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(54) Title: CARBON FIBRILS, METHOD FOR PRODUCING SAME, AND COMPOSITIONS CONTAINING SAME		
(57) Abstract <p>An essentially cylindrical discrete carbon fibril characterized by a substantially constant diameter between about 3.5 and about 70 nanometers, e.g. between about 7 and 25 nanometers, length greater than about 10² times the diameter, an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core region, each of the layers and core disposed substantially concentrically about the cylindrical axis of the fibril. Preferably the entire fibril is substantially free of thermal carbon overcoat. The invention further concerns a plurality of such fibrils. The fibril or plurality of fibrils of this invention may be produced by contacting for an appropriate period of time and at suitable pressure a suitable metal-containing particle with a suitable gaseous, carbon-containing compound, at a temperature between about 850°C and 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal containing particle being at least about 100:1.</p> <div data-bbox="730 1249 1439 2094" style="text-align: right;"> </div>		

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CARBON FIBRILS, METHOD FOR PRODUCING SAME,
AND COMPOSITIONS CONTAINING SAME

BACKGROUND OF THE INVENTION

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This invention relates to the production of graphitic carbon fibrils having high surface area, high Young's modulus of elasticity and high tensile strength. More specifically, it relates to such fibrils grown catalytically from inexpensive, readily available carbon precursors without the need for usual and expensive graphitizing temperatures (approximately 2900°C).

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Fiber-reinforced composite materials are becoming increasingly important because their mechanical properties, notably strength, stiffness and toughness, are superior to the properties of their separate components or of other non-composite materials. Composites made from carbon fibers excel in strength and stiffness per unit weight, hence are finding rapid acceptance in aerospace and sporting goods applications. Their high cost, however, inhibits their wider use.

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Carbon fibers are currently made by controlled pyrolysis of continuous filaments of precursor organic polymers, notably cellulose or polyacrylonitrile, under carefully maintained tension, needed to insure good orientation of the anisotropic sheets of carbon atoms in the final filaments. Their high cost is a consequence of the cost of the preformed organic fibers, the weight loss in carbonization, the slow rate of carbonization in expensive equipment and the careful handling necessary to avoid breaks in the continuous filaments.

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There has been intense development of methods of spinning

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and carbonizing hydrocarbon pitch fiber to reduce precursor filament cost and weight loss. So far, the pitch pre-treatment, spinning conditions and post-treatments needed to insure correct orientation of the sheets of carbon atoms in the final products have been nearly as expensive as the previously noted method involving organic polymers. Both methods require use of continuous filaments to achieve high orientation and best properties. There is a practical lower limit of fiber diameter, 6 to 8 micrometers, below which fiber breakage in spinning and post-treatments becomes excessive.

An entirely distinct approach to carbon fiber formation involves the preparation of carbon filaments through the catalytic decomposition at metal surfaces of a variety of carbon containing gases, e.g., CO/H₂, hydrocarbons, and acetone. These filaments are found in a wide variety of morphologies (e.g., straight, twisted, helical, branched) and diameters (e.g., ranging from tens of angstroms to tens of microns). Usually, a mixture of filament morphologies is obtained, frequently admixed with other, non-filamentous carbon (cf. Baker and Harris, Chemistry and Physics of Carbon, Vol. 14, 1978). Frequently, the originally formed carbon filaments are coated with poorly organized thermal carbon. Only relatively straight filaments possessing relatively large graphitic domains oriented with their c-axes perpendicular to the fiber axis and possessing little or no thermal carbon overcoat will impart the properties of high strength and modulus required in reinforcement applications.

