



(51) International Patent Classification:

C01B 31/02 (2006.01) *C08F 120/44* (2006.01)
C09C 1/48 (2006.01)

(21) International Application Number:

PCT/US2015/066769

(22) International Filing Date:

18 December 2015 (18.12.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/094,330 19 December 2014 (19.12.2014) US

(71) Applicant: STC.UNM [US/US]; Suite 101, 801 University Blvd., SE, Albuquerque, New Mexico 87106 (US).

(72) Inventors: KEMP, Richard Alan; 9027 Lazy Brook Ct. NE, Albuquerque, New Mexico 87113 (US). TAHA, Mahmoud Reda; 9300 Thornton Avenue NE, Albuquerque, New Mexico 87109 (US).

(74) Agent: VOGT, Keith A.; Vogt IP, Suite 200, 1033 South Blvd., Oak Park, Illinois 60302 (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).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: METHODS OF USING N-CONTAINING COMPOUNDS WITH CARBON BLACK TO REPLACE PAN AND FORM CARBON FIBERS

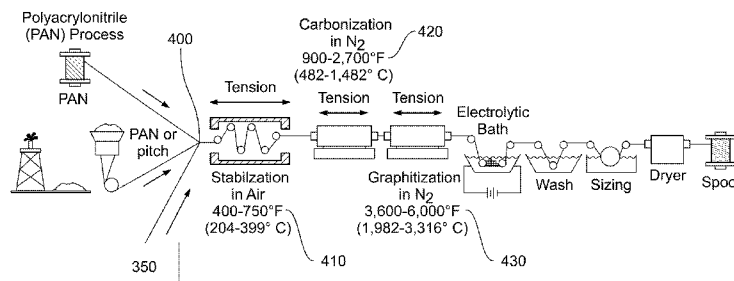


FIG. 4

(57) Abstract: A method and precursor for making carbon fibers and the like comprising carbon black modified with at least one cyclic compound promoter. A source of the carbon black may be recycled materials such as recycled tires or recycled plastics. The carbon black is modified by attaching at least one cyclic compound promoter to the outer periphery of the carbon black.

TITLE

Methods of Using N-Containing Compounds with
Carbon Black to Replace PAN and Form Carbon Fibers

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/094,330 filed on December 19, 2014 and herein incorporated by reference.

STATEMENT REGARDING FEDERALLY SPONSORED**RESEARCH & DEVELOPMENT**

[0002] Not applicable.

INCORPORATION BY REFERENCE OF MATERIAL**SUBMITTED ON A COMPACT DISC**

[0003] Not applicable.

BACKGROUND OF THE INVENTION

[0004] In order to produce carbon fibers, an expensive nitrogen-containing polymer (polyacrylonitrile, or PAN) is generally used which is heated to ultimately give the pure carbon fibers.

BRIEF SUMMARY OF THE INVENTION

[0005] In one embodiment, the present invention provides an inexpensive and efficient method to produce pure carbon fibers. The resulting carbon fibers may be used in products such as graphene sheets and high tech composites.

[0006] In another embodiment, inexpensive carbon blacks are combined with one or more compounds that promote the formation of a cyclic carbon black

compound that may be used to replace or be used in combination with the expensive PAN and/or pitch.

[0007] In another embodiment, inexpensive carbon blacks are combined with one or more nitrogen-containing organic compounds to replace or be used with part of the expensive PAN and/or pitch.

[0008] In other embodiments, the present invention simulates producing PAN-based carbon fibers by substituting recycled carbon blacks that have been modified with inexpensive nitrogen (N)-containing compounds for all or part of the expensive PAN polymer material.

[0009] In other embodiments, the present invention replaces pitch and/or PAN precursors with a precursor made from recycled carbon black that has been modified with at least one N-containing compound.

[0010] In other embodiments, the present invention chemically attaches N-containing compounds to the periphery of the carbon black to create a precursor that is similar to the chemistry associated with a PAN precursor.

[0011] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0012] In the drawings, which are not necessarily drawn to scale, like numerals may describe substantially similar components throughout the several views.

Like numerals having different letter suffixes may represent different instances of substantially similar components. The drawings illustrate generally, by way of

example, but not by way of limitation, a detailed description of certain embodiments discussed in the present document.

[00013] FIG. 1A is a full atomic schematic of the structural changes of PAN-based carbon fiber during the stabilization step of the manufacturing process.

[00014] FIG. 1B is a simpler schematic (equivalent to the full atomic schematic) of the structural changes of PAN-based carbon fiber during the stabilization step of the manufacturing process.

[00015] FIG. 2A illustrates the structural changes of PAN-based carbon fiber during the carbonization step of the manufacturing process.

[00016] FIG. 2B illustrates the structural changes of PAN-based carbon fiber during the graphitization step of the manufacturing process.

[00017] FIG. 2C illustrates a putative carbon black structure with attached cyclic compound promoters that may be used in accordance with an embodiment of the present invention.

[00018] FIG. 3 illustrates generic and exemplary N-containing compounds that may be used with an embodiment of the present invention.

[00019] FIG. 4 illustrates a method of producing carbon fiber in accordance with an embodiment of the present invention.

[00020] FIG. 5 illustrates mix proportions for producing carbon black based PAN-like material in accordance with an embodiment of the present invention.

[00021] FIG. 6 illustrates load-indentation depths of carbon black based PAN-like material produced in accordance with an embodiment of the present invention.

[00022] FIG. 7 illustrates the stiffness achieved by carbon black based PAN-like material produced in accordance with an embodiment of the present invention.

[00023] FIG. 8 illustrates the hardness (strength) achieved by carbon black based PAN-like material produced in accordance with an embodiment of the present invention.

[00024] FIGS. 9A and 9B illustrate the scatter of carbon black based PAN-like material in hardness versus modulus plot showing the new material to have very similar mechanical properties to PAN

DETAILED DESCRIPTION OF THE INVENTION

[00025] Detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed structure. Further, the terms and phrases used herein are not intended to be limiting, but rather to provide an understandable description of the invention.

