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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 December 2016 (15.12.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/200469 A1

(51) International Patent Classification:
H01B 1/14 (2006.01) *H01L 21/78* (2006.01)

(21) International Application Number:
PCT/US2016/025338

(22) International Filing Date:
31 March 2016 (31.03.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/173,041 9 June 2015 (09.06.2015) US

(71) Applicant: **GARMOR INC.** [US/US]; 6317 McCoy Road, Suite 100, Orlando, FL 32822 (US).

(72) Inventors: **McINNIS, Matt**; 3569 Khayyam Avenue, Apt.6, Orlando, FL 32826 (US). **BULLINGTON, Jeff**; 55 W. Church Street, #2406, Orlando, FL 32801 (US). **RESTREPO, David**; 4500 Loring Place, Orlando, FL 32812 (US). **STOLTZ, Richard**; 3321 Swanson Drive, Plano, TX 75025 (US). **CHRISTIANSEN, Sean**; 4050 Shorecrest Drive, Orlando, FL 32804 (US).

(74) Agents: **CHALKER, Daniel J.** et al.; Chalker Flores, LLP, 14951 Norht Dallas Parkway, Suite 400, Dallas, TX 75254 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2016/200469 A1

(54) **Title**: GRAPHITE OXIDE AND POLYACRYLONITRILE BASED COMPOSITE

(57) **Abstract**: The present method includes graphene, preferably in the form of flat graphene oxide flakes with, by mass, preferably between 0.5% and 35% PAN. The graphene oxide and conductive-polymer PAN is in a co-suspension in water and is co-deposited on a surface. The deposited PAN with a high-percentage graphene-oxide layer is dried. Our tests have produced electrical conductivities 1000 times more conductive than the PAN by itself. Our testing indicates that using flakes that are flat is essential to getting very high conductivity, and that controlled oxidation is very important in suspending graphene oxide in water.

GRAPHITE OXIDE AND POLYACRYLONITRILE BASED COMPOSITE

TECHNICAL FIELD OF THE INVENTION

The present invention relates in general to the field of high electrical conductivity nanocomposites, and more particularly, to graphene based additives to enhance electrical conductivity.

BACKGROUND OF THE INVENTION

Without limiting the scope of the invention, its background is described in connection with compound conductive materials.

Polyacrylonitrile (PAN) is a synthetic resin prepared by the polymerization of acrylonitrile. PAN is the starting precursor for the creation of carbon fiber. PAN is first polymerized and pulled into a fiber. The pulled fiber has an initial diameter on the order of 200μm. The PAN fiber goes through a series of thermal and chemical treatments to produce a carbon fiber or filament on the order of 10μm. Creating a carbon fiber structure with a 250μm diameter to weave a fabric requires an excessive amount of PAN. PAN has none of the hazardous properties of the monomer due to the formation of strong chemical bonds between the nitrile (CN) groups. PAN does not melt without decomposing, and in most cases, the polymer is dissolved in a Dimethylformamide (DMF) dimethylsulphoxide (DMSO) or other solvent prior to being spun or pulled into a fiber. PAN is not as widely used as the simple acrylics because of the higher cost of the precursor. The GNFs have an entangled micro-fibril structure.

The synthesis of carbon fibers from a PAN fiber in general involves three processing steps: i) stabilization, ii) carbonization and iii) graphitization. The stabilization processing step is where PAN is heated to 200-300°C in an oxygen-containing atmosphere. Heating the PAN 200-300°C in an oxygen stabilizes the molecular structure and prevents reactions between the fiber in the subsequent processing stems at higher temperatures. This also prevents chain scission and mass loss that occurs when a PAN fiber is heated in an inert atmosphere without stabilization. The carbonization processing step requires 500°C, in an inert atmosphere or vacuum. The graphitization processing step requires 1500°C.

