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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number
WO 2004/052447 A1

(51) International Patent Classification[7]: A61N 1/05

(21) International Application Number:
PCT/US2003/038955

(22) International Filing Date: 8 December 2003 (08.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/431,330 6 December 2002 (06.12.2002) US
10/403,329 31 March 2003 (31.03.2003) US

(71) Applicant: **MEDTRONIC, INC.** [US/US]; MS LC340, 710 Medtronic Parkway N.E., Minneapolis, MN 55432 (US).

(72) Inventors: **GARDESKI, Kenneth, C.**; 10405 45th Avenue North, Plymouth, MN 55442 (US). **BRABEC, Scott, J.**; 13822 211th Avenue Northwest, Elk River, MN 55330 (US).

(74) Agents: **MCDOWALL, Paul, H.** et al.; MC LC340, 710 Medtronic Parkway, Minneapolis, MN 55432 (US).

(81) Designated States *(national)*: CA, JP.

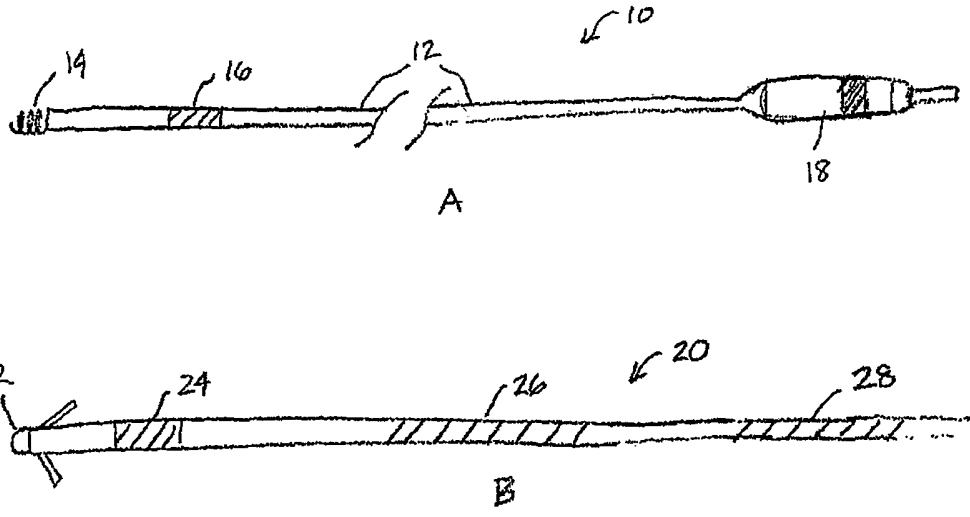
(84) Designated States *(regional)*: European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

Declaration under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MEDICAL DEVICES INCORPORATING CARBON NANOTUBE MATERIAL AND METHODS OF FABRICATING SAME



(57) Abstract: The present invention relates generally to medical devices; in particular and without limitation, to unique electrodes and/or electrical lead assemblies for stimulating cardiac tissue, muscle tissue, neurological tissue, brain tissue and/or organ tissue; to electrophysiology mapping and ablation catheters for monitoring and selectively altering physiologic conduction pathways; and, wherein said electrodes, lead assemblies and catheters optionally include fluid irrigation conduit(s) for providing therapeutic and/or performance enhancing materials to adjacent biological tissue, and wherein each said device is coupled to or incorporates nanotube structures or materials therein. The present invention also provides methods for fabricating, deploying, and operating such medical devices.

WO 2004/052447 A1

MEDICAL DEVICES INCORPORATING CARBON NANOTUBE MATERIAL AND METHODS OF FABRICATING SAME

The present invention relates generally to medical devices; in particular and without limitation, to unique electrodes and/or electrical lead assemblies for stimulating cardiac tissue, muscle tissue, neurological tissue, brain tissue and/or organ tissue; to electrophysiology mapping and ablation catheters for monitoring and selectively altering physiologic conduction pathways; and, wherein said electrodes, lead assemblies and catheters optionally include fluid irrigation conduit(s) for providing therapeutic and/or performance enhancing materials to adjacent biological tissue, and wherein each said device is coupled to or incorporates nanotube structures or materials therein. The present invention also provides methods for fabricating, deploying, and operating such medical devices. For the uninitiated, to get an idea of scale - one nanometer is one one-thousandth of a micrometer; in comparison, a strand of human hair is typically 50 to 100 micrometers thick.

Even brief study of the prior art relating to medical electrical leads will reveal that such leads typically incorporate at least one electrode and the lead assembly should be compact and resilient, should yield a low threshold for stimulation, should sense the low amplitude electrical signals naturally generated by a body. In addition, such leads should be biocompatible with the adjacent body tissue and body fluids, which it contacts. Various attempts have been made to improve these characteristics, especially with respect to medical electrodes electrically coupled to the lead body of a cardiac pacing lead. Generally these attempts are aimed at increasing the interfacial, or active, surface area of an electrode by the use of surface treatments or coatings that are considered highly biocompatible.

As is known in the art, electrochemical reactions occur at the electrode-tissue interface when an electrical stimulation pulse is delivered through a medical electrical lead assembly. This phenomenon is referred to as "polarization," which is known to interfere with efficient delivery of the stimulation pulses. High interfacial impedance due to the

effects of polarization reduces the effective charge transfer of the stimulation pulse to the targeted tissue. Therefore low polarization electrodes have been developed to reduce this effect and improve the transfer of charge from the electrode to the tissue.

One method for reducing polarization effects is to increase electrode surface area. However, a design trade-off exists in increasing the electrode size since medical leads and the electrodes they carry are preferably of small dimensions such that they may be easily implanted. For example, presently available cardiac pacing leads typically have cross-sectional diameters of greater than about three or four French and a typical diameter of an electrophysiology catheter is about six French. For reference, a single French unit of measurement equals one third of a millimeter. In any event, to overcome this trade-off, methods for increasing the active surface area of a geometrically down-sized electrode have been proposed. For example, treatments or coatings that yield a porous, irregular or grooved surface increase the active surface area of the electrode and thereby diminish the effects of polarization. Various coatings have been proposed and put into commercial use for producing low polarization electrodes such as platinum black, pyrolytic carbon, iridium oxide, vitreous carbon, titanium nitride and others.