[00026] The production of carbon fibers begins with a precursor that is typically made from polyacrylonitrile (PAN) which is a synthetic, semicrystalline organic polymer resin, with the linear formula ($C_3 H_3 N$). Another less common precursor are pitches, which are generally complex blends of polyaromatic molecules and heterocyclic compounds. Pitches are often obtained from petroleum refining, coal,

asphalt, or the pyrolysis of PVC. However, the vast majority of carbon fibers are made from PAN precursors.

[00027] As is known in the art, PAN precursor formation begins with an acrylonitrile monomer, which is combined in a reactor with plasticized acrylic comonomers and a catalyst to promote polymerization to create long-chain polymers that can be formed into acrylic fibers. FIGS. 1A-1B and FIGS. 2A-2B illustrate the structural changes PAN undergoes through the manufacturing processes described above and below.

[00028] As shown in FIGS. 1A and 1B, PAN (left side) is first heated to convert the compound from a chain-like structure to form cyclic or ringed structures (right side). To promote the formation of carbocycles and heterocycles, the compound is subject to one or more processing steps such as dehydrogenation (FIG. 2A) and denitrogenation (FIG. 2B). These steps are performed to remove hydrogen and nitrogen to promote the formation of carbocycles and heterocycles.

[00029] The PAN precursors generally undergo a process called spinning where the precursor is extruded through holes to create filaments which may repeatedly be drawn and stretched to continue orienting the PAN polymer. Next, the fiber is oxidized to cause the polymer chains to begin crosslinking to increase fiber density. In the end, the oxidized (stabilized) PAN fiber contains about 50 to 65 percent carbon molecules, with the balance a mixture of hydrogen, nitrogen and oxygen. The fibers are then carbonized to remove non-carbon molecules. The crystallization of the carbon molecules may be optimized to produce a finished fiber that is more than 90 percent carbon.

[00030] In a preferred embodiment, the present invention provides a process for making a PAN-like material for making carbon fibers by providing a carbon black precursor, a source of which may be used tires or other recycled products, modified with one or cyclic compound promoters. In other embodiments, fresh carbon black may be used as well.

[00031] In other preferred embodiments, the present invention provides a substitute for the PAN polymer precursor by attaching one or more cyclic compound promoters (CCPs) 100-102 (not drawn to scale or in number used) to carbon black as shown in FIG. 2C, to make a carbon black precursor 120. FIG. 2C shows an exemplary carbon black structure 110 and other carbon black structures are within the scope of the present invention.

[00032] CCPs 100-102 may be a single compound or a mixture of compounds. CCPs 100-102 may also be a monomer, a polymer or a mixture of monomers and polymers. In a preferred embodiment, CCPs 100-102 are chemically attached to carbon black structure 110. In other embodiments, CCPs 100-102 are chemically attached to the periphery and/or outer periphery of carbon black structure 110. In still further embodiments, CCPs 100-102 may also be attached to one or more functional groups 130-132.

[00033] In a preferred embodiment, the present invention uses one or more N-containing compounds, monomers, and/or polymers as the CCPs. In yet other embodiments, one or more of the compounds shown in FIG. 3 may be used as the CCPs.

[00034] Representative examples of CCPs include, but are not limited to, organics containing di-cyano groups, cyanamide, carbodiimides, pyridine, 2,2-bipyridine, ammonia, hydrazine, 2-aminopyridine, 2-cyanopyridine, and related compounds. Other compounds that may be used may or may not contain cyano-groups, but would have functionalities that simulate the cyano group cyclization process.

[00035] It is possible to generate CCPs *in situ* by utilizing synthetic routes that generate nitriles from other precursors, such as organic amides, organic halides, or related compounds. Other CCPs may rely on atoms that resemble the N atom in the various structure in function, yet are not N. It is well-known in the chemical literature that elements such as P which reside in the same family as N, often have similar chemistry and are capable of forming cyclic structures. Compounds as shown in Fig. 3 in which N is substituted by P would be exemplary.

[00036] Carbon black structure 110 with the attached CCPs form carbon black precursor 120 which may be processed to remove the CCPs to promote the formation of carbocycles and/or heterocycles. The processing may include one or more of the following steps 1) stabilization such as shown in FIG. 1A, 2) carbonization such as shown in FIG. 2A, and 3) graphitization such as shown in FIG. 2B. One or more of steps 1-3 may be repeated, omitted and/or performed out of order.

[00037] In one embodiment, carbon black precursor 120 may replace PAN or pitch in the production of carbon fibers. In yet other embodiments, carbon black

precursor 120 may be used in combination with PAN or pitch in the production of carbon fibers, sheets and other materials.

[00038] FIG. 4 illustrates a method of processing carbon fibers in accordance with several embodiments of the invention. As shown, carbon black precursor 350 may replace Pan or pitch or be used in combination with PAN and/or a pitch in step 400 to create a precursor for processing. The precursor is stabilized in step 410 and then undergoes carbonization in step 420. The final step, 430, is graphitization and thereafter the carbon fibers are sized and packaged. As described above, the steps may be repeated and/or performed out of order and in differing combinations.

[00039] FIG. 5 illustrates mixtures of PAN, pitch and carbon black precursor 120 used in accordance with several embodiments of the invention. As shown in FIGS. 6-9, carbon fibers produced from mixture 4 have similar performance to fibers made from PAN that is mixture 1.

[00040] The lower cost of using carbon black (available from many industrial processing and recycling sources) with inexpensive CCPs, such as N-containing compounds, provides economic advantages not found in the prior art. In other embodiments, the present invention achieves approximately most of the strength of PAN-based carbon fibers using carbon black. Other forms of carbon black that may be used with the present invention include, but are not limited to, carbon black subtypes such as acetylene black, channel black, furnace black, lamp black and thermal black. Other sources of the carbon black that may also be used with the present invention include soot and the material produced by the incomplete

combustion of petroleum products such as FCC tar, coal tar, ethylene cracking tar as well as fossil fuels, biofuels, biomass and vegetable oil.

[00041] While the foregoing written description enables one of ordinary skill to make and use what is considered presently to be the best mode thereof, those of ordinary skill will understand and appreciate the existence of variations, combinations, and equivalents of the specific embodiment, method, and examples herein. The disclosure should therefore not be limited by the above described embodiment, method, and examples, but by all embodiments and methods within the scope and spirit of the disclosure.

