improved. With the increase of cobalt chloride dosage, the dry breaking strength and dry elongation at break of the obtained fiber showed a trend of increasing and then decreasing. When cobalt chloride was 0.17 ppm, the swelling and dissolving effects were the best, making the fiber spun

by the entire gel system have high strength and desirable toughness. When the cobalt chloride exceeded 0.17 ppm, there was a too low polymerization degree of the gel solution, resulting in a decrease in the quality of the spun fiber.

[0039] In order to further study the influence of cobalt chloride on the properties of the prepared Juncao regenerated cellulose fiber staples, the Juncao regenerated cellulose fibers obtained in the following Examples 6 to 7 and Comparative Example 2 were all staples, and spinning equipment was a continuous spinning machine.

Example 6:

[0040] A preparation method of an NMMO solvent method-based Juncao regenerated cellulose fiber included the following steps:

(1) 3 kg of a Juncao pulp was sterilized and disinfected with a 1.2% ethanol solution, and dried for later use;
(2) a DMSO/NMMO mixed solvent was added into a dried Juncao pulp obtained in step (1), and then propyl gallate and cobalt chloride were added to allow mixing uniformly to obtain a mixed system; where
the mixed solvent included 90 wt% of a DMSO solution and 96 wt% of an NMMO solution at a ratio of 15:85; the propyl gallate was added at 0.01 wt% of the Juncao pulp, and the Juncao pulp in the mixed system had a concentration of 4 wt%; the cobalt chloride was added at 0.09 ppm;
(3) the mixed system obtained in step (2) was subjected to swelling fully at 35°C for 120 min, and then heated to 100°C to continue dissolving for 4.5 h to obtain a Juncao fiber gel solution; and
(4) the Juncao fiber gel solution was filtered, defoamed, and spun to obtain the Juncao regenerated cellulose fiber; where
the coagulation bath was a 5 wt% NMMO aqueous solution at 23°C, and the spinning was conducted at a spinning speed of 60 m/min, a sizing amount of 1.3%, and a metering pump flow rate of 0.835 mL/r.

Example 7:

[0041] Example 7 was substantially the same as Example 6, except that 0.10 ppm of cobalt chloride was added in step (2).

Comparative Example 2:

[0042] Comparative Example 2 was substantially the same as Example 6, except that no cobalt chloride was added in step (3).

Performance Test:

[0043] The dry breaking strength and dry elongation at break of the Juncao regenerated cellulose fibers obtained in Examples 6 and 7 and Comparative Example 2 were tested. The results were shown in Table 2, where a fiber variety was 1.67d×38mm, mm represented a length of the staple fiber and d represented the mass of 9 km fiber (i.e., fineness).

Table 2 Influence of cobalt chloride dosage on fiber filament properties

Item name	Example 6	Example 7	Comparative Example 2
DMSO-NMMO (solution mass ratio)	15:85	15:85	15:85
Cobalt chloride dosage (ppm)	0.09	0.10	0
Spinning speed (m/min)	60	60	60
Fiber variety	1.67d×38mm	1.67d×38mm	1.67d×38mm
Dry breaking strength (CN/dtex)	1.89	2.03	1.71
Dry elongation at break (%)	16.2	15.72	15.4
Fiber quality	First-class staple	First-class staple	Qualified

[0044] As shown in Table 2, when cobalt chloride was not added during the swelling and dissolving, the prepared fiber staples had low strength and poor toughness. The strength and toughness of the prepared fiber staples after adding cobalt chloride during the dissolving were significantly improved. When the cobalt chloride was added at 0.1 ppm, the dry breaking strength and dry elongation at break of the regenerated cellulose fiber staples were 2.03 CN/dtex and 15.72%,

respectively, showing an excellent quality of first-class staples.

Example 8:

[0045] Example 8 was substantially the same as Example 1, except that:
the DMSO solution and the NMMO solution in step (2) were mixed at a mass ratio of 10:90, and the cobalt chloride was added at 0.08 ppm.

Example 9:

[0046] Example 9 was substantially the same as Example 1, except that: the DMSO solution and the NMMO solution in step (2) were mixed at a mass ratio of 20:80.

Example 10:

[0047] Example 10 was substantially the same as Example 1, except that: the DMSO solution and the NMMO solution in step (2) were mixed at a mass ratio of 2.5:97.5.

[0048] The performance indicators of the Juncao regenerated cellulose fibers obtained in Examples 8 to 10 were shown in Table 3.