Most reports that cite formation of filamentous carbon do not document the particular type of filaments formed, so that it is impossible to determine whether the filaments are suitable for reinforcement applications. For example,

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5 Baker et al., in British Patent 1,499,930 (1977), disclose that carbon filaments are formed when an acetylene or diolefin is decomposed over catalyst particles at 675-775°C. No description of the structure of these filaments is given, however. In European Patent Application EP 56,004 (1982), Tates and Baker describe the formation of filamentous carbon over FeO_x substrates, but again do not disclose any information concerning the structure of the carbon filaments formed. Bennett et al., in United Kingdom Atomic Energy Authority Report AERE-R7407, describe the formation of filamentous carbon from catalytic decomposition of acetone, but also fail to give any indication of the morphology, and hence suitability for reinforcement applications, of the carbon formed.

15 Several groups of workers have disclosed the formation of straight carbon filaments through catalytic decomposition of hydrocarbons. Oberlin, Endo, and Koyama have reported that aromatic hydrocarbons such as benzene are converted to carbon fibers with metal catalyst particles at temperatures of around 1100°C, Carbon 14:133 (1976). The carbon filaments contain a well ordered, graphitic core of approximately the diameter of a catalyst particle, surrounded by an overcoat of less organized thermal carbon. Final filament diameters are in the range of 0.1 to 80 microns. The authors infer that the graphitic core grows rapidly and catalytically, and that thermal carbon subsequently deposits on it, but state that the two processes cannot be separated "because they are statistically concomitant". Journal of Crystal Growth 32:335 (1976). The native fibers, coated with thermal carbon, possess low strength and stiffness, and are not useful as a reinforcing filler in composites. An additional high temperature treatment at 2500-3000°C is necessary to convert the entire filament to highly ordered graphitic carbon. While this procedure may be an im-

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5 improvement on the difficult and costly pyrolysis of preformed organic fibers under tension, it suffers from the drawback that a two step process of fiber growth and high temperature graphitization is required. In addition, the authors state nothing regarding deliberate catalyst preparation, and catalyst particles appear to be adventitious. In more recent work, preparation of catalytic particles is explored, but the two processes of catalytic core growth and thermal carbon deposition are again not separated, Extended Abstracts, 16th Biennial Conference on Carbon: 523 (1983).

15 Tibbetts has described the formation of straight carbon fibers through pyrolysis of natural gas in type 304 stainless steel tubing at temperatures of 950-1075°C, Appl. Phys. Lett. 42(8):666 (1983). The fibers are reported to grow in two stages similar to those seen by Koyama and Endo, where the fibers first lengthen catalytically and then thicken by pyrolytic deposition of carbon. Tibbetts states that these stages are "overlapping", and is unable to grow filaments free of pyrolytically deposited carbon. In addition, Tibbetts's approach is commercially impracticable for at least two reasons. First, initiation of fiber growth occurs only after slow carbonization of the steel tube (typically about ten hours), leading to a low overall rate of fiber production. Second, the reaction tube is consumed in the fiber forming process, making commercial scale-up difficult and expensive.

30 It has now unexpectedly been found that it is possible to catalytically convert hydrocarbon precursors to carbon filaments substantially free of pyrolytically deposited thermal carbon, and thereby to avoid the thickening stage reported in the prior art as "overlapping" and "concomitant" with the filament lengthening stage. This ability allows the direct formation of high strength fibrils useful in the

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reinforcement of matrices, in the preparation of electrode materials of very high surface area, and in the shielding of objects from electromagnetic radiation.

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SUMMARY OF THE INVENTION

5 This invention concerns an essentially cylindrical discrete carbon fibril characterized by a substantially constant diameter between about 3.5 and about 70 nanometers, e.g. between about 7 and 25 nanometers, length greater than about 10^2 times the diameter, an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core region, each of the layers and core
10 disposed substantially concentrically about the cylindrical axis of the fibril. Preferably the entire fibril is substantially free of thermal carbon overcoat.

15 The inner core of the fibril may be hollow or may contain carbon atoms which are less ordered than the ordered carbon atoms of the outer region, which are graphitic in nature.

20 The fibril of this invention may be produced by contacting for an appropriate period of time and at a suitable pressure a suitable metal-containing particle with a suitable gaseous, carbon-containing compound, at a temperature between about 850°C and 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal-containing particle being at least about 100:1.

