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(54) **Title:** POLYARENAZOLE MICROFILAMENTS AND PROCESS FOR MAKING SAME

(57) **Abstract:** Provided is a polymer filament having an average diameter of about 20 to 5000 nm, the filament comprising a polyarenazole polymer having an inherent viscosity of greater than about 20g/dl. Also provided are yarns comprising such filaments. Additional aspects concern fabrics and garments comprising such filaments and/or yarns.

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POLYARENAZOLE MICROFILAMENTS AND PROCESS FOR MAKING SAME

RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Patent Application US Provisional Patent Application 60/834,426 filed 7/31/06, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention concerns polyarenazole microfilaments and processes for making such filaments.

BACKGROUND OF THE INVENTION

[0003] Certain low denier fibers have been shown to be useful in a variety of end uses such as filtration media, cell & tissue cultures, drug delivery systems, and specialty textiles.

[0004] U.S. Patent No. No. 4,263,245 describes certain low denier, high-strength polybibenzimidazole filaments that are 20 to 200 microns in diameter.

[0005] Filtration mediums, fine particle wipe mediums and absorbent mediums containing a mixture of submicron and greater than submicron fibers are disclosed in U.S. Patent No. 6,315,806. Preferred fibers are said to be made from polypropylene polymer. Published U.S. Application No. 20050026526 discloses filter media having a mixture of course fibers and fine fibers of diameter less than 1 μm.

[0006] PCT Patent Application No. WO 03/080905 discloses the preparation of a nanofiber web by an electro-blown spinning process. PCT Patent Application No. WO 05/026398 describes production of nanofibers by reactive electrospinning.

[0007] A method for producing a webbed fibrillar material is disclosed in published U.S. Application No. 20050048274. The process injects polymer through an electric field towards an electrically charged target.

[0008] There is an ongoing need for web containing nanofibers that have improved properties.

SUMMARY OF THE INVENTION

[0009] Provided is a polymer filament having an average diameter of about 20 to 5000 nm, the filament comprising a polyarenazole polymer having an inherent viscosity of greater than about 20g/dl. In some embodiments, the average diameter is in the range of about 20 to 1000 nm. In certain embodiments, the average diameter is in the range of about 20 to 800 nm. In yet other embodiments, the average diameter is in the range of about 100 to 500 nm.

[0010] In some embodiments, the polyarenazole polymer has an inherent viscosity of greater than about 25g/dl. In other embodiments, the inherent viscosity is greater than about 28 g/dl. Useful polyarenazole polymers include polypyridoazole polymers. One useful polypyridoazole polymer is poly[2,6-diimidazo[4,5-b:4,5-e]- pyridinylene–1,4-(2,5-dihydroxy)phenylene).

[0011] Also provided are yarns comprising filaments described herein. In some embodiments, the yarn has a filament tenacity of greater than about 10 g / denier.

[0012] The invention also concerns fabrics and garments comprising the filaments and/or yarns described herein.

[0013] The invention also provides a polyarenazole polymer filament comprising:

--extruding a solution comprising polyarenazole polymer through a spinneret having a first applied voltage; and

-- collecting the extruded polyarenazole polymer on a collection surface optionally having a second applied voltage that is opposite in polarity to the first applied voltage.

[0014] In some embodiments, the solution comprising polyarenazole polymer comprises polyphosphoric acid as a solvent.

[0015] In some methods, the first applied voltage is in the range of ±1kV to ±300kV. In certain methods, the second applied voltage is opposite in polarity to the first applied voltage and in the range of 0 to ±10kV.

[0016] In some embodiments, the method additionally comprises the step of passing the extruded polyarenazole polymer solution through an air gap. The extruded polymer can be accelerated in the air gap by providing air flow along the direction between the spinneret and collection surface In certain embodiments, the second applied voltage is zero.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0017] Provided is a polymer filament having an average diameter of about 20 to 5000 nm, the filament comprising a polyarenazole polymer having an inherent viscosity of greater than about 20g/dl. Also provided are yarns comprising such filaments. Additional aspects concern fabrics and garments comprising such filaments and/or yarns.