Table 3 Properties of products obtained under different solvent ratios

Item name	Example 8	Example 9	Example 10
DMSO-NMMO (solution mass ratio)	10:90	20:80	2.5:97.5
Cobalt chloride dosage (ppm)	0.08	0.08	0.08
Spinning speed (m/min)	100	100	100
Fiber variety	120D/38F	120D/38F	120D/38F
Dry breaking strength (CN/dtex)	3.37	3.24	3.29
Dry elongation at break (%)	13.62	13.53	13.57
Fiber quality	First-class filament	First-class filament	First-class filament

[0049] The above examples are specific implementations of the present disclosure, but the implementation of the present disclosure is not limited by the above examples. Any other combinations, changes, modifications, substitutions, and simplifications that do not exceed the design idea of the present disclosure shall fall within the protection scope of the present disclosure.

Claims

1. A preparation method of an N-methylmorpholine-N-oxide (NMMO) solvent method-based Juncao regenerated cellulose fiber, comprising the following steps:

   (1) adding a dimethyl sulfoxide (DMSO)/NMMO mixed solvent into a Juncao pulp, and then adding an antioxidant and cobalt chloride to allow mixing uniformly to obtain a mixed system; and
   (2) subjecting the mixed system to swelling and dissolving to obtain a Juncao fiber gel solution, and then subjecting the Juncao fiber gel solution to filtration, defoaming, and spinning to obtain the Juncao regenerated cellulose fiber.

2. The preparation method according to claim 1, wherein the cobalt chloride in the mixed system has a content of 0.01 ppm to 0.5 ppm.

3. The preparation method according to claim 2, wherein the Juncao pulp in the mixed system in step (1) has a concentration of 3 wt% to 5 wt%.

4. The preparation method according to claim 1, 2, or 3, wherein the DMSO/NMMO mixed solvent is obtained by mixing a

DMSO solution and an NMMO solution at a mass ratio of (2-20):(80-98).

5. The preparation method according to claim 4, wherein the DMSO solution has a concentration of 85 wt% to 99 wt%, and the NMMO solution has a concentration of 50 wt% to 98 wt%.

6. The preparation method according to claim 5, wherein the swelling in step (2) is conducted at 35°C to 50°C for 30 min to 120 min.

7. The preparation method according to claim 6, wherein the dissolving in step (2) is conducted at 80°C to 120°C for 2 h to 5 h.

8. The preparation method according to claim 1, wherein the spinning in step (2) is conducted in an NMMO solution with a concentration of 1 wt% to 8 wt% as a coagulation bath.

9. The preparation method according to claim 8, wherein the coagulation bath is at 15°C to 30°C.

10. The preparation method according to claim 1, wherein the spinning is conducted at a spinning speed of 60 m/min to 180 m/min, a sizing amount of 0.1% to 3.5%, and a spinning metering pump flow rate of 0.54 mL/r to 0.835 mL/r.

11. The preparation method according to claim 1, wherein the antioxidant in step (1) is propyl gallate.

12. The preparation method according to claim 1 or 11, wherein the antioxidant is added at 0.01 wt% to 0.05 wt% of the Juncao pulp.

13. A Juncao regenerated cellulose fiber prepared by the preparation method according to any one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/110467

A. CLASSIFICATION OF SUBJECT MATTER

D01F2/02(2006.01)i; D01F1/02(2006.01)i; D01D5/06(2006.01)i; D01D1/02(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: D01F,D01D

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

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

CJFD, CNABS, CNTXT, ENTXTC, WPABSC, VEN, CNKI, ISI: 二甲基亚砜, 纺丝, 甲基吗啉, 金属, 菌草, 抗氧化剂, 氯化镍, 氯化铁, 氯化亚铁, 氯化钴, 没食子酸, 没食子酸丙酯, 溶解, 溶液, 溶胀, 纤维, 纤维素, 再生纤维, 溴化钴, 钴, co, DMSO, NMMO, cocl??, cellulose, cobalt, fiber, fibre, juncao, spinning

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 115537955 A (XINXIANG CHEMICAL FIBER CO., LTD.) 30 December 2022 (2022-12-30) description, paragraphs 0004-0027	1-13
Y	CN 101187081 A (SHENZHEN YUANJIU HITECH CO., LTD.) 28 May 2008 (2008-05-28) description, page 4, paragraph 2 to page 9, paragraph 1	1-13
Y	CN 108250460 A (ZHEJIANG FASHION INSTITUTE OF TECHNOLOGY et al.) 06 July 2018 (2018-07-06) description paragraphs 0003-0012	1-13
Y	JP H07229016 A (MITSUBISHI RAYON CO., LTD.) 29 August 1995 (1995-08-29) description, paragraphs 0008-0033	1-13
Y	CN 111304767 A (HEBEI JIGAO CHEMICAL FIBER CO., LTD.) 19 June 2020 (2020-06-19) description, paragraphs 0008-0052	1-13

☑ 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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"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 September 2023	**09 October 2023**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 113305971 A (ZHONGFU STRAITS (PINGTAN) DEVELOPMENT CO., LTD.) 27 August 2021 (2021-08-27) entire document	1-13

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
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JP	H07229016	A	29 August 1995	None			
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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