WHAT IS CLAIMED IS:

1. A method of making carbon fibers by providing a precursor used to make the carbon fiber, said precursor comprising carbon black modified with at least one cyclic compound promoter.
2. The method of claim 1 wherein said carbon black is from recycled materials.
3. The method of claim 2 wherein said carbon black is from recycled tires or recycled plastics.
4. The method of claim 1 wherein said carbon black is modified by attaching said at least one cyclic compound promoter to the periphery of the carbon black.
5. The method of claim 1 wherein said at least one cyclic compound promoter is a nitrogen (N)-containing compound.
6. The method of claim 5 wherein said carbon black is modified by attaching said nitrogen (N)-containing compound to the outer periphery of the carbon black.
7. The method of claim 6 wherein said N-containing compound is from the group including organics containing di-cyano groups, cyanamide, carbodiimides, pyridine, 2,2-bipyridine, ammonia, hydrazine, 2-aminopyridine, 2-cyanopyridine, and related compounds.
8. The method of claim 6 wherein said N-containing compound contains cyano-groups that simulate the cyano group cyclization process.

9. A method of making carbon fibers by providing a precursor used to make the carbon fiber, said precursor comprising carbon black modified with at least one cyclic compound promoter and PAN.

10. The method of claim 9 wherein said carbon black is from recycled materials.

11. The method of claim 10 wherein said carbon black is from recycled tires.

12. The method of claim 9 wherein said carbon black is modified by attaching said at least one cyclic compound promoter to the periphery of the carbon black.

13. The method of claim 9 wherein said at least one cyclic compound promoter is a nitrogen (N)-containing compound.

14. The method of claim 13 wherein said carbon black is modified by attaching said nitrogen (N)-containing compound to the outer periphery of the carbon black.

15. The method of claim 14 wherein said N-containing compound is from the group including organics containing di-cyano groups, cyanamide, carbodiimides, pyridine, 2,2-bipyridine, ammonia, hydrazine, 2-aminopyridine, 2-cyanopyridine, and related compounds.

16. The method of claim 13 wherein said N-containing compound contains cyano-groups that simulate the cyano group cyclization process.

17. The method of claim 13 wherein the precursor contains around 7 parts PAN and around 1 part carbon black N-containing compound.

18. The method of claim 13 wherein the precursor is made using methyl acrylate, itaconic acid and fumaronitrile.

19. The method of claim 18 wherein the precursor is made using around 0.6 parts methyl acrylate, around 0.1 parts itaconic acid and around 1 part fumaronitrile.

20. A method of making carbon fibers by providing a precursor used to make the carbon fiber, said precursor comprising carbon black modified with at least one nitrogen (N)-containing compound, PAN, methyl acrylate, itaconic acid and fumaronitrile.

21. The method of claim 20 wherein said N-containing compound is from the group including organics containing di-cyano groups, cyanamide, carbodiimides, pyridine, 2,2-bipyridine, ammonia, hydrazine, 2-aminopyridine, 2-cyanopyridine, and related compounds.

22. The method of claim 21 wherein said N-containing compound contains cyano-groups that simulate the cyano group cyclization process.

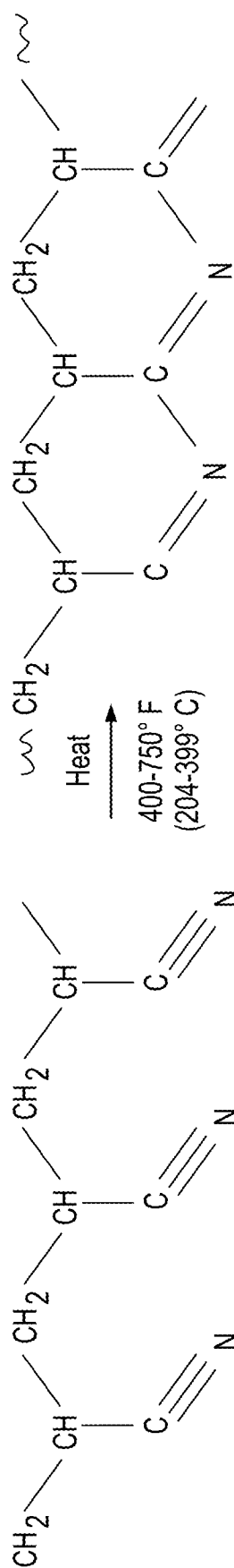


FIG. 1A

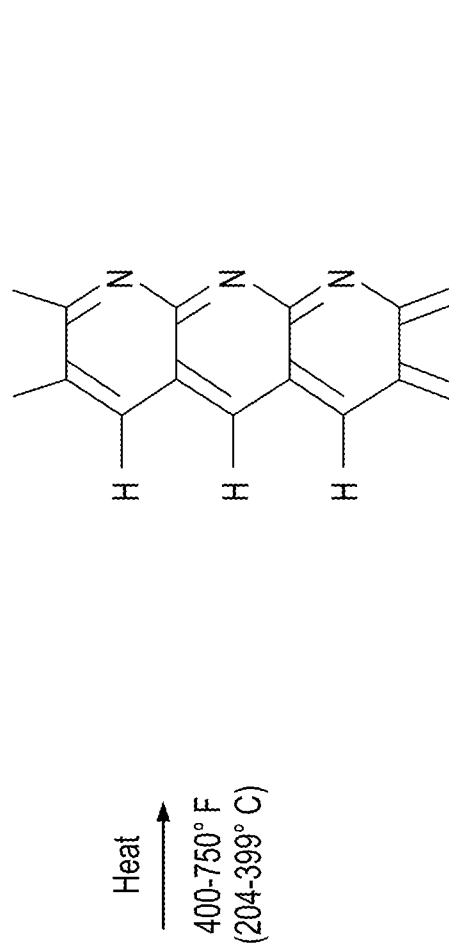
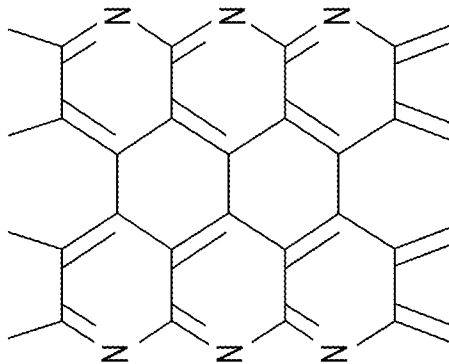