A further benefit of increasing electrode interfacial or active surface area can be improved electrode sensing performance. Cardiac signals, including action potentials that are relatively low amplitude, monophasic signals, may be more readily sensed when the active surface area of the electrode is increased. Moreover, an evoked response following delivery of a stimulation pulse may be more readily detected when post-pace polarization artifact is diminished.

Recently, as reported in the Journal of the American Chemical Society (JACS), research personnel at Washington University in St. Louis and their collaborators report that they have made boron "nanowhiskers" by chemical vapor deposition. The particles have diameters in the range of 20 to 200 nanometers and the whiskers (also called nanowires) are semiconducting and show properties of elemental boron.

The group at Washington University in St. Louis turned to boron, one spot to the left of carbon in the periodic table, to see if it would be a good candidate. They postulated that if nanotubes could be made of boron and produced in large quantities, they should have the advantage of having consistent properties despite individual variation in diameter

and wall structure. The discovery that the "nanowhiskers" are semiconducting make them promising candidates for nanoscale electronic wires. Boron nitride nanotubes, which are similar in structure to carbon nanotubes, are electrically insulating. Boron nanotubes on the other hand may be grown into long thin wire-like structures. At first they appeared hollow, but after closer examination, they were determined to be dense whisker-like structures, not hollow nanotube structures. The notion of boron nanotubes creates more excitement in nanotechnology than nanowhiskers because of their unique structure, which could be likened to a distinct form of an element. Carbon, for instance, is present as graphite and diamond, and, recently discovered, in "buckyball" and nanotube conformations. Also, boron nanotubes are predicted by theory to have very high conductivity especially when bulk boron is "doped" with other atoms to increase conductivity. Carbon nanotubes also have been doped, as have various other kinds of nanowires, and assembled in combinations of conducting and semiconducting ones to make for several different microscale electronic components such as rectifiers, field-effect transistors and diodes.

The present invention is directed at providing a class of improved medical electrical lead assemblies featuring carbon nanotube material. Carbon nanotubes, discovered in about 1991, are formed from a cage-like hollow lattice structure of carbon molecules arranged into tubes having a diameter on the order of nanometers. Considerable interest in the use of carbon nanotubes in various applications such as batteries, capacitors, flat panel displays and microelectronics, has grown due to the unique properties of this newly discovered material including its high strength, stable state, low weight, and so-called ballistic (or near-superconducting) electrical properties. In addition, boron nanotubes and carbon nanotube "nanowires" are now becoming available. The inventors have discovered that these developments enable invention of discrete technologies providing significant value to patients suffering from diverse afflictions while advancing the medical device field in several important ways.

Nanotubes made exclusively from carbon are chemically inert and are therefore, the inventors suggest, are highly biocompatible. Carbon nanotubes may be formed to have metallic conductor or semi-conductor properties and are capable of sustaining a high

current density, on the order of hundreds of times greater than common metals. Carbon nanotubes are thin, long tubular macromolecules with diameters on the order of a 1-200 nanometers (molecules are on the order of a few nanometers) and with lengths on the order of micrometers to millimeters. Bundles of such nanotubes create nanostructures which are characterized by a large surface area. In short, these characteristics of carbon nanotubes may make them particularly well-suited for diverse uses in conjunction with medical electrical lead assemblies and medical electrodes for improving electrode performance.

The inventors have discovered that carbon nanotubes may be adapted to render greatly improved medical electrical leads and/or medical electrodes. The present invention provides such leads and/or electrodes in one or more of the following ways. Nanotube structures coupled to, layered upon or coated upon a electrically conductive or non-conductive electrode or lead body structure. In addition, a variety of polymers and other resin-based materials when combined, encapsulated or impregnated with nanotubes can be used to render the resulting structures electrically conductive. In the context of the present invention, such structures may be configured as elongated medical lead body structures, electrode structures and the like. In addition, carbon nanotubes may be employed in lieu of a metallic coil conductor (or other type) of primary electrical conductor for all or a portion of the body of an extremely thin, resilient and flexible medical electrical lead. The resulting structure may be porous and itself impregnated with diverse materials such as steroid material, electrically conductive fluid or paste materials, and the like.

One embodiment of the present invention features a medical electrical lead carrying one or more tip-, ring-, defibrillation coil-, neurological-, brain-, skeletal muscle-, or organ-electrodes for sensing and/or delivering electrical stimulation pulses to a portion of cardiac tissue, neurological tissue, brain tissue, skeletal tissue, organ tissue and the like.

In embodiments involving cardiac tissue, the active surface area of the electrodes, which is contact with blood or bodily tissue, is increased by depositing carbon nanotubes on the electrode surface. Furthermore, carbon nanotubes at the electrode/tissue interface emit electrons from the tip portions of the nanotubes at relatively low voltages and sustain current densities hundreds of times greater than common metals. Such field emission

properties can be obtained by mixing nanotubes into a composite paste with polymers such as polyurethane or silicone, applying the paste to an electrode surface, and then applying a voltage to align the nanotubes on end. Such alignment can form extremely consistent, tightly packed arrays of nanotubes or may be less consistent. In either case, a vast surface area is created which is very advantageous as is known to those of skill in the art. Such arrays of nanotubes may be impregnated with diverse materials such as biological, genetic or pharmacological substances so that over time said arrays elute the materials into adjacent tissue or body fluid. Some representative diverse materials include steroid material, electrically conductive fluid materials such as isotonic saline solution or other biologically compatible fluids.

In another embodiment, a carbon nanotube coating may be applied to a metallic electrode substrate, such as platinum, platinum-iridium, titanium, alloys of the foregoing and other metals by chemical vapor deposition or other methods known in the art for growing and depositing carbon nanotubes on a substrate. The surface area of the carbon nanotubes, which may include the outer surface and the inner surface of the tubes, effectively increases the active electrode surface area of the metallic electrode substrate.