Graphene is an allotrope of carbon. Graphene's structure can be a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb or hexagonal crystal lattice. The carbon-carbon bond length in graphene is about 1.42Å. Graphene sheets stack to form graphite with an inter-planar spacing of 3.35Å. Multiple graphene sheets/flakes are bonded together by van der Waals forces.

Graphene can be oxidized by a number of processes including thermal, chemical or mechanochemical. Reduction of graphite oxide monolayer films e.g. by hydrazine, annealing in argon/hydrogen was reported to yield graphene films of low quality; the flakes are not flat.

Graphene oxide can be produced in significant quantities from microcrystalline graphite that is treated with a mixture of acids such as sulfuric, nitric, and other oxidizing chemicals in combination with mechanical and/or thermal energy elements. This processing will produce graphene oxide flakes with diameters ranging from a few nanometers to tens of microns depending on the specific processing environment. If one uses a shaker mill in conjunction with an oxidizing agent the time duration in the mill will determine the size of the flake of graphene oxide. In general, the longer the processing time in the mill, the smaller the graphene oxide flake. The oxidizing process can produce a carboxyl group on the perimeter of the flake. The graphene flakes can be suspended in a number of solutions including but not limited to: tetrahydrofuran, tetrachloromethane, water, and/or dichloroethane.

Graphene is one of the strongest materials and most electrically conductive ever tested. Measurements have shown that graphene has a breaking strength 200 times greater than steel, with a tensile modulus (stiffness) of 1 TPa (150,000,000 psi). An Atomic Force Microscope (AFM) has been used to measure the mechanical properties of a suspended graphene sheet. Graphene sheets, held together by Van der Waals forces, were suspended over SiO_2 cavities where an AFM tip was probed to test its mechanical properties. Its spring constant was in the range 1–5 N/m and the Young's modulus was 0.5 TPa (500GPa) thereby demonstrating that graphene can be mechanically very strong and rigid. Measurements of the electrical properties showed to be more conductive than copper. The enhanced conductivity is associated with the electrons being transmitted on the sp^2 orbitals that extend out of the plane of the two dimensional graphene structure. Graphene and graphene oxide nanocomposites have superior mechanical, thermal, and electrical properties. Improvement in the physicochemical properties of the nanocomposites depends on the distribution of the graphene oxide layers as well as interfacial bonding between the graphene oxide layers and the host.

SUMMARY OF THE INVENTION

In one embodiment, the present invention includes a method of making an electrical and/or thermal conductor, comprising: providing a surface; providing a co-suspension of at least one of graphene (G) or graphene oxide (GO) flakes and polyacrylonitrile (PAN), comprising between 1% and 25% by mass PAN and between 99% and 75% by mass flakes, in a dimethylformamide (DMF) solvent to form a G/GO-PAN layer. In one aspect, the method further comprises the step

of casting or extruding an arbitrary structure of the co-suspension in a water-containing fluid. In another aspect, the method further comprises the step of casting or extruding an arbitrary shape of the co-suspension of G/GO-PAN structure in water. In another aspect, the method further comprises the step of forming a G/GO-PAN structure by at least one of: drying the G/GO-PAN structure by heating, vacuum, or a combination of heating and vacuum; stabilizing the G/GO-PAN structure by heating the structure in an oxygen containing atmosphere; carbonizing the G/GO-PAN structure by heating the layer up to 800°C in an inert atmosphere or vacuum; or graphitizing the G/GO-PAN structure by heating the layer up to 1,500°C in an inert atmosphere or vacuum. In another aspect, the G/GO-PAN layer is compacted by a press applying up to 300MPA. In another aspect, the PAN is between 0.5% and 35% weight to volume. In another aspect, the G/GO flakes are 5 to 50 micron across. In another aspect, the G/GO flakes are 1 to 20 micron across. In another aspect, the G/GO flakes are 0.05 to 1 micron across. In another aspect, the G/GO-PAN structure is diffused with a non-Newtonian fluid in voids in the surface or a substrate. In another aspect, the method further comprises the step of pressing the G/GO-PAN through a stylist, or spinneret to form a fiber.