FIG. 1B

2/8



Dehydrogenation
↑
900-2,700° F
(482-1,482° C)

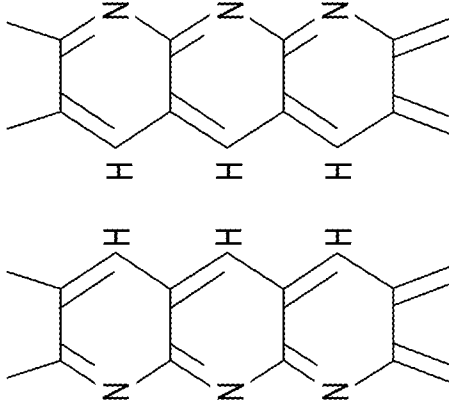
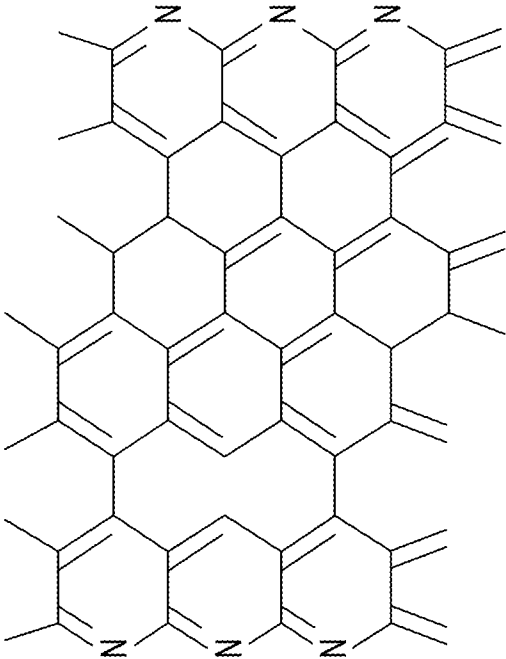


FIG. 2A



Denitrogenation
↑
3,600-6,000° F
(1,982-3,316° C)