The carbon nanotube coating provides a highly biocompatible electrode surface. Moreover, the carbon nanotube coating provides a low electrode-tissue interface impedance allowing for improved sensing of low frequency, intrinsic cardiac signals as well as evoked responses from cardiac tissue. The high-energy density properties of carbon nanotubes further provides lower stimulation thresholds for capturing a heart during pacing and/or when delivering defibrillation therapy to a heart.

While chemical vapor deposition (CVD) represents one manner of mass producing apparatus according to the present invention, CVD generally has a higher density of structural defects and a subsequently a larger variation in resistivity. Metallic catalysts such as nickel, iron, cobalt, molybdenum and ruthenium are usually necessary for formation of consistent, high yield films using CVD. Achieving good contact resistances to the substrate material is still a matter of adapting the catalyst and substrate to one another, among other variables. If the formation of thin oxide layers, on the atomic scale, occur between the nanotubes and metal substrate, high ohmic-contact resistance is often the result. As research continues with respect to high yield, mass production of carbon

nanotube coatings, there are now presently available highly ordered single-wall and multi-wall nanotube structures on substrates in a very ordered manner.

In this patent disclosure the term "nanotube(s)" is intended to refer to nanostructures in general; that is, substantially one dimensional so-called nanowires (or "nanowhiskers"), two dimensional, substantially planar structures such as fullerenes (e.g., a convex cage of atoms with only hexagonal and/or pentagonal faces) having a cylindrical shape, and three-dimensional structures such as the so-called buckyballs, closed- and open-ended nanotubes, and the like. The inventors suggest that when incorporated into suitably adapted structures the fully variety of nanostructures may be used to improve the electrical performance of myriad medical electrical leads. In some applications, the nanostructures may also be used to retain and/or release over time the above-noted diverse materials, such as electrically conductive fluids, biological, genetic and/or pharmacological substances. Thus, the terms used in the present patent disclosure may differ from the evolving convention(s) for referring to a broad variety of different nano-scale structures. For example, typically, a nanotube is any tube having nanoscale dimensions, but is often intended to generally refer to carbon nanotubes. In this disclosure the reverse is true. Thus, in this disclosure "nanotube" or "nanostructure" is intended to include carbon nanotubes and other nanostructures, and shall also be deemed to cover a often mentioned non-carbon variety of nanotube made of boron and the like. In general, then, nanotubes are sheets of graphite rolled up to make a tube. The dimensions are variable (down to 0.4 nm in diameter) and a single nanotube can be formed or disposed within another nanotube, leading to a distinction between multi-walled and single-walled nanotubes ("MWNT" and "SWNT," respectively).

Apart from remarkable tensile strength, nanotubes exhibit varying electrical properties (depending on the way the graphite structure spirals around the tube, and other factors), and can be insulating, semiconducting or conducting (metallic).

Nanotubes can be either electrically conductive or semiconductive, depending on their helicity, leading to nanoscale wires and electrical components. These one-dimensional fibers exhibit electrical conductivity as high as copper, thermal conductivity as high as diamond, strength 100 times greater than steel at one sixth the weight, and high strain to failure.

Carbon nanotubes exhibit extraordinary mechanical properties: the Young's modulus is over 1 Tera Pascal and as stiff as diamond with an estimated tensile strength of about 200 Giga Pascal. These properties are ideal for reinforced composites and nanoelectromechanical systems, among others.

Carbon nanotube transistors exploit the fact that nm-scale nanotubes are ready-made molecular wires and can be rendered into a conducting, semiconducting, or insulating state, which make them valuable for future nanocomputer design. Carbon nanotubes are quite popular now for their prospective electrical, thermal, and even selective-chemistry applications.

While the present invention will be described primarily with reference to single- and multi-walled carbon nanotubes (SWNT/MWNT), it is not to be construed as being limited solely to such materials. For example, the present invention may be practiced using so-called "nanowires" or "nanowhiskers" (NW). Such NW may be produced of carbon or other related elements such as boron and the NW (and SWNT/MWNT) may be doped or modified so they readily conduct electricity, are semi-conductive, or even insulative.

The foregoing summary is intended to briefly introduce the reader to the basic concepts of the present invention and should not be construed as limiting the invention hereof. Likewise, the following drawings (and those incorporated herein) are illustrative of only a few embodiments of the present invention, are not drawn to scale and should not be viewed as limiting the scope of the present invention. In fact, those of skill in the art will quickly recognize variations of the described and depicted embodiments of the present invention, and each such variation is intended to be covered by this patent disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a plan view of a cardiac pacing lead that may be used in conjunction with the present invention. It should be noted that the pacing lead may have one or more anode rings.

FIG. 1B is a plan view of the distal end of a cardiac pacing and defibrillation lead that may be used in conjunction with the present invention.

FIG. 2 is a flow diagram summarizing a method for manufacturing a carbon nanotube coated medical electrode.

FIG. 3 is an illustration of a magnified, side view of a carbon nanotube coated electrode wherein the nanotubes are aligned.

FIG. 4 is an illustration of a magnified, side view of a carbon nanotube coated electrode wherein the nanotubes are randomly ordered.

FIG. 5 is an illustration of a magnified, side view of a carbon nanotube coated electrode wherein the nanotubes are coiled and randomly arranged.

FIG. 6 is a flow chart summarizing an alternative method for manufacturing a carbon nanotube coated medical electrode.

DETAILED DESCRIPTION OF THE INVENTION

As described above, the present invention is directed at providing a medical lead having improved electrode performance by providing carbon nanotube coated electrodes. **FIGS. 1A and 1B** depict exemplary medical leads of the type that may be used with the present invention. **FIG. 1A** is a plan view of a medical lead 10 that may typically be used for cardiac pacing and/or sensing. Lead 10 is provided with an elongated lead body 12, a helical tip electrode 14 located at the distal end of the lead and a ring electrode 16 spaced proximally from tip electrode 14. A connector assembly 18 at the proximal end of lead 10 is used to connect the lead to a medical device, such as a pacemaker. Conductors extending the length of lead body 12 electrically couple the tip electrode 14 and ring electrode 16 to respective connectors carried by the connector assembly 18.

FIG. 1B is a plan view of the distal end of a medical lead 20 of the type that may be used for pacing, sensing, cardioversion and/or defibrillation. Lead 20 is provided with a tip electrode 22 and a ring electrode 24, which are generally used for pacing and/or sensing, and two defibrillation coil electrodes 26 and 28 for delivering high-energy shocking pulses for cardioversion or defibrillation.