Another embodiment of the present invention includes a method of fabricating an electronic device; comprising of a high surface area electrode for an energy storage devices by: providing a surface or structure; providing a co-suspension of at least one of graphene (G) or graphene oxide (GO) flakes and polyacrylonitrile (PAN), comprising between 1% and 25% by mass PAN and between 99% and 75% by mass flakes, in a dimethylformamide (DMF) solvent to form a G/GO-PAN layer; and forming a G/GO-PAN structure by at least one of: drying the G/GO-PAN structure by heating, vacuum, or a combination of heating and vacuum; stabilizing the G/GO-PAN structure by heating the structure in an oxygen containing atmosphere; carbonizing the G/GO-PAN structure by heating the layer up to 800°C in an inert atmosphere or vacuum; or graphitizing the G/GO-PAN structure by heating the layer up to 1,500°C in an inert atmosphere or vacuum. In one aspect, the G/GO-PAN structure is diffused with a non-Newtonian fluid in voids in the substrate or structure. In another aspect, the G/GO-PAN layer is compacted by a press applying up to 300MPA. In another aspect, the PAN is between 0.5% and 35% weight to volume. In another aspect, the G/GO flakes are 5 to 50 micron across. In another aspect, the G/GO flakes are 1 to 20 micron across. In another aspect, the G/GO flakes are 0.05 to 1 micron across. In another aspect, the method further comprises the step of casting or extruding an arbitrary structure of the co-suspension in a water-containing fluid. In another aspect, the method further comprises the step of casting or extruding an arbitrary shape of the co-suspension of G/GO-PAN structure in water.

The present method includes compositions and methods for using graphene in the form of graphene oxide flakes with oxidation between 0.01% and 25% by weight; preferably between 2% and 20%. The graphene oxide and Polyacrylonitrile (PAN) can be suspended in Dimethylformamide (DMF).

DETAILED DESCRIPTION OF THE INVENTION

While the making and using of various embodiments of the present invention are discussed in detail below, it should be appreciated that the present invention provides many applicable inventive concepts that can be embodied in a wide variety of specific contexts. The specific embodiments discussed herein are illustrative of ways to make and use the invention and do not delimit the scope of the invention.

As used herein, the term “graphene” refers to a polycyclic hexagonal lattice with carbon atoms covalently bonded to each other. The covalently bonded carbon atoms can form a six-member ring as a repeating unit, and may also include at least one of a five-member ring and a seven-member ring. Multiple graphene layers are referred to in the art as graphite. Thus, graphene may be a single layer, or also may comprise multiple layers of graphene that are stacked on other layers of graphene yielding graphene oxide. Generally, graphene oxide can have a maximum thickness of about 100 nanometers (nm), specifically about 0.5 nm to about 90 nm.

As used herein, the term “graphene oxide flake” refers to a crystalline or "flake" form of graphene oxide that has been oxidized and includes many graphene sheets oxidized and stacked together and can have oxidation levels ranging from 0.01% to 25% by weight in ultra pure water. The flakes are preferably substantially flat.

As used herein, the term suspension refers to a combination of PAN/GO suspension in a DMF solvent.

The present method includes graphene in the form of graphene oxide flakes with oxidation between 0.01% and 25% by weight; preferably between 2% and 20%. The graphene oxide and Polyacrylonitrile (PAN) can be suspended in Dimethylformamide (DMF). The novel loading herein of PAN relative to the GO is between 0.1% and 50% by weight; this can be suspended in the DMF. The suspension can then be extruded into water-containing fluid. The PAN hydrolyzes in the water to form a gel that envelops the GO flakes. The resulting hydrolyzed-PAN and GO material can be shaped or stamped in any form; e.g. a fiber, cube, etc. The hydrolyzed-PAN and GO material may be injected into a mold. The hydrolyzed PAN (H-PAN) and GO molded structure shall be known herein as H-PAN/GO molded structure. The H-PAN/GO molded structure can be heated in three processing steps: i) stabilization, ii)