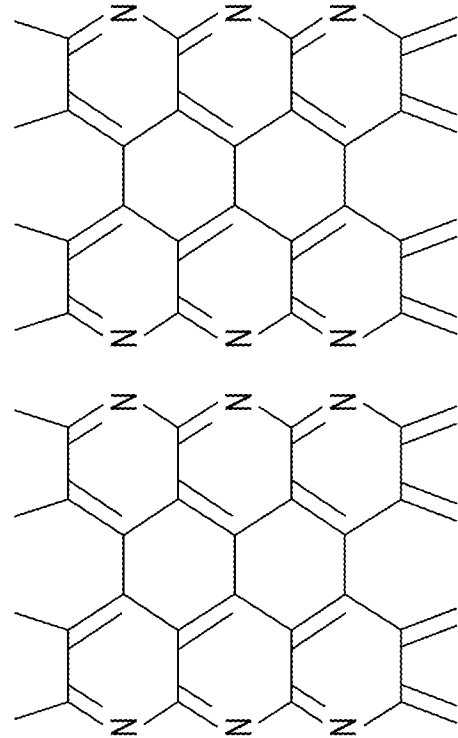


FIG. 2B

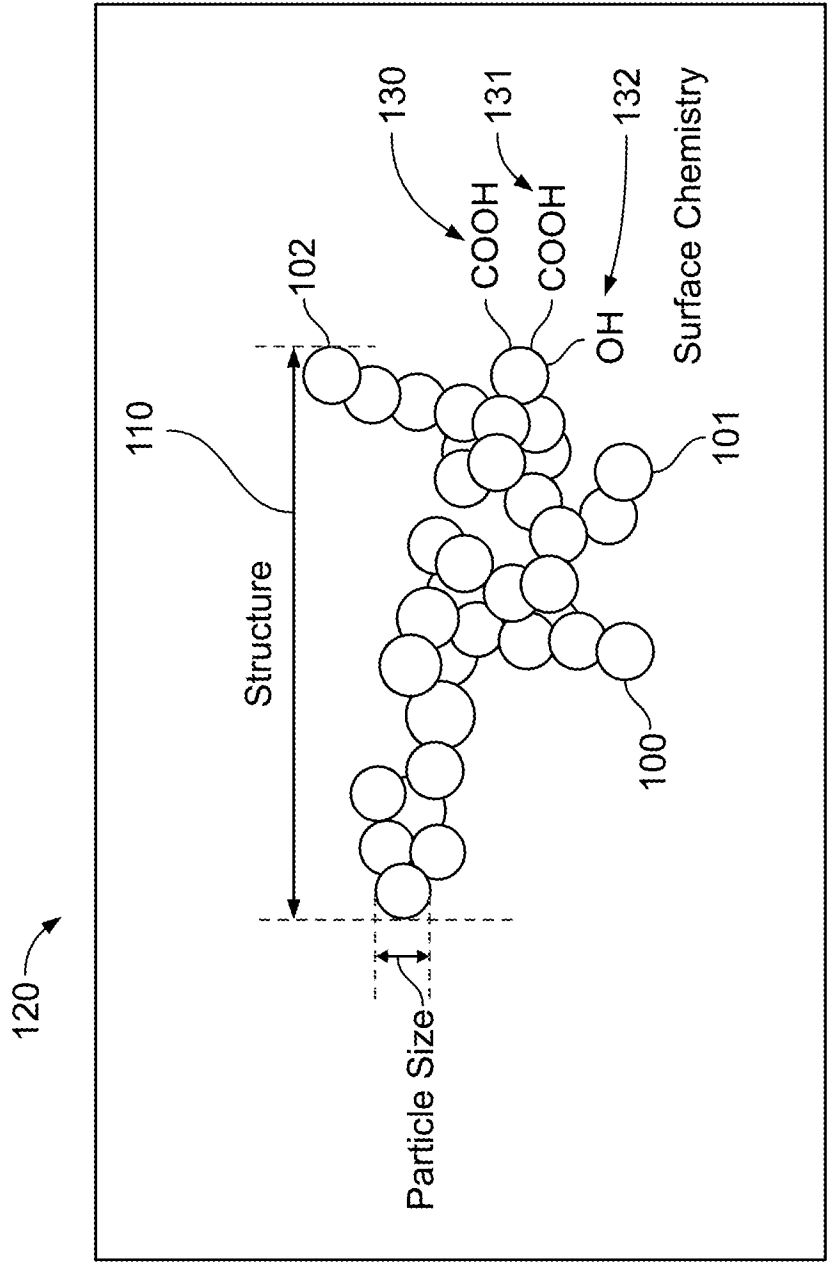
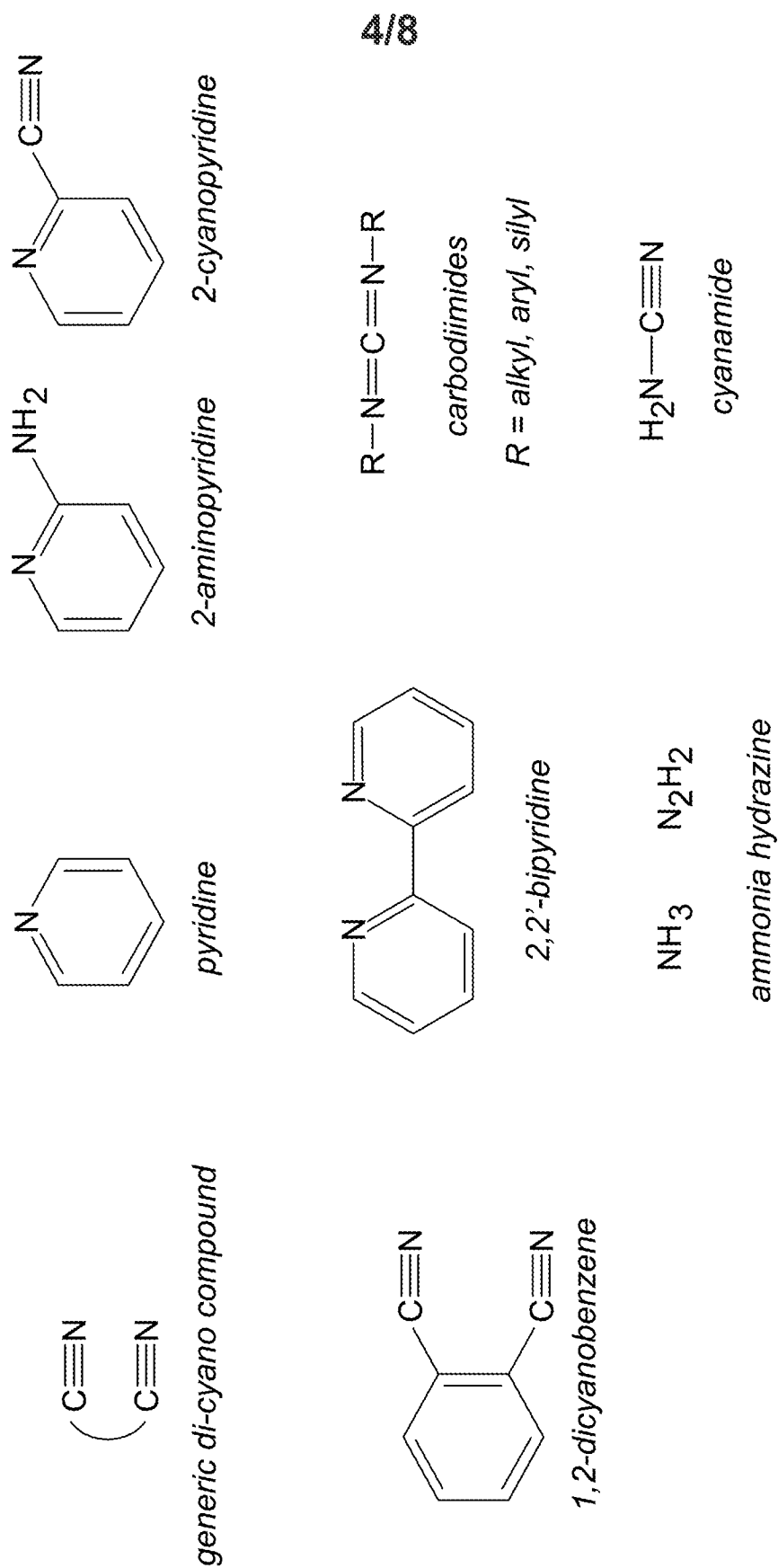