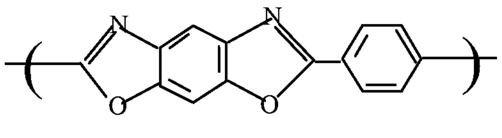
[0018] The filaments and yarns of the instant invention utilize polyarenazole microfibers. Polyareneazole polymer may be made by reacting a mix of dry ingredients with a polyphosphoric acid (PPA) solution. The dry ingredients may comprise azole-forming monomers and metal powders. Accurately weighed batches of these dry ingredients can be obtained through employment of at least some of the preferred embodiments of the present invention.

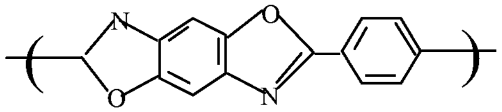
[0019] Exemplary azole-forming monomers include 2,5-dimercapto-p-phenylene diamine, terephthalic acid, bis-(4-benzoic acid), oxy-bis-(4-benzoic acid), 2,5-dihydroxyterephthalic acid, isophthalic acid, 2,5-pyridodicarboxylic acid, 2,6-napthalenedicarboxylic acid, 2,6-quinolinedicarboxylic acid, 2,6-bis(4-carboxyphenyl) pyridobisimidazole, 2,3,5,6-tetraaminopyridine, 4,6-diaminoresorcinol, 2,5-diaminohydroquinone, 1,4-diamino-2,5-dithiobenzene, or any combination thereof. Preferably, the azole forming monomers include 2,3,5,6-tetraaminopyridine and 2,5-dihydroxyterephthalic acid. In certain embodiments, it is preferred that that the azole-forming monomers are phosphorylated. Preferably, phosphorylated azole-forming monomers are polymerized in the presence of polyphosphoric acid and a metal catalyst.

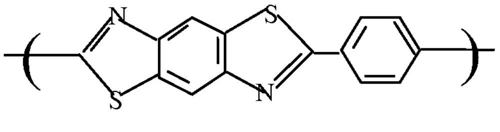
[0020] Metal powders can be employed to help build the molecular weight of the final polymer. The metal powders typically include iron powder, tin powder, vanadium powder, chromium powder, and any combination thereof.

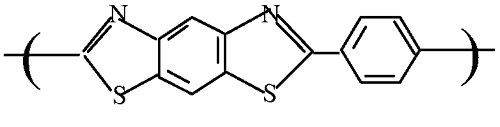
[0021] The azole-forming monomers and metal powders are mixed and then the mixture is reacted with polyphosphoric acid to form a polyareneazole polymer solution. Additional polyphosphoric acid can be added to the polymer solution if desired.

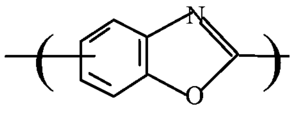
[0022] Polybenzoxazole (PBO) and polybenzothiazole (PBZ) two suitable polymers. These polymers are described in PCT Application No. WO 93/20400. Polybenzoxazole and polybenzothiazole are preferably made up of repetitive units of the following structures:

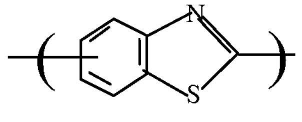












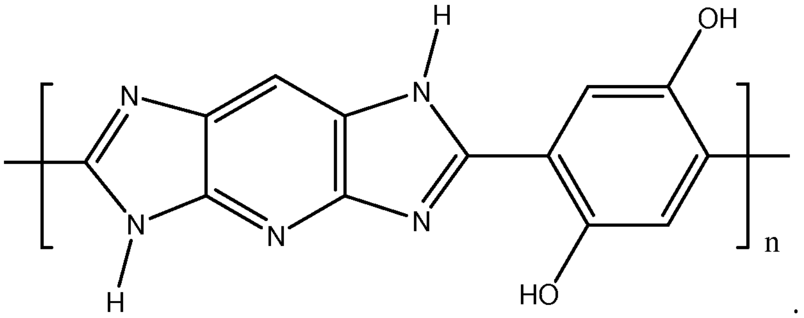
[0023] Polybibenzimidazole polymer is useful for making fiber used in this invention. Such products can be made by the processes disclosed in U.S. Patent 2,895,948 and U.S. Reissue 26,065. Polybibenzimidazole fibers can be made by known processes such as those disclosed in U.S. Patent 3,441,640 and U.S. Patent 4,263,245.

[0024] In some embodiments, the polybenzimidazole (PBI) fiber comprises polybibenzimidazole polymer. One useful polybibenzimidazole polymer is poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole) polymer. One commercial PBI polymer is prepared from tetra-aminobiphenyl and diphenyl isophthalate.

[0025] While the aromatic groups shown joined to the nitrogen atoms may be heterocyclic, they are preferably carbocyclic; and while they may be fused or unfused polycyclic systems, they are preferably single six-membered rings. While the group shown in the main chain of the bis-azoles is the preferred para-phenylene group, that group may be replaced by any divalent organic group which doesn't interfere with preparation of the polymer, or no group at all. For example, that group may be aliphatic up to twelve carbon atoms, tolylene, biphenylene, bis-phenylene ether, and the like.

[0026] The polybenzoxazole and polybenzothiazole used to make fibers of this invention should have at least 25 and preferably at least 100 repetitive units. Preparation of the polymers and spinning of those polymers is disclosed in the aforementioned PCT application WO 93/20400.

[0027] Polypyridobisimidazole fibers are particularly suited for use in the instant invention. These fibers are made from rigid rod polymers that are of high strength. The polypyridobisimidazole fiber has an inherent viscosity of at least 20 dl/g or at least 25 dl/g or at least 28 dl/g. Such fibers include PIPD fiber (also known as M5® fiber and fiber made from poly[2,6-diimidazo[4,5-b:4,5-e]- pyridinylene–1,4(2,5-dihydroxy)phenylene). PIPD fiber is based on the structure:



[0028] Polypyridobisimidazole fiber can be distinguished from the well known commercially available PBI fiber or polybenzimidazole fiber in that that polybenzimidazole fiber is a polybibenzimidazole. Polybibenzimidazole fiber is not a rigid rod polymer and has low fiber strength and low tensile modulus when compared to polypyridobisimidazoles.

[0029] PIPD fibers have been reported to have the potential to have an average modulus of about 310 GPa (2100 grams/denier) and an average tenacities of up to about 5.8 Gpa (39.6 grams/denier). These fibers have been described by Brew, *et al.*, *Composites Science and Technology* **1999**, 59, 1109; Van der Jagt and Beukers, *Polymer* **1999**, 40, 1035; Sikkema, *Polymer* **1998**, 39, 5981; Klop and Lammers, *Polymer*, **1998**, 39, 5987; Hageman, *et al.*, *Polymer* **1999**, 40, 1313.

[0030] One method of making rigid rod polypyridoimidazole polymer is disclosed in detail in United States Patent 5,674,969 to Sikkema *et al.* Polypyridoimidazole polymer may be made by reacting a mix of dry ingredients with a polyphosphoric acid (PPA) solution. The dry ingredients may comprise pyridobisimidazole-forming monomers and metal powders. The polypyridobisimidazole polymer used to make the rigid rod fibers used in the fabrics of this invention should have at least 25 and preferably at least 100 repetitive units.