carbonization, and iii) graphitization. The stabilization processing step is heated to 200-300°C in an oxygen-containing atmosphere. The heating of the H-PAN/GO molded structure 200-300°C in oxygen can stabilize the PAN molecular structure for subsequent processing stems at higher temperatures. This also reduces mass loss that occurs when a H-PAN/GO molded structure is heated in an inert atmosphere. The carbonization of PAN in the H-PAN/GO molded structure occurs when it is at 500°C to 800°C, in an inert atmosphere or vacuum.

A carbonized H-PAN/GO molded structure will be sufficient for many commercial applications without graphitization. The graphitization processing step for the H-PAN/GO molded structure requires 1500°C, in an inert atmosphere or vacuum. Graphitization is required for forming strong chemical and mechanical bonds within the H-PAN/GO molded structure mainly for mechanical and strength applications. The heating profile may also be accomplished in a mechanical press to further improve the physical properties.

In some embodiments, the GO flakes are 5 to 50 micron across; e.g. 5 to 20 micron across; 0.05 to 5 micron across; or 5 to 14 micron across.

In some embodiments the H-PAN/GO suspension in DMF is pressed through a stylist, or spinneret to form a fiber.

It will be understood that particular embodiments described herein are shown by way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the claims.

All publications and patent applications mentioned in the specification are indicative of the level of skill of those skilled in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference.

The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to

only alternatives and "and/or." Throughout this application, the term "about" is used to indicate that a value includes the inherent variation of error for the device, the method being employed to determine the value, or the variation that exists among the study subjects.

As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

The term "or combinations thereof" as used herein refers to all permutations and combinations of the listed items preceding the term. For example, "A, B, C, or combinations thereof" is intended to include at least one of: A, B, C, AB, AC, BC, or ABC, and if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, AB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context. In certain embodiments, the present invention may also include methods and compositions in which the transition phrase "consisting essentially of" or "consisting of" may also be used.

As used herein, words of approximation such as, without limitation, "about", "substantial" or "substantially" refers to a condition that when so modified is understood to not necessarily be absolute or perfect but would be considered close enough to those of ordinary skill in the art to warrant designating the condition as being present. The extent to which the description may vary will depend on how great a change can be instituted and still have one of ordinary skilled in the art recognize the modified feature as still having the required characteristics and capabilities of the unmodified feature. In general, but subject to the preceding discussion, a numerical value herein that is modified by a word of approximation such as "about" may vary from the stated value by at least ±1, 2, 3, 4, 5, 6, 7, 10, 12 or 15%.

All of the compositions and/or methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and

modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

What is claimed is:

1. A method of making an electrical and/or thermal conductor, comprising:

providing a surface;

providing a co-suspension of at least one of graphene (G) or graphene oxide (GO) flakes and polyacrylonitrile (PAN), comprising between 1% and 25% by mass PAN and between 99% and 75% by mass flakes, in a dimethylformamide (DMF) solvent to form a G/GO-PAN layer.

2. The method of claim 1, further comprising the step of casting or extruding an arbitrary structure of the co-suspension in a water-containing fluid.

3. The method of claim 1, further comprising the step of casting or extruding an arbitrary shape of the co-suspension of G/GO-PAN structure in water.

4. The method of claim 1, further comprising the step of forming a G/GO-PAN structure by at least one of:

drying the G/GO-PAN structure by heating, vacuum, or a combination of heating and vacuum;

stabilizing the G/GO-PAN structure by heating the structure in an oxygen containing atmosphere;

carbonizing the G/GO-PAN structure by heating the layer up to 800°C in an inert atmosphere or vacuum; or

graphitizing the G/GO-PAN structure by heating the layer up to 1,500°C in an inert atmosphere or vacuum.