25 The contacting of the metal-containing particle with the carbon-containing compound may be carried out in the presence of a compound, e.g. CO₂, H₂ or H₂O, capable of reaction with carbon to produce gaseous products.

30 Suitable carbon-containing compounds include hydrocarbons, including aromatic hydrocarbons, e.g. benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene or mixtures thereof; non-aromatic hydrocarbons, e.g., methane, ethane, propane, ethylene, propylene or acetylene or mixtures thereof; and oxygen-con-
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taining hydrocarbons, e.g. formaldehyde, acetaldehyde, acetone, methanol, or ethanol or mixtures thereof; and include carbon monoxide.

5 The suitable metal-containing particle may be an iron-, cobalt-, or nickel-containing particle having a diameter between about 3.5 and about 70 nanometers.

10 Such particles may be supported on a chemically compatible, refractory support, e.g., a support of alumina, carbon, or a silicate, including an aluminum silicate.

15 In one embodiment the surface of the metal-containing particle is independently heated, e.g. by electromagnetic radiation, to a temperature between about 850°C and 1800°C, the temperature of the particle being higher than the temperature of the gaseous, carbon-containing compound.

20 In a specific embodiment, the metal-containing particle is contacted with the carbon-containing compound for a period of time from about 10 seconds to about 180 minutes at a pressure of from about one-tenth atmosphere to about ten atmospheres. In this embodiment, the metal-containing particle is an iron-containing particle, the gaseous
25 carbon-containing compound is benzene, the reaction temperature is between 900°C and 1150°C and the ratio of carbon-containing compound to metal-containing particle is greater than about 1000:1. The contacting may be carried out in the presence of gaseous hydrogen. Additionally, the
30 iron-containing particle may be supported on a chemically compatible, refractory support of, e.g., alumina or carbon.

35 In addition to the above-mentioned method and carbon fibril produced thereby this invention also concerns a method for producing a substantially uniform plurality of essentially cylindrical, discrete carbon fibrils which comprises con-

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tacting for an appropriate period of time and at a suitable pressure, suitable metal-containing particles with a suitable gaseous, carbon-containing compound, at a temperature between about 850°C and 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal-containing particles being at least about 100:1. Preferably, each of the fibrils so produced has a diameter substantially equal to the diameter of each other fibril. In one embodiment the metal-containing particles are pre-formed.

The fibrils are useful in composites having a matrix of e.g., an organic polymer, an inorganic polymer or a metal. In one embodiment the fibrils are incorporated into structural materials in a method of reinforcement. In other embodiments the fibrils may be used to enhance the electrical or thermal conductivity of a material, to increase the surface area of an electrode or an electrolytic capacitor plate, to provide a support for a catalyst, or to shield an object from electromagnetic radiation.

Brief Description of the Figures

Fig. 1. A dispersion of catalyst particles comprised of Fe_3O_4 .

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Fig. 2. A dispersion of catalyst particles comprised of Fe_3O_4 .

Fig. 3. Catalyst particles encapsulated in 50-150 angstrom carbon sheaths.

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Fig. 4. Numerous 100-450 angstrom diameter fibrils, together with catalyst support and reaction debris.

Fig. 5. A fibril with a diameter of approximately 250 angstroms, together with catalyst support and reaction debris.

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DETAILED DESCRIPTION OF THE INVENTION

An essentially cylindrical carbon fibril may be produced in accordance with this invention, said fibril being characterized by a substantially constant diameter between
5 about 3.5 and about 70 nanometers, a length greater than about 10^2 times the diameter, an outer region of multiple layers of ordered carbon atoms and a distinct inner core region, each of the layers and core disposed concentrically
10 about the cylindrical axis of the fibril. Preferably the entire fibril is substantially free of thermal carbon overcoat. The term "cylindrical" is used herein in the broad geometrical sense, i.e., the surface traced by a straight line moving parallel to a fixed straight line and intersecting a curve. A circle or an ellipse are but two of
15 the many possible curves of the cylinder.