The exemplary leads 10 and 20 of **FIGS. 1A and 1B** are shown to illustrate the various types of electrodes, including ring electrodes (16 and 24), coil electrodes (26 and 28), helical electrodes (14), or generally hemispherical electrodes (22), with which the present invention may be used. Other electrodes of various geometries may exist that may

also benefit from the use of carbon nanotube coating as provided by the present invention. The application of the present invention is therefore not limited to the types of electrodes depicted in **FIG. 1A and 1B**. The present invention may also be used in conjunction with electrodes for neurological stimulation or sensing, smooth or skeletal muscle sensing or stimulation or any other types of medical electrodes that may benefit from increased active surface area and/or increased current density capacity.

An electrode used with the present invention is preferably fabricated from a conductive biocompatible material appropriate for depositing carbon nanotubes thereto. CVD methods begin with supported catalyst particles that are exposed to a carbon feedstock gas (e.g., acetylene or methane). Carbon atoms from the dissociation of these molecules at the catalyst surface dissolve in the catalyst particles to reappear on the surface, where they organize to form nanotubes. Depending on the growth conditions (e.g. gas mixture, gas flows, reaction temperature, reaction time, and catalyst), the catalyst particle either remains on the surface (base growth) or is lifted from the surface by the nanotube (tip growth).

As mentioned earlier, adapting the catalyst to the substrate is critically important and note that catalysts can also be deposited to the substrate surface before introducing the carbon nanotubes. Noble metal substrates such as gold are known to suppress growth. The problem is most likely due to alloy formation with the catalyst material. Refractory metals and their nitrides can act as a diffusion barrier to the chosen catalyst. Also, applying an AC or DC electric field helps in nanotube growth.

The electrode material may be, for example, platinum, platinum-iridium, iridium, titanium or alloys , tantalum, and other non-noble metals. The electrode surface may also be treated or coated to enhance the surface for nanotube deposition, as will be further described below.

Carbon nanotubes may be grown and deposited onto a surface by at least three methods: 1) chemical vapor deposition, 2) carbon arc deposition, and 3) laser evaporation deposition. Chemical vapor deposition methods generally use a metal catalyst substrate at a high temperature to which a hydrocarbon gas is exposed. Carbon nanotubes are deposited on the catalyst surface and may be grown in various structures such as straight tubes that may be well-aligned or coiled tubes. A method for growing densely packed,

uniform nanotube arrays perpendicular to a substrate is generally disclosed in U.S. Pat. No. 6,361,861 issued to Gao et al., incorporated herein by reference in its entirety.

Carbon arc deposition methods include evaporating material from a graphite electrode in an electric arc discharge between two graphite electrodes. Carbon nanotubes deposit on the other graphite electrode and are generally straight but may be impure with a high percentage of nanoparticles. Laser evaporation techniques involve forming carbon nanotubes in a plume of carbon vapor evaporated from a graphite target by a laser at high temperature.

Methods for growing and depositing carbon nanotubes on a substrate may produce varying purity, density, alignment, structure, and size of the nanotubes. Carbon nanotubes are formed as one or more concentric shells of graphite and therefore may be single-walled, double-walled or multi-walled tubes. Nanotubes may be straight or may have irregular curving or coiling shapes. Nanotubes reportedly range in diameter from 1 nanometer to several hundred nanometers. Nanotubes may be grown to be on the order of 1 micron to several hundred microns in length. Future methods for carbon nanotube growth and deposition may be developed that improve the purity, increase uniformity or achieve desired geometries or properties of the nanotubes, such as desired electrical properties.

In the present state of the art, carbon nanotube coated electrodes are contemplated to be produced by chemical vapor deposition methods, though any of the above described methods or modifications thereof or newly developed methods may be used. **FIG. 2** is a flow chart depicting one method for producing a carbon nanotube coated electrode. The method may begin by preparing an electrode surface for deposition of the carbon nanotubes at step 102. The electrode is preferably fabricated from platinum or platinum-iridium. The electrode may take the form of any known types of electrodes, such as those shown in **FIGS. 1A and 1B**. The platinum iridium surface of the electrode may be a sufficient catalyst for carbon deposition. Alternatively, the electrode surface may be prepared by creating a more porous surface and/or coating the surface with an alternative biocompatible catalyst to promote strong bonding of the carbon nanotubes to the electrode surface or to enhance the deposition process. For example, a platinum electrode may be coated with a porous coating of catalytic nanoparticles. The porous coating may provide a

better catalyst for carbon nanotube deposition in that the growth direction, size, and density of the nanotubes may be controlled by the pores (see Li et al., Science, 1996;274(5239):1701-3.

The electrode may then be mounted in a vacuum chamber at step 104 through which an inert gas flows, such as a helium-argon gas, to raise the pressure in the chamber at step 106. The temperature of the substrate is raised at step 108. The temperature may typically be raised to a level on the order of 500 to 1000 degrees C. Resistive heating elements may be used to heat the substrate, although other equivalent means may be employed.

A carbon source in the form of a hydrocarbon gas, which may be, for example, acetylene gas, methylene gas, or ethylene gas, is then allowed to flow through the chamber at step 110. At step 112, nanotube deposition and growth are allowed to occur. The time required for adequately coating the electrode surface with a carbon nanotube coating may range from several minutes to several hours. The size of the nanotubes and their uniformity and density may be controlled by the flow rate of the hydrocarbon gas, the temperature of the substrate, the density of the catalyst on the substrate or other conditions.

Verification of the carbon nanotube coating may be performed by scanning electron microscopy or other methods at step 114. Verification may be performed to ensure a desired density or size of the nanotubes has been achieved or to ensure that the nanotubes are well attached to the electrode surface. The carbon nanotube coated electrode may then be assembled onto a lead at step 116 and electrically coupled to a conductor extending through the lead body.