5. The method of claim 1, wherein the G/GO-PAN layer is compacted by a press applying up to 300MPA.

6. The method of claim 1, wherein the PAN is between 0.5% and 35% weight to volume.

7. The method of claim 1, wherein the G/GO flakes are 5 to 50 micron across.

8. The method of claim 1, wherein the G/GO flakes are 1 to 20 micron across.

9. The method of claim 1, wherein the G/GO flakes are 0.05 to 1 micron across.

10. The method of claim 1, wherein the G/GO-PAN structure is diffused with a non-Newtonian fluid in voids in the surface or a substrate.

11. The method of claim 1, further comprising the step of pressing the G/GO-PAN through a stylist, or spinneret to form a fiber.

12. A method of fabricating an electronic device comprising of a high surface area electrode for an energy storage devices by:

providing a surface or structure;

providing a co-suspension of at least one of graphene (G) or graphene oxide (GO) flakes and polyacrylonitrile (PAN), comprising between 1% and 25% by mass PAN and between 99% and 75% by mass flakes, in a dimethylformamide (DMF) solvent to form a G/GO-PAN layer; and

forming a G/GO-PAN structure by at least one of:

drying the G/GO-PAN structure by heating, vacuum, or a combination of heating and vacuum;

stabilizing the G/GO-PAN structure by heating the structure in an oxygen containing atmosphere;

carbonizing the G/GO-PAN structure by heating the layer up to 800°C in an inert atmosphere or vacuum; or

graphitizing the G/GO-PAN structure by heating the layer up to 1,500°C in an inert atmosphere or vacuum.

13. The method of claim 12, wherein the G/GO-PAN structure is diffused with a non-Newtonian fluid in voids in the substrate or structure.

14. The method of claim 12, wherein the G/GO-PAN layer is compacted by a press applying up to 300MPA.

15. The method of claim 12, wherein the PAN is between 0.5% and 35% weight to volume.

16. The method of claim 12, wherein the G/GO flakes are 5 to 50 micron across.

17. The method of claim 12, wherein the G/GO flakes are 1 to 20 micron across.

18. The method of claim 12, wherein the G/GO flakes are 0.05 to 1 micron across.

19. The method of claim 12, further comprising the step of casting or extruding an arbitrary structure of the co-suspension in a water-containing fluid.

20. The method of claim 12, further comprising the step of casting or extruding an arbitrary shape of the co-suspension of G/GO-PAN structure in water.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/025338

A. CLASSIFICATION OF SUBJECT MATTER

H01B 1/14(2006.01)i, H01L 21/78(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)
H01B 1/14; D04H 1/728; H01M 4/1393; H01M 2/14; C08K 3/04; D04H 1/4242; H01M 4/1391; C08K 5/20; C08L 33/20; H01L 21/78

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
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: Graphite oxide, G/GO, polyacrylonitrile, PAN, co-suspension, DMF, conductor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2014-0018480 A1 (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 16 January 2014 See abstract; claim 6; and paragraphs [0006], [0054]-[0060].	1-20
Y	CN 103757823 A (ZHEJIANG SANZHI TEXTILES CO., LTD.) 30 April 2014 See abstract; claim 1; and paragraphs [0003]-[0004], [0008]-[0019].	1-20
Y	WO 2011-014242 A1 (SEARETE, LLC) 03 February 2011 See abstract; claims 1, 34-35, 41; and pages 3-4.	10,13
A	CN 104319372 A (HUNAN UNIVERSITY) 28 January 2015 See abstract; and claim 1.	1-20
A	CN 103408880 A (FUDAN UNIVERSITY) 27 November 2013 See abstract; claims 1, 2; and paragraphs [0007]-[0022].	1-20

☐ 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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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
21 July 2016 (21.07.2016)	**25 July 2016 (25.07.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
CHO, KI YUN
Telephone No. +82-42-481-5655

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2016/025338

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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