[0031] For the purposes of this invention, the relative molecular weights of the polypyridoimidazole polymers are suitably characterized by diluting the polymer products with a suitable solvent, such as methane sulfonic acid, to a polymer concentration of 0.05 g/dl, and measuring one or more dilute solution viscosity values at 30°C. Molecular weight development of polypyridoimidazole polymers of the present invention is suitably monitored by, and correlated to, one or more dilute solution viscosity measurements. Accordingly, dilute solution measurements of the relative viscosity ("V_{rel}" or "η_{rel}" or "n_{rel}") and inherent viscosity ("V_{inh}" or "η_{inh}" or "n_{inh}") are typically used for monitoring polymer molecular weight. The relative and inherent viscosities of dilute polymer solutions are related according to the expression

$$V_{inh} = ln\ (V_{rel}) / C,$$

where *ln* is the natural logarithm function and C is the concentration of the polymer solution. V_{rel} is a unitless ratio of the polymer solution viscosity to that of the solvent free of polymer, thus V_{inh} is expressed in units of inverse concentration, typically as deciliters per gram ("dl/g"). Accordingly, in certain aspects of the present invention the polypyridoimidazole polymers are produced that are characterized as providing a polymer solution having an inherent viscosity of at least about 20 dl/g at 30°C at a polymer concentration of 0.05 g/dl in methane sulfonic acid. Because the higher molecular weight polymers that result from the invention disclosed herein give rise to viscous polymer solutions, a concentration of about 0.05 g/dl polymer in methane sulfonic acid is useful for measuring inherent viscosities in a reasonable amount of time.

[0032] It is well known in the art that ultra-fine fibers can be prepared by flash spinning, electrostatic spinning, and melt-blown spinning. Ultra-fine fibers, such as microfibers, and nonwoven webs can be produced by a process that utilizes an electro-blown spinning process. In such a process, a polymer solution is discharged through a spinning nozzle to which a high voltage has been applied. The fiber spun from the nozzle is collected on a grounded suction collector. Typically, compressed air is injected at the lower end of the spinning nozzle. Such a processes for making microfibers and webs containing such fibers can be found in PCT Patent Application WO03/080905, the disclosure of which is incorporated herein in its entirety.

[0033] As used herein the term "fiber" is defined as a relatively flexible, macroscopically homogeneous body having a high ratio of length to width across its cross-sectional area perpendicular to its length. The fiber cross section can be any shape, but is typically round. Herein, the term “filament” or “continuous filament” is used interchangeably with the term “fiber.”

[0034] As used herein, “basis weight” cam be determined by ASTM D-3776, which is hereby incorporated by reference and reported in g/m^2.

[0035] As used herein, “fiber diameter” can be determined as follows. Ten scanning electron microscope (SEM) images at 5,000x magnification were taken of each microfiber layer sample. The diameter of eleven (11) clearly distinguishable microfibers were measured from each SEM image and recorded. Defects were not included (i.e., lumps of microfibers, polymer drops, intersections of microfibers). The average fiber diameter for each sample was calculated.

[0036] The terms “tenacity” and “tensile strength” refer to the strength of a fiber, yarn or fabric (ISO 5081) as measured using ASTM D638. Tensile properties of the nonwoven web are being determined by (ISO 1924) “Paper and Board - Determination of Tensile Properties”.

[0037] The present invention may be understood more readily by reference to the following detailed description of illustrative and preferred embodiments that form a part of this disclosure. It is to be understood that the scope of the claims is not limited to the specific devices, methods, conditions or parameters described and/or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of the claimed invention. Also, as used in the specification including the appended claims, the singular forms “a,” “an,” and “the” include the plural, and reference to a particular numerical value includes at least that particular value, unless the context clearly dictates otherwise. When a range of values is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. All ranges are inclusive and combinable.

Examples

[0038] The invention is illustrated by, but is not intended to be limited by the following examples.

Example 1

Polymer Process

[0039] 11,580 grams of polyphosphoric acid (PPA) (84.7% P_2O_5) at 120 °C is fed from a weigh tank into a 10CV DIT Helicone mixer that has a nitrogen atmosphere of 1 atmosphere.