Nanotubes may be deposited in an orderly, aligned fashion using various deposition methods. **FIG. 3** is an illustration of a side view of an ordered nanotube "forest" 30 as it may be deposited on the surface of an electrode 32. The nanotube "forest" 30 may be grown such that the nanotubes are well aligned with one another and each generally have one end attached to the electrode surface. The nanotubes may be on the order of 0.1 to 300 microns in length and one to 200 nanometers in diameter depending on the deposition method used. A preferred range of diameters is in the range of approximately about one nm to about 20 nm but the present invention is not to be strictly

limited to this range. In certain embodiments of the present invention a highly ordered array of SWNT members disposed approximately perpendicular to a supporting member having a diameter dimension on the order of approximately about one to about five nm diameters. But that does not mean an excellent electrode couldn't be had with random MWNT's about 200 nm diameter in a urethane paste and the like.

FIG. 4 illustrates an alternative arrangement of deposited nanotubes on a medical electrode surface. Nanotubes 36 may be deposited in a disorderly fashion wherein nanotubes 36 are straight but not aligned with respect to each other. The tubes will still have one end generally attached to the electrode surface 38.

FIG. 5 illustrates yet another arrangement of deposited nanotubes 40 on a medical electrode surface 42. In this embodiment, coiled nanotubes 40, having one end attached to the electrode surface 42, are arranged randomly on electrode surface 42. Deposition methods resulting in coiled nanotubes have been described previously in the prior art.

The paste method described earlier is a preferred manner of coupling nanostructures to chronically implanted medical devices. In an alternative embodiment, carbon nanotubes may be grown and purified in a first process and then deposited onto an electrode surface as a coating in a second process. A method for depositing a purified carbon nanotube material onto a conductive substrate is generally disclosed in U.S. Pat. No. 6,280,697 issued to Zhou et al., incorporated herein by reference in its entirety.

FIG. 6 is a flow chart summarizing this alternative method for manufacturing carbon nanotube coated electrodes. Carbon nanotubes are grown at step 122 and purified at step 124. For example, carbon nanotubes may be formed by arc or laser deposition methods, or any known method, and purified by an appropriate method such as filtering through a microporous membrane. Alternatively, carbon nanotube materials that may be suitable for coating medical electrodes may be obtained directly from commercial sources such as NanoLab, Brighton, MA; CarboLex, Lexington, KY; Materials and Electrochemical Research Corporation, Tucson, AZ, among a growing number of other suppliers.

At step 126, the nanotubes are suspended in a solvent, such as alcohol. An electrode to be coated may then be placed in a vessel with the suspension of carbon nanotubes at step 128. The solvent is then driven off at step 130 leaving a coating of

nanotubes on the surface of the electrode. The nanotube coating may be verified at step 132 as described above. The electrode may then be assembled onto a medical lead at step 134.

The increase in active surface area created by a carbon nanotube coating is expected to be a minimum of 1,000X to potentially on the order of about 10,000X. This increase is theorized to result in a reduction in interfacial impedance at low frequencies from approximately 1000X, associated with prior known electrode coating methods such as sputtered porous titanium nitride, and iridium oxide. That is, the increase in active surface area created by a carbon nanotube coating is expected to be on the order off 1,000 to about 10,000X. The low frequencies referred to hereinabove, are on the order of less than about 0.1 Hz (or lower). Such a decrease in interfacial impedance improves electrode sensing performance which is very important for certain medical applications, such as cardiac rhythm management. This reduction in interfacial impedance and the high current density properties of carbon nanotubes also reduces pacing and/or defibrillation thresholds.

Methods for increasing the defects in the walls of the deposited nanotubes or for opening the ends of the tubes may be used to further increase the active surface area of the electrode. For example mechanical ball-milling or exposure to ultrasonic energy as generally disclosed in U.S. Pat. No. 6,280,697 may be applied to increase the available, accessible surface area. Theoretically, by creating more openings in the nanotubes, electrolytes may enter the tubes, which would expectedly further reduce the interfacial impedance, improving the electrode performance.

As depicted in the flow chart of **FIG. 7**, a nanotube coated electrode can be processed according to another embodiment of the present invention wherein at step 150 a nanotube polymer composite adhesive material is prepared. The material comprising a biocompatible polymer in combination with a sufficient volume of nanotube material to provide for electrical conductivity. The adhesive may comprise a thermoset composite material or otherwise curable material (e.g., using ultraviolet, infrared or other radiation, etc.) and the like. At step 152 the surface portion of an electrode is prepared to receive the material prepared at step 150. Such surface preparation may include mechanical grinding, etching, sanding and the like and/or application of one or more fluid materials to prepare

the surface. While a vast number of fluid materials may be used, a few representative fluids include compressed air, water, solvents (aqueous and non-aqueous), various inert so-called "cover gases" and the like. After the surface is adequately prepared at step 152 the material prepared at step 150 is applied to the electrode surface at step 154. Single- or multiple-layer applications of the material may be applied at step 154 with optional material curing processes performed following application of a layer. Following application of the material at step 154, electrical potential is applied to the electrode at step 156 to complete and/or confirm an operative bond between the electrode surface and the nanotube-bearing material. The electrical potential may be applied as a simple ascending ramp waveform, descending ramp waveform, using a pulsed wave delivery and/or a constant voltage and the like. The amount and type of electrical energy (e.g., single or multiple phase having a frequency and wavelength characteristic whether electrical potential or electrical current) applied to the electrode assembly may vary but should remain within required tolerances of expected when the electrode is operatively coupled to electronic circuitry. For example, in the event that the electrode surface forms a portion of the surface of a cardiac defibrillation electrode the electrical energy should include rapid discharge of 20-40 joules of energy.

An improved medical lead having carbon nanotube coated electrodes and method for manufacture provided by the present invention has been described according to specific embodiments. It is recognized that one knowledgeable in the art may conceive variations of these embodiments that generally gain the benefits provided by a carbon nanotube coated electrode. The above described embodiments should therefore not be considered limiting in regard to the following claims.

We Claim:

1. A medical device, comprising:

an elongated conductor; and

at least one electrode electrically coupled to the elongated conductor;

wherein a nanotube material is disposed on at least a portion of said at least one electrode.