The inner core region of the fibril may be hollow, or may comprise carbon atoms which are less ordered than the
20 ordered carbon atoms of the outer region. "Ordered carbon atoms," as the phrase is used herein means graphitic domains having their c -axes substantially perpendicular to the cylindrical axis of the fibril.

In one embodiment, the length of the fibril is greater than
25 about 10^3 times the diameter of the fibril. In another embodiment, the length of the fibril is greater than about 10^4 times the fibril diameter. In one embodiment, the fibril diameter is between about 7 and about 25 nanometers. In
30 another embodiment the inner core region has a diameter greater than about 2 nanometers.

More specifically, a method for producing an essentially
cylindrical, discrete carbon fibril according to this invention comprises contacting for an appropriate period of
35 time and at a suitable pressure a catalyst, i.e., a suitable,

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discrete metal-containing particle, with a suitable precursor, i.e., a suitable gaseous, carbon-containing compound, at a temperature between about 850°C and about 1200°C. The ratio on a dry weight basis of carbon-containing compound (precursor) to metal-containing particle (catalyst) is suitably at least about 100:1.

It is contemplated that a variety of carbon-containing compounds are suitable as precursors when used with an appropriate combination of reaction parameters, in accordance with this invention. In one embodiment, exemplified herein, the precursor is benzene. Other contemplated suitable precursors include hydrocarbons and carbon monoxide. The hydrocarbon precursor may be aromatic, e.g. benzene (exemplified herein), toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene or mixtures thereof. Alternatively, the hydrocarbon may be non-aromatic, e.g. methane, ethane, propane, ethylene, propylene or acetylene or mixtures thereof. The hydrocarbon may also contain oxygen, e.g. alcohols such as methanol or ethanol, ketones such as acetone, and aldehydes such as formaldehyde or acetaldehyde or mixtures thereof.

Important reaction parameters, in addition to the particular precursor, include catalyst composition and pretreatment, catalyst support, precursor temperature, catalyst temperature, reaction pressure, residence time or growth time, and feed composition, including the presence and concentrations of any diluents (e.g., Ar) or compounds capable of reaction with carbon to produce gaseous products (e.g., CO₂, H₂, or H₂O). It is contemplated that the reaction parameters are highly interdependent, and that the appropriate combination of reaction parameters will depend on the specific precursor carbon-containing compound.

It is further contemplated that a variety of transition

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metal-containing particles are suitable as catalysts when used with an appropriate combination of reaction parameters. In a presently preferred embodiment, the metal-containing particle comprises a particle having a diameter between about 3.5 and about 70 nanometers and contains iron, cobalt or nickel, or an alloy or mixture thereof.

In one embodiment, the metal-containing particle is contacted with the carbon-containing compound in the presence of a compound capable of reaction with carbon to produce gaseous products. In one such embodiment, the compound capable of reacting with carbon is CO_2 , H_2 , or H_2O .

It is desirable that catalyst particles be of reasonably uniform diameter and that they be isolated from one another, or at least held together in only weakly bonded aggregates. The particles need not be in an active form before they enter the reactor, so long as they are readily activated through a suitable pretreatment or under reaction conditions. The choice of a particular series of pretreatment conditions depends on the specific catalyst and carbon-containing compound used, and may also depend on other reaction parameters outlined above. Exemplary pretreatment conditions are provided in the Examples which follow. The metal-containing particles may be precipitated as metal oxides, hydroxides, carbonates, carbonylates, nitrates, etc., for optimum physical form. Well-known colloidal techniques for precipitating and stabilizing uniform, very small particles are applicable. For example, the techniques described by Spiro et al. for precipitating hydrated ferric oxide into easily dispersable uniform spheres a few nanometers in diameter, are very suitable for catalyst preparation, J. Am. Chem. Soc. 8(12):2721-2726(1966); 89(22):5555-5559 and 5559-5562(1967). These catalyst particles may be deposited on chemically compatible, re-

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fractory supports. Such supports must remain solid under reaction conditions, must not poison the catalyst, and must be easily separated from the product fibrils after they are formed. Alumina, carbon, quartz, silicates, and aluminum
5 silicates such as mullite are all suitable support materials. For ease of removal, their preferred physical form is thin films or plates which can easily be moved into and out of the reactor.