(The mixer blades are stopped so as not to obscure the addition port.) After the PPA is in the mixer, the mixer blades are run at 40 rpm and the jacket cooling water is started to cool the PPA to 70 °C. When the PPA is cooled, the water flow is stopped and the mixer blades are stopped so as not to obscure the addition port.

[0040] 3400 grams of P_2O_5 are weighed into a transfer bin in a weigh chamber under dry nitrogen (N_2). The 1 atmosphere (absolute) nitrogen pressure in the mixer is equalized to the 1 atmosphere pressure in the N_2–blanketed weigh chamber. The P_2O_5 is transferred to the 10CV mixer, and then the transfer valve is closed. The mixer blades are started and their speed is ramped to 40 rpm. Water cooling is restarted and a vacuum is slowly applied to degas the mixture as the P_2O_5 is blended into the PPA. Water cooling is controlled to maintain the contents of the mixer at 75 (+/- 5) °C. The pressure in the mixer is reduced to 50 mm Hg and mixing is continued for an additional 10 minutes. The water flow is then stopped and the mixer blades are stopped so as not to obscure the addition port. N_2 is admitted to bring the pressure up to 1 atmosphere (absolute).

[0041] 10174 grams of monomer-complex are weighed into a transfer bin in a dry N_2 weigh chamber. In addition, 51 grams of tin powder (approx. 325 mesh) and 25 grams of benzoic acid are weighed into a separate N_2–blanketed transfer vessel in the same weigh chamber.

[0042] The 1 atmosphere (absolute) pressure in the mixer is equalized to the 1 atmosphere pressure in the N_2–blanketed weigh chamber. The monomer complex, tin, and benzoic acid are transferred to the 10CV mixer, and then the transfer valve is closed. The mixer blades are started and their speed is ramped to 40 rpm. Water cooling is restarted when the agitator starts, and the monomer complex, tin, and benzoic acid are blended into the PPA mixture for 10 minutes after the mixer blades have reached the 40 rpm rate. Then a vacuum is slowly applied to degas the mixture as the blending continues. Water cooling is controlled to maintain the contents of the mixer at 75 (+/-5) °C. The pressure in the mixer is reduced to 50 mm Hg pressure and mixing is continued for 10 minutes. Then the mixer blade speed is reduced to 12 rpm and water cooling is reduced to allow the temperature of the contents in the mixer to rise to 85 (+/-5) °C. The mixer blades are then stopped, N_2 is admitted to bring the pressure up to 1 atmosphere, and the contents of the mixer are then transferred to a feed tank having two agitators (a DIT 10SC mixer).

[0043] The reactant mixture in the feed tank is maintained at a temperature of 110 °C and a pressure of 50 mm Hg absolute. Both agitators are run at 40 rpm. The reactant mixture is pumped from the tank at an average rate of 10,050 grams/hour through a heat exchanger, to increase the temperature of the mixture to 137 °C, and into a series of three static mixer reactors, allowing a 3-hour hold-up time for oligomer formation. Exiting the static mixer reactors, superphosphoric acid (SPA) (76 % P_2O_5) is injected into the oligomer mixture at an average rate of 1079 grams/hour.

[0044] The oligomer mixture with SPA is then well blended through a static mixer and transferred to a stirred surge tank any volatiles are removed by a vacuum. The stirred surge tank is a DIT 5SC mixer, having a temperature maintained at 137 °C. Average hold-up time in the surge tank is 1¼ hr.

Polymerization of the Mixture

[0045] The oligomer mixture is then further polymerized to the desired molecular weight at a temperature of 180 °C. The oligomer mixture is first pumped through a heat exchanger to raise the temperature of the mixture to 180 C and then through a reactor system of static mixers and a rotating Couette-type-shearing reactor imparting 5 sec^{-1} shear rate to the polymerizing solution. The reactor system is maintained at 180 °C (+/- 5 degrees) and the hold-up time in the reactor system is 4 hours. A solution containing a polymer having an inherent viscosity of 25 dl/g is obtained.