2. A medical device according to claim 1, wherein the at least one electrode is at least a one of the following:

a tip electrode, a ring electrode, a defibrillation electrode, a subcutaneous electrode, a button electrode, a coil-type electrode, a helical electrode, a can electrode, a neurological stimulation electrode, a deep brain electrode, an organ electrode, a cuff electrode.

3. A medical device according to claim 1, wherein the at least one electrode comprises at least one of the following materials: a platinum material, a platinum-iridium material, a titanium material, a gold material, a tantalum material, a niobium material, a cobalt-chromium alloy material, or another electrically conductive material.

4. A medical device according to claim 1, further comprising either an electrically conductive adhesive layer or a metallic layer disposed on said portion of the electrode and coupled to said nanotube material.

5. A medical device according to claim 1, wherein said nanotube material is a one of the following: a carbon nanotube material, a boron nanotube material, a doped nanotube material, an electrically modified nanotube material.

6. A medical device according to claim 5, wherein said nanotube material comprises a single-wall nanotube material or a multiple-wall nanotube material.

7. A medical device according to claim 6, wherein at least a majority of said nanotube material is aligned substantially normal to an adjacent portion of said electrode and in close proximity to a plurality of adjacent discrete nanotube material units.

8. A medical device according to claim 6, wherein at least a majority of said nanotube material is randomly oriented with respect to an adjacent portion of said electrode.

9. A medical device according to claim 1, further comprising an elongated electrical conductor electrically coupled to said electrode.

10. A medical device according to claim 9, wherein said elongated medical conductor comprises an electrically conductive nanotube material.

11. A medical device according to claim 10, wherein said electrically conductive nanotube material is disposed within a relatively flexible biocompatible material.

12. A medical device according to claim 11, wherein said relatively flexible biocompatible material is electrically conductive and further comprising an electrically insulative material surrounding substantially all or the entire surface of the relatively flexible biocompatible material.

13. A medical device according to claim 9, 10, 11 or 12, and further comprising a flexible elongated sheath removeably coupled around the medical device.

14. A medical device according to claim 13, wherein said medical device has a substantially geometric lateral cross section having a dimension in the range of about 8 French units to less than about one French unit.

15. A medical device according to claim 9, and further comprising at least one additional elongated conductor disposed within the relatively flexible biocompatible material and electrically insulated from the elongated electrical conductor.

16. A medical device according to claim 15, further comprising at least one of the following structures electrically coupled to the at least one additional elongated conductor: a sensor, a transducer, an electrode.

17. A medical device according to claim 16, wherein the sensor is at least a one of the following: an oxygen sensor, including without limitation, an oxygen saturation sensor, a partial pressure oxygen sensor, a blood oximetry sensor; a lactate sensor; a pH sensor; a glucose sensor; a fluid flow sensor; a temperature sensor; a pressure sensor; an optical sensor.

18. A medical device according to claim 5, further comprising a fluid material in contact with said nanotube material.

19. A medical device according to claim 18, wherein said fluid material is a steroid material.

20. A medical device according to claim 18, wherein said fluid material is an electrically conducting material.

21. A medical device according to claim 20, wherein said electrically conducting material comprises at least a portion of an electrically conducting solid material.

22. A medical device according to claim 21, wherein said at least a portion of the electrically conducting solid material is a nanotube material.

23. A medical device according to claim 22, wherein said nanotube material is a carbon nanotube material, a boron nanotube material or a combination of carbon and boron nanotube material.

24. A medical device according to claim 21, 22, or 23, further comprising a biologically inert paste coupled to the at least one electrode.

25. A medical device, comprising:

an electrode member having an exterior surface portion; and

an elongated conductor having a distal end electrically coupled to said electrode member;

wherein a plurality of nanotubes are disposed over at least a portion of said exterior surface portion.

26. A medical device according to claim 25, wherein the elongated conductor comprises at least a one of the following: a single metallic strand; a multi-filar strand; a metallic braided conductor; a carbon nanotube material; a boron nanotube material; a conductive polymer material; a material comprised of a nanotube material impregnated with a electrically conductive polymer material.

27. A medical device according to claim 25, wherein said plurality of nanotubes are disposed either in an irregular array or a substantially regular array with respect to an adjacent group of nanotubes.

28. A medical device according to claim 27, further comprising a metallic layer disposed over the exterior surface portion of the electrode and coupled to the plurality of nanotubes.

29. A medical device according to claim 28, wherein said metallic layer comprises: a platinum layer, a platinum-iridium layer, a titanium layer, a gold layer, a

tantalum layer, a niobium layer, a cobalt-chromium alloy layer, or other another electrically conductive material layer.

30. A medical device according to claim 25, wherein said electrode is configured as a cardiac sense electrode, a cardiac pacing electrode, a neurological stimulation electrode, a brain stimulation electrode, an organ stimulation electrode, and/or a cardiac defibrillation electrode.

31. A medical device according to claim 25, further comprising a steroid material disposed about at least a portion of said plurality of nanotubes.

32. A medical device according to claim 25, further comprising an electrically conductive paste coupled to at least a portion of said plurality of nanotubes.

33. A method for manufacturing a medical electrode having an electrode surface adapted for electrical communication with biological tissue, comprising the step of depositing a plurality of nanotube structures on at least a portion of the electrode surface.

34. A method according to claim 31, wherein the electrode surface comprises a platinum material, a platinum-iridium material, a titanium material, a gold material, a tantalum material, or a cobalt-chromium alloy material.

35. A method according to claim 31, wherein said medical electrode is a distal end portion of a helical coil and further comprising the steps of:

spreading the coil at said distal end portion to form a helical screw portion so that the helix can perform as an active fixation lead.

36. A method according to claim 31, wherein during the depositing step, performing the following sub-step:

applying an alternating-current or direct-current electric field to orient the nanotubes structures relative to the electrode surface.

37. A method according to claim 32, wherein the medical electrode structure is formed with a hollow portion for conveying a fluid or paste to said biological tissue.

38. A method according to claim 35, further comprising the step of:

mechanically coupling an elongated medical electrical lead to said electrode, wherein said lead has a fluid conduit formed therein and said fluid conduit is in fluid communication with said hollow portion and wherein an electrical conductor disposed within said lead is in electrical communication with said medical electrode.