10 Small metal particles may also be formed by thermolysis of metal-containing vapor in the reactor itself. For example, iron particles may be formed from ferrocene vapor. This method has the advantage that fibril growth is initiated throughout the reactor volume, giving higher productivity
15 than when the catalyst particles are introduced on supports.

The reaction temperature must be high enough to cause the catalyst particles to be active for fibril formation, yet low enough to avoid significant thermal decomposition of the
20 gaseous carbon-containing compound with formation of pyrolytic carbon. The precise temperature limits will depend on the specific catalyst system and gaseous carbon-containing compound used. For example, benzene is kinetically thermally stable to about 1100°C, methane to about 950°C, and
25 acetylene to about 500°C. In cases where thermal decomposition of the gaseous carbon-containing compound occurs at a temperature near or below that required for an active, fibril-producing catalyst, the catalyst particle may be heated selectively to a temperature greater than that
30 of the gaseous carbon-containing compound. Such selective heating may be achieved, for example, by electromagnetic radiation.

35 The carbon fibril of this invention may be produced at any desirable pressure, and the optimum pressure will be dictated by economic considerations. Preferably, the reaction

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pressure is between one-tenth and ten atmospheres. More preferably, the reaction pressure is atmospheric pressure.

5 In one exemplified embodiment, ~~the fibril is produced by~~
contacting for about 180 minutes and at a pressure of about
one atmosphere, a suitable iron-containing particle with
benzene (gaseous) in an approximately 9:1 hydro-
10 gen:benzene mixture at a temperature of about 900°C, the
ratio on a dry weight basis of carbon-containing compound to
iron-containing particle being greater than about 1000:1.
In another exemplified embodiment the fibril is produced by
contacting for from about one to about five minutes and at
a pressure of about one atmosphere, a suitable iron-con-
15 taining particle with benzene (gaseous) in an approximately
9:1 hydrogen:benzene mixture at a temperature of about
1100°C, the ratio on a dry weight basis of carbon-containing
compound to iron-containing particle being greater than
about 1000:1. In a preferred embodiment of this method, the
20 iron-containing particle is supported on a chemically
compatible, refractory support, as previously described.
Preferably such refractory support is alumina.

Fibrils made according to this invention are highly gra-
phitic as grown. The individual graphitic carbon layers are
25 concentrically arranged around the long axis of the fiber
like the growth rings of a tree, or like a scroll of
hexagonal chicken wire. There is usually a hollow core a few
nanometers in diameter, which may be partially or wholly
filled with less organized carbon. Each carbon layer around
30 the core may extend as much as several hundred nanometers.
The spacing between adjacent layers may be determined by
high resolution electron microscopy, and should be only
slightly greater than the spacing observed in single crystal
graphite, i.e., about 0.339 to 0.348 nanometers.

35 There are no methods for direct measurement of the physical

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properties of such small fibrils. However, the stiffness of composites containing the fibrils are those expected from the Young's moduli which have been measured on larger, well graphitized carbons.

5 Another aspect of this invention concerns a method for producing a substantially uniform plurality of essentially cylindrical, discrete carbon fibrils. The plurality of fibrils is substantially uniform in the sense that the
10 diameter of each fibril is substantially equal to the diameter of each other fibril. Preferably each of the fibrils is substantially free of thermally deposited carbon. The method for producing such a plurality involves contacting for an appropriate period of time and at a
15 suitable pressure, suitable metal-containing particles, with a suitable gaseous carbon-containing compound as previously discussed, at a temperature between about 850°C and 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal-containing particle being at least about
20 100:1. By this method a substantially uniform plurality of fibrils, e.g. each having a diameter substantially equal to the diameter of each other fibril, may be obtained.