FIG. 2C



4/8

FIG. 3

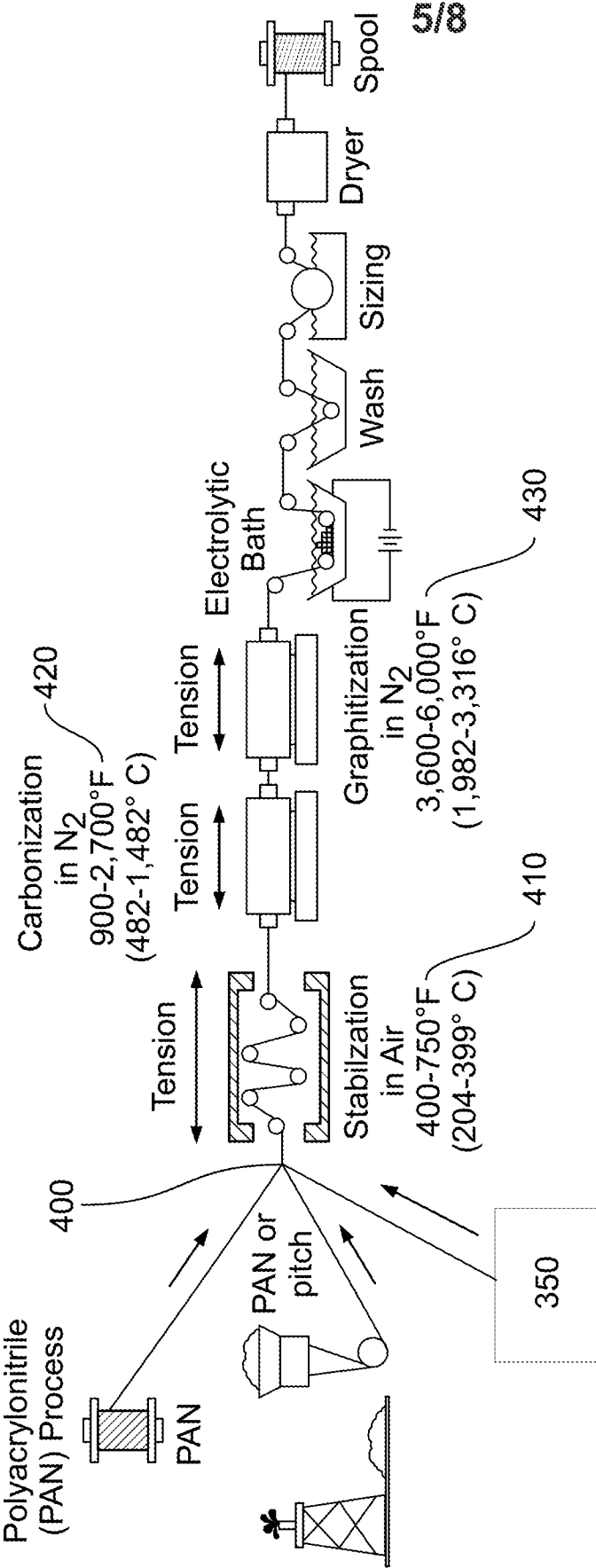


FIG. 4

6/8

1	Pan 9.3	methyl acrylate 0.6	itaconic acid 0.1		
2	Pan 8.3	methyl acrylate 0.6	itaconic acid 0.1	CB 1	
3	Pan 7.3	methyl acrylate 0.6	itaconic acid 0.1	CB 1	bipyridiyl 1
4	Pan 7.3	methyl acrylate 0.6	itaconic acid 0.1	CB 1	fumaronitrile 1
5	Pan 7.3	methyl acrylate 0.6	itaconic acid 0.1	CB 1	nn-diisopropylcarbidiimide 1
6	Pan 7.3	methyl acrylate 0.6	itaconic acid 0.1	CB 1	azodisobutylnitrile 1