39. A method of treating a portion of biological tissue, comprising the steps:

advancing a hollow electrode member into contact with a portion of biological tissue wherein said hollow electrode member is fluidly coupled to a source of substantially biologically inert solution; and

dispensing a small amount of the substantially biologically inert solution into the contact portion between the hollow electrode member and the portion of biological tissue, wherein said substantially biologically inert solution comprises a sufficient plurality of electrically conductive nanotube structures to render the substantially biologically inert solution electrical conductive.

40. A method according to claim 37, wherein said portion of biological tissue comprises a one of the following: a cardiac tissue, a muscle tissue, an organ tissue, a brain tissue, a myocardial infarct tissue, a neurological tissue,

41. A method according to claim 37, wherein said small amount of solution is approximately about 100 microliters of solution.

42. A method according to claim 37, wherein said advancing step means piercing said portion of biological tissue and further comprising the steps:

withdrawing the hollow electrode member;

moving the hollow electrode member to an adjacent portion of biological tissue;

piercing said adjacent portion of biological tissue;

dispensing an second small amount of substantially biologically inert solution into said adjacent biological tissue.

43. A method according to claim 40, wherein said piercing step comprises at least two sub-piercing steps, a first sub-piercing step comprises the step of advancing the hollow electrode member to a first depth in said biological tissue and wherein at least a second sub-piercing step comprises advancing or retracting said hollow electrode member to a second depth different from the first depth.

44. A method according to claims 37 through 41, further comprising the steps of:

electrically coupling the hollow electrode member to a pulse generator circuit having pulse sensing capabilities;

stimulating the portion and/or the adjacent portion of biological tissue with at least one electrical pulse delivered by the hollow electrode member;

sensing a resulting evoked response from a remote electrode or from a sensor coupled to the subject.

45. A method according to claim 42, wherein said remote electrode is a one of the following: a transcutaneous electrode, a percutaneous electrode, a subcutaneous electrode, an epicardial electrode, an endocardial electrode, a pericardial electrode.

46. A method of fabricating an electrode surface, comprising:

preparing a volume of an electrically conducting nanotube-bearing composite adhesive material;

preparing a surface portion of an electrode to receive the electrically conducting nanotube-bearing composite adhesive material;

applying the electrically conducting nanotube-bearing composite adhesive material to the surface portion; and

applying electrical energy to the electrode surface.

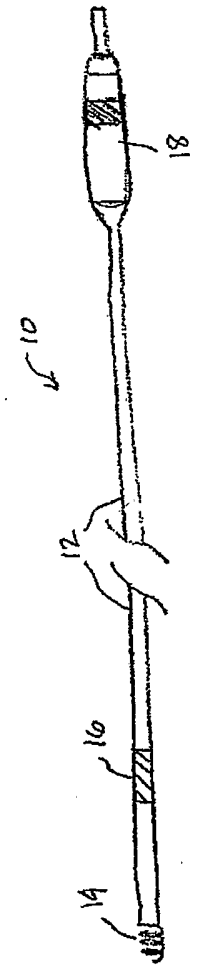


FIG. 1A

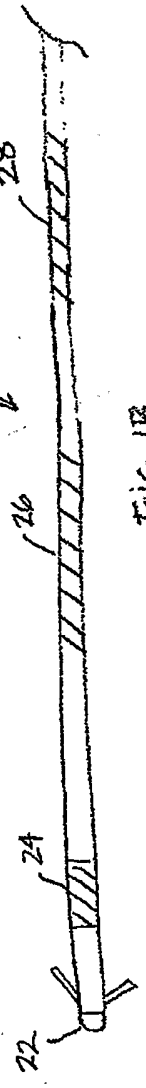


FIG. 1B

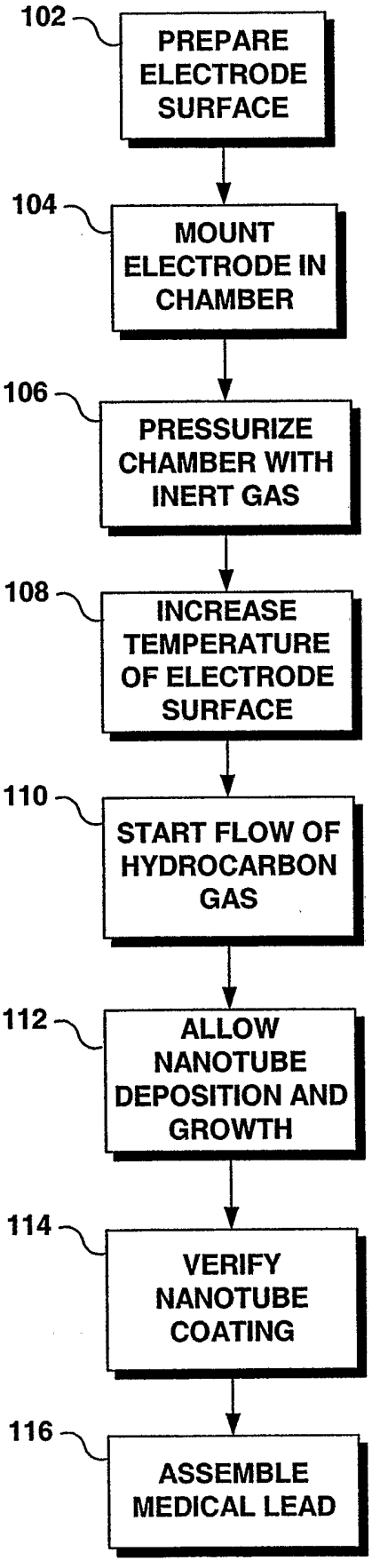

102
PREPARE ELECTRODE SURFACE
104
MOUNT ELECTRODE IN CHAMBER
106
PRESSURIZE CHAMBER WITH INERT GAS
108
INCREASE TEMPERATURE OF ELECTRODE SURFACE
110
START FLOW OF HYDROCARBON GAS
112
ALLOW NANOTUBE DEPOSITION AND GROWTH
114
VERIFY NANOTUBE COATING
116
ASSEMBLE MEDICAL LEAD