Spinning Process

Fiber Formation & Quenching

Electro-Blowing:

[0046] A 20 weight percent solution of 25 IV polymer in PPA (having a strength of equivalent of 81.5 percent P2O5 is forwarded to a spinnerette pack having electrically charged spinning nozzles. The spinning nozzles have a diameter of about 0.25mm, an L/d ratio of about 10, DCD of 300mm, a spinning pressure of about 6 kg/cm^2, and an applied voltage of about 50kV. The number of spinning nozzles in the spinnerette pack is 51.

[0047] Surrounding the spinning nozzles are air nozzles that provide high pressure air for the electro-blowing process. The air velocity is about 3000meters/minute and the air temperature is about 100 degrees Celsius.

[0048] The spun filaments are collected on a moving belt by suction to form a web. The distance between the spinnerette nozzle and suction collection belt is 30cm.

Hydrolysis, Washing, & Drying

[0049] The web is sprayed with water at 40 degrees Celsius for 20 seconds. The web is then passed through an oven operating at a temperature of 300 °C for a residence time of 60 seconds. The web is then washed with a water spray. The water temperature is 40 °C. The web is then dried by passing the web through an oven operating at 150 °C for a residence time of 40 seconds.

Example 2

[0050] The process of example 1 is repeated except that the air velocity is 0 meters / minute.

Example 3

[0051] The process of example 1 is repeated except that no voltage is applied to the spin nozzle.

Example 4

[0052] This example illustrates the optional heat treatment of the web made in the previous examples. The process of a preceding example is repeated, except after drying, a volatile antistatic finish is applied to theweb instead of a textile finish, and the web is immediately conveyed to an oven instead of being wound on a bobbin.

Heat Treatment

[0053] The dried web is conveyed to an electrically heated belt, which raises the temperature of the web to 400 °C. The web is then conveyed into a N_2-blanketed tube oven which raises the temperature of the yarn to 500 °C. Before exiting the N_2 atmosphere, the web is cooled in a room temperature N_2 atmosphere for 2 seconds, and a finish is applied. The web is then collected.

What is Claimed:

1. A polymer filament having an average diameter of about 20 to 5000 nm, the filament comprising a polyarenazole polymer having an inherent viscosity of greater than about 20g/dl.

2. The polymer filament of claim 1 wherein the average diameter is in the range of about 20 to 1000 nm.

3. The polymer filament of claim 2 wherein the average diameter is in the range of about 20 to 800 nm.

4. The polymer filament of claim 3 wherein the average diameter is in the range of about 100 to 500 nm.

5. The polymer filament of claim 1 wherein the polyarenazole polymer has an inherent viscosity of greater than about 25g/dl.

6. The polymer filament of claim 1 wherein the polyarenazole polymer is a polypyridoazole polymer.

7. The polymer filament of claim 6 wherein the polypyridoazole polymer is poly[2,6-diimidazo[4,5-b:4,5-e]- pyridinylene–1,4-(2,5-dihydroxy)phenylene).

8. A yarn comprising a polyarenazole filament having an average diameter of about 20 to 5000 nm and a filament tenacity of greater than about 10 g / denier.

9. The yarn of claim 8 wherein the polyarenazole filament comprises polypyridoazole polymer.

10. The yarn of claim 9 wherein the polypyridoazole is poly[2,6-diimidazo[4,5-b:4,5-e]-pyridinylene–1,4-(2,5-dihydroxy)phenylene).

11. A fabric comprising filament of claim 1.

12. A garment comprising fabric of claim 11.

13. A method of producing a polyarenazole polymer filament comprising:

extruding a solution comprising polyarenazole polymer through a spinneret having a first applied voltage; and

collecting the extruded polyarenazole polymer on a collection surface optionally having a second applied voltage that is opposite in polarity to the first applied voltage.

14. The method of claim 13 wherein the solution comprising polyarenazole polymer comprises polyphosphoric acid as a solvent.