CB is carbon black and quantities are in gm

FIG. 5

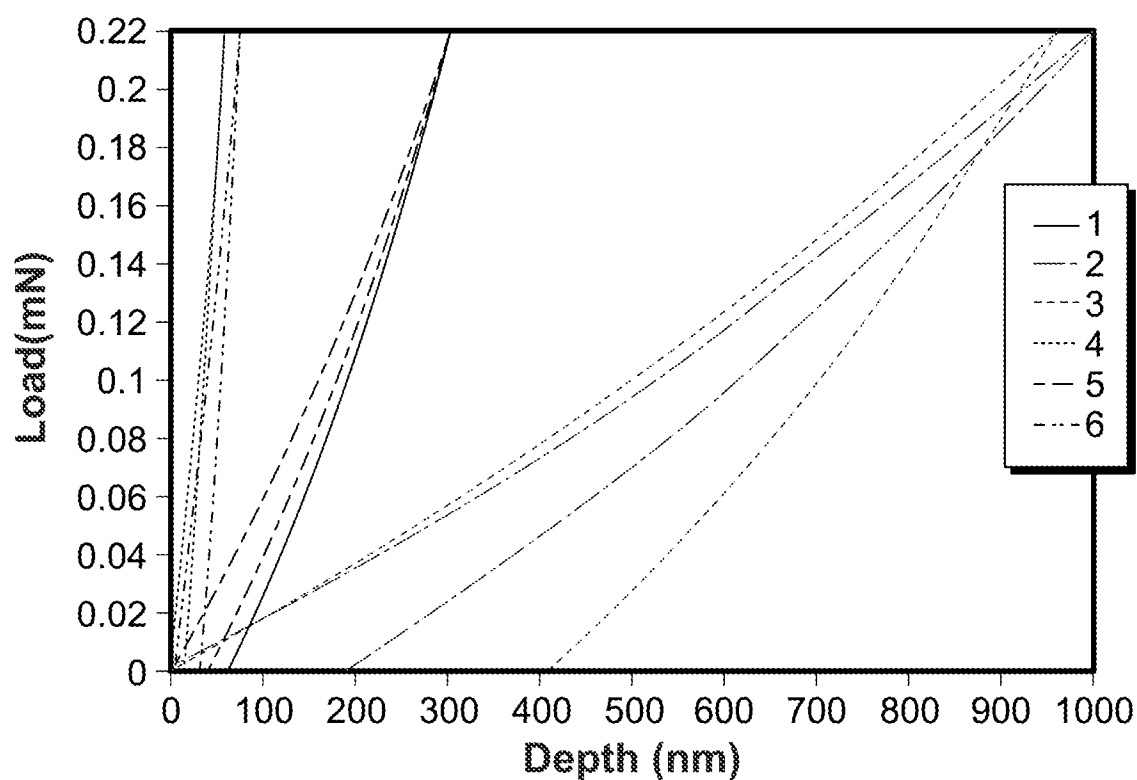


FIG. 6

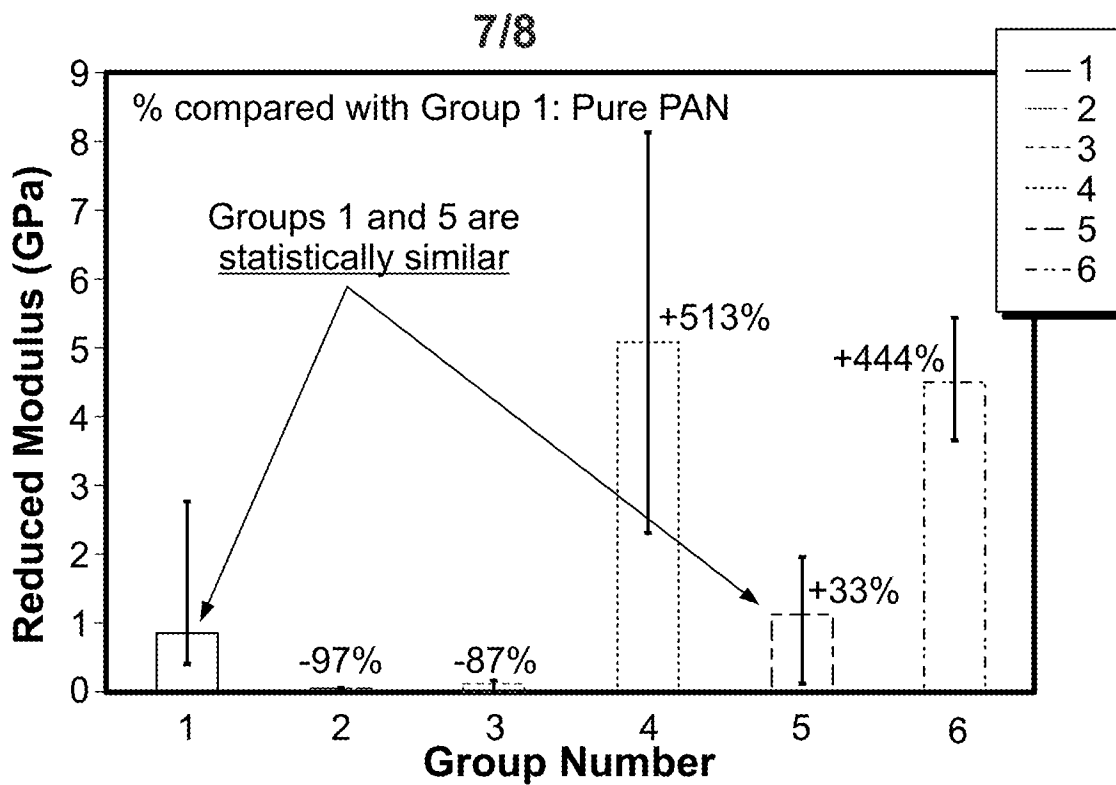


FIG. 7

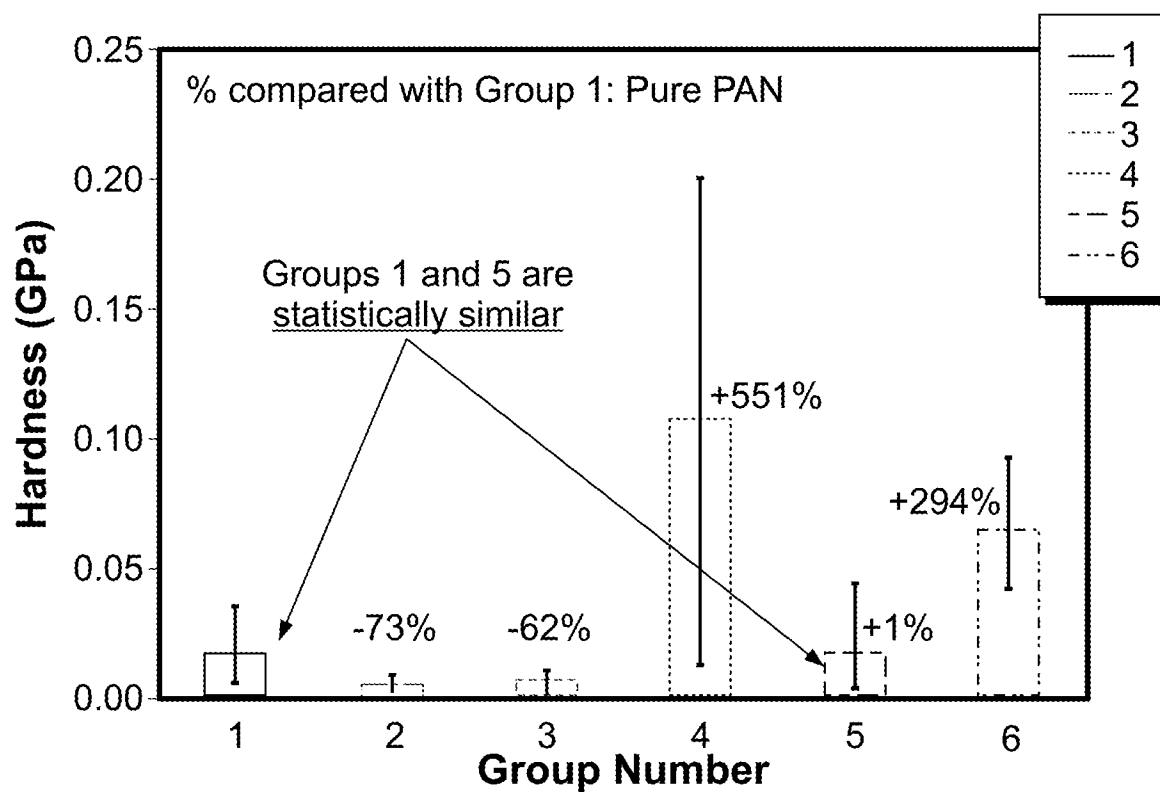


FIG. 8

8/8

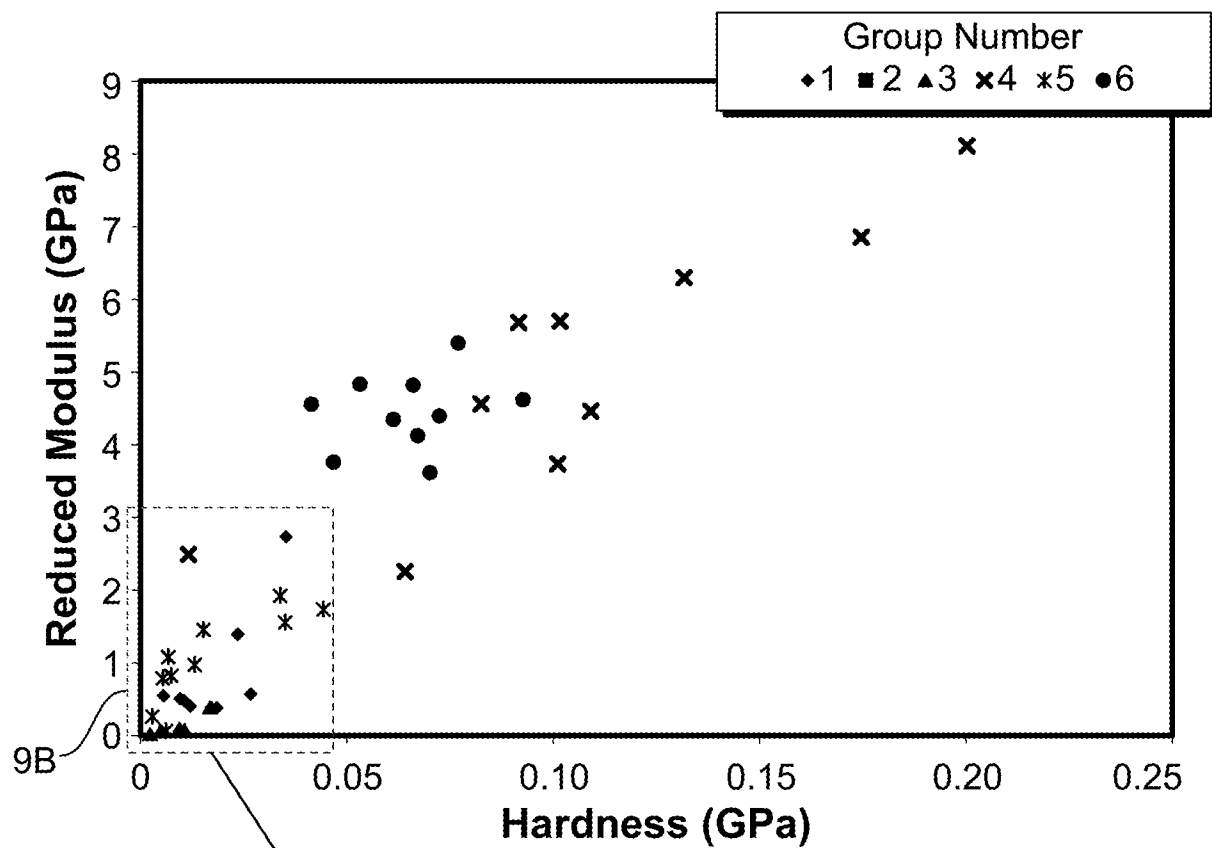


FIG. 9A

Groups 1 and 5 lie
within the same cluster

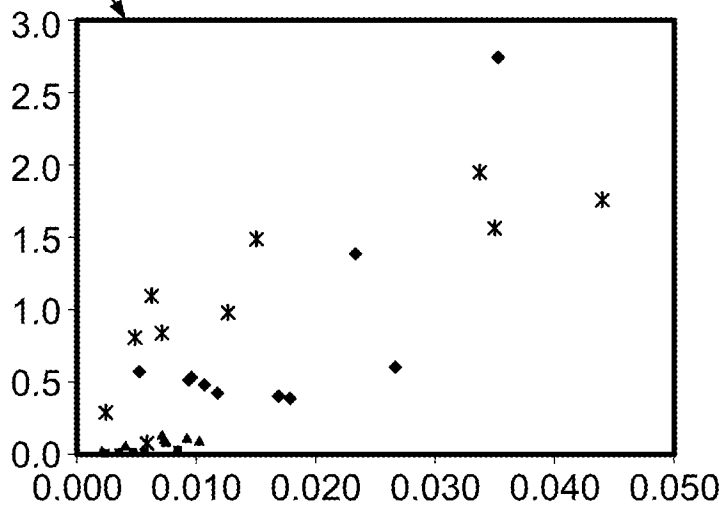


FIG. 9B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/066769**A. CLASSIFICATION OF SUBJECT MATTER****C01B 31/02(2006.01)i, C09C 1/48(2006.01)i, C08F 120/44(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)

C01B 31/02; D01F 9/12; C09C 1/48; C08F 120/44

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: carbon fiber, low cost carbon fiber, modified carbon black, cyclic compound promoter, n-containing organic compound, polyacrylonitrile (PAN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BAKER, DARREN A. et al., "Recent advances in low-cost carbon fiber manufacture from lignin," Journal of Applied Polymer Science, 2013, vol. 130, no. 2, pages 713-728 See abstract; page 715, left column, line 15-right column, line 2; and figures 1, 3.	1-22
A	MALDONADO, STEPHEN et al., "Direct preparation of carbon nanofiber electrodes via pyrolysis of iron (II) phthalocyanine: electrocatalytic aspects for oxygen reduction," Journal of Physical Chemistry B, 2004, vol. 108, no. 31, pages 11375-11383 See abstract; and page 11376, left column, line 45-right column, line 13.	1-22
A	HUANG, XIAOSONG, "Fabrication and properties of carbon fibers," Materials, 2009, vol. 2, no. 4, pages 2369-2403 See abstract; page 2375, line 16-page 2378, line 26; and figures 4, 5.	1-22