25 Another aspect of this invention concerns a composite which comprises carbon fibrils as described above, including composites serving as structural materials. Such a composite may also comprise a matrix of pyrolytic or non-pyrolytic carbon or an organic polymer such as a poly-
amide, polyester, polyether, polyimide, polyphenylene, polysulfone, polyurethane or epoxy resin, for example.
30 Preferred embodiments include elastomers, thermoplastics and thermosets.

In another embodiment, the matrix of the composite is an
35 inorganic polymer, e.g. a ceramic material or polymeric inorganic oxide such as glass. Preferred embodiments in-

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clude fiberglass, plate glass and other molded glass, silicate ceramics, and other refractory ceramics such as aluminum oxide, silicon carbide, silicon nitride and boron nitride.

5 In still another embodiment the matrix of the composite is a metal. Suitable metals include aluminum, magnesium, lead, copper, tungsten, titanium, niobium, hafnium, vanadium, and alloys and mixtures thereof.

10 The carbon fibrils are also useful in various other applications. One embodiment is a method for increasing the surface area of an electrode or electrolytic capacitor plate by attaching thereto one or more carbon fibrils of this invention. In another embodiment the fibril can be used in
15 a method for supporting a catalyst which comprises attaching a catalyst to the fibril. Such catalyst may be an electrochemical catalyst.

20 The carbon fibrils are also useful in a method of enhancing the electrical conductivity of a material. According to this method an effective electrical conductivity enhancing amount of carbon fibrils is incorporated in the material.

25 A further use of the carbon fibrils is in a method of enhancing the thermal conductivity of a material. In this method an effective thermal conductivity enhancing amount of carbon fibrils is incorporated in the material.

30 An additional use of the carbon fibrils is in a method of shielding an object from electromagnetic radiation. In this method an effective shielding amount of carbon fibrils is incorporated in the object.

35 This invention is illustrated in the examples which follow. The examples are set forth to aid in an understanding of the

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invention but are not intended to, and should not be construed to, limit in any way the invention as set forth in the claims which follow thereafter.

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ExamplesMaterials

5 The following materials used in the examples below may be
obtained from commercial sources: Benzene (reagent
grade), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baker Analyzed Crystal), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
(Baker Analyzed Granular), KNO_3 (Baker Analyzed Crystal)
and NaHCO_3 (Baker Analyzed Crystal) may all be obtained
10 from J.T. Baker Chemical Company, Phillipsburg, New
Jersey. CO (C.P. Grade) may be obtained from Air Products
and Chemicals, Inc., Allentown, Pennsylvania. KOH (C.P.
Pellets) may be obtained from Mallinckrodt Inc., Lodi, New
Jersey. Water used in the examples was deionized. Vycor®
15 glass tubes may be obtained from Corning Glass Works,
Corning, New York.

Davison SMR-37-1534 SRA alumina is an α -boehmite with an
average crystallite size of 15 angstroms, an average ag-
glomerate size of 0.2 microns, and an average particle size
20 of 15 microns.

Degussa Aluminum Oxid C is a γ -alumina with a surface area
of $100 \text{ m}^2/\text{g}$, an average particle size of 200 angstroms, and
an apparent bulk density of 60 g/L.
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Cabot Sterling R V-9348 carbon powder is a furnace black
with a minimum carbon content of 99.5%, a surface area of
25 m^2/g , an average particle size of 750 angstroms, and an
apparent density of 16 lb/ft³.
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Analyses

All electron micrographs were obtained from a Zeiss EM-10
Electron Microscope.
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Catalyst Preparations

Example 