15. The method of claim 13 wherein the first applied voltage is in the range of 1kV to 300kV.

16. The method of claim 13 wherein the second applied voltage is in the range of 0 to 10kV.

17. The method of claim 13 wherein the polyarenazole polymer is poly[2,6-diimidazo[4,5-b:4,5-e]- pyridinylene–1,4-(2,5-dihydroxy)phenylene).

18. The method of claim 13 wherein the method additionally comprises the step of passing the extruded polyarenazole polymer solution through an air gap.

19. The method of claim 18 wherein the method additionally comprises the step of accelerating the extruded polymer solution in the air gap by providing air flow along the direction between the spinneret and collection surface.

20. The method of claim 19 where the second applied voltage is zero.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/074465

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G73/00 C08G73/18 C08G73/22 D01D5/12 D01D5/26

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)
C08G 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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 263 245 A (TAN MARSHALL) 21 April 1981 (1981-04-21)	1-12
Y	column 1, line 7 - column 9, line 54; claims 1-30; examples	13-20
X	US 5 976 447 A (MILLS MICHAEL E [US] ET AL) 2 November 1999 (1999-11-02)	1-12
Y	column 1, line 14 - column 7, line 54; claims 1-19; examples	13-20
X	US 5 273 703 A (ALEXANDER WILLARD E [US] ET AL) 28 December 1993 (1993-12-28)	1-12
Y	column 1, line 6 - column 7, line 28; claims 1-10; examples	13-20
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☒ 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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"P" document published prior to the international filing date but later than the priority date claimed

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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Kiebooms, Rafaël

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/074465

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P Y,P	WO 2006/105230 A (DU PONT [US]; MAGELLAN SYSTEMS INTERNATIONAL [US]; ALLEN STEVEN [US];) 5 October 2006 (2006-10-05) page 1 - page 32; claims 1-20; examples	1-12 13-20
X Y	US 5 674 969 A (SIKKEMA DOETZE JAKOB [NL] ET AL) 7 October 1997 (1997-10-07) column 1, line 6 - column 13, line 64; claims 1-19; examples	1-12 13-20
Y	WO 03/080905 A (NANO TECHNICS CO LTD [KR]; KIM YONG MIN [KR]; SUNG YOUNG BIN [KR]; JAN) 2 October 2003 (2003-10-02) page 1, line 5 - page 8, line 16; claims 1-16; examples	13-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2007/074465

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4263245 A	21-04-1981	NONE	
US 5976447 A	02-11-1999	EP 0799334 A1	08-10-1997
		JP 3613719 B2	26-01-2005
		JP 8209445 A	13-08-1996
		WO 9620303 A1	04-07-1996
US 5273703 A	28-12-1993	CA 2142279 A1	03-03-1994
		CN 1087138 A	25-05-1994
		EP 0655092 A1	31-05-1995
		JP 8510791 T	12-11-1996
		WO 9404726 A1	03-03-1994
		US 5411694 A	02-05-1995
WO 2006105230 A	05-10-2006	NONE	
US 5674969 A	07-10-1997	AT 169317 T	15-08-1998
		CA 2161663 A1	10-11-1994
		CN 1121728 A	01-05-1996
		DE 69412250 D1	10-09-1998
		DE 69412250 T2	11-02-1999
		DK 696297 T3	10-05-1999
		WO 9425506 A1	10-11-1994
		EP 0696297 A1	14-02-1996
		ES 2120042 T3	16-10-1998
		JP 3527740 B2	17-05-2004
		JP 8509516 T	08-10-1996
		MX PA94003094 A	18-11-2003
		ZA 9402967 A	19-01-1995
WO 03080905 A	02-10-2003	AU 2002354313 A1	08-10-2003
		CN 1511200 A	07-07-2004
		EP 1495170 A1	12-01-2005
		JP 2005520068 T	07-07-2005
		KR 20030077384 A	01-10-2003
		US 2005067732 A1	31-03-2005