A	ZHANG, HUIHUI et al., "Nano-carbon black filled lyocell fiber as a precursor for carbon fiber," Journal of Applied Polymer Science, 2006, vol. 99, issue 1, pages 65-74 See abstract; and page 66.	1-22

☒ 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

01 April 2016 (01.04.2016)

Date of mailing of the international search report

04 April 2016 (04.04.2016)

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, Han Sol

Telephone No. +82-42-481-5580



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2015/066769

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LALANDE, G. et al., "Catalytic activity and stability of heat-treated iron phthalocyanines for the electroreduction of oxygen in polymer electrolyte fuel cells," Journal of Power Sources, 1996, vol. 61, nos. 1-2, pages 227-237 See abstract; and page 228, left column, lines 22-38.	1-22
A	US 4275051 A (BARR, JOHN B.) 23 June 1981 See abstract; and claim 1.	1-22
A	US 4572813 A (ARAKAWA, KOHEI) 25 February 1986 See abstract; and example 1.	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/066769

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4275051 A	23/06/1981	EP 0014161 A2	06/08/1980
		EP 0014161 A3	17/09/1980
		EP 0014161 B1	30/03/1983
		JP 55-128020 A	03/10/1980
		JP 63-011447 B2	14/03/1988
		US 4276278 A	30/06/1981
US 4572813 A	25/02/1986	JP 04-013447 B2	09/03/1992
		JP 04-013448 B2	09/03/1992
		JP 60-185818 A	21/09/1985
		JP 60-224815 A	09/11/1985