FIG. 2

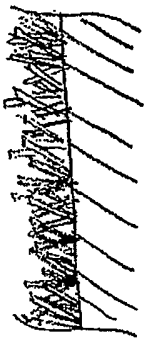


Fig. 4

Fig. 3

Fig 5

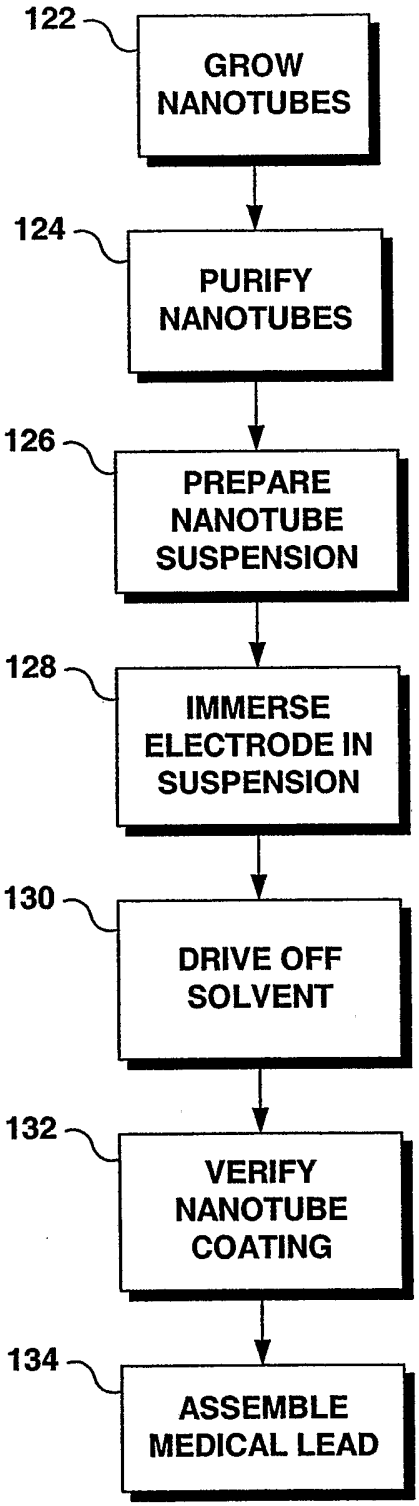

122
GROW NANOTUBES
124
PURIFY NANOTUBES
126
PREPARE NANOTUBE SUSPENSION
128
IMMERSE ELECTRODE IN SUSPENSION
130
DRIVE OFF SOLVENT
132
VERIFY NANOTUBE COATING
134
ASSEMBLE MEDICAL LEAD

FIG. 6

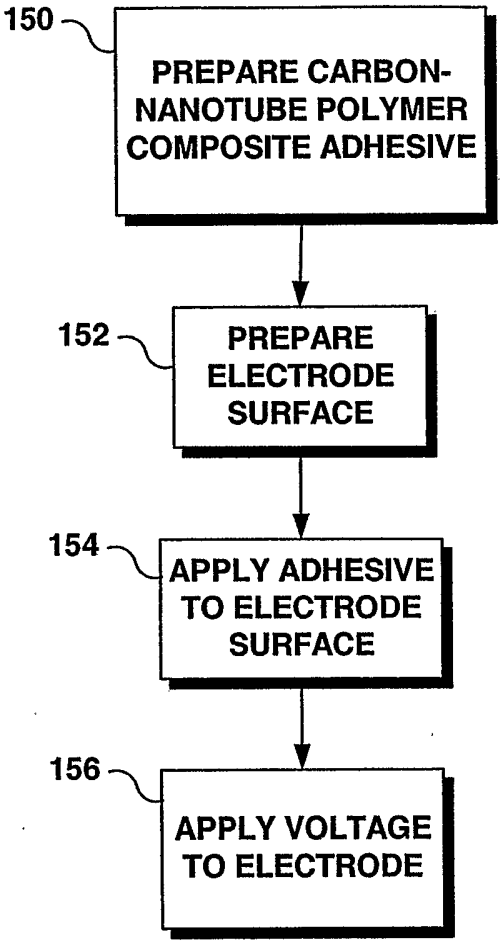

150
PREPARE CARBON-NANOTUBE POLYMER COMPOSITE ADHESIVE
152
PREPARE ELECTRODE SURFACE
154
APPLY ADHESIVE TO ELECTRODE SURFACE
156
APPLY VOLTAGE TO ELECTRODE

FIG. 7

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 03/38955

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61N1/05

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 7 A61N A61B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 057 877 A (MEDTRONIC INC) 18 August 1982 (1982-08-18) page 5, line 36 -page 6, line 37; figures	1,25,33, 39,46
A	US 6 240 320 B1 (MACHEK JAMES E ET AL) 29 May 2001 (2001-05-29) column 3, line 9 - line 31; figures	1,25,33, 39,46
A	EP 1 174 076 A (BIOTRONIK MESS & THERAPIEG) 23 January 2002 (2002-01-23) page 2, column 1, line 38 -page 3, column 3, line 21; figures	1,25,33, 39,46
A	US 6 273 875 B1 (DOVE JEFF ET AL) 14 August 2001 (2001-08-14) column 6, line 64 -column 7, line 44; figures	1,25,33, 39,46

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document 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
4 May 2004	12/05/2004

Name and mailing address of the ISA	Authorized officer
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	Rakotondrajaona, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int onal Application No
PCT/US 03/38955

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0057877 A	18-08-1982	CA 1173114 A1	21-08-1984
		DE 3264606 D1	14-08-1985
		EP 0057877 A1	18-08-1982
		JP 57128852 U	11-08-1982
US 6240320 B1	29-05-2001	CA 2334268 A1	09-12-1999
		EP 1083964 A1	21-03-2001
		JP 2002516731 T	11-06-2002
		WO 9962591 A1	09-12-1999
		US 6134478 A	17-10-2000
		US 6526321 B1	25-02-2003
EP 1174076 A	23-01-2002	DE 10040366 A1	31-01-2002
		EP 1174076 A2	23-01-2002
		US 2002042570 A1	11-04-2002
US 6273875 B1	14-08-2001	AU 5127299 A	06-03-2000
		WO 0009177 A1	24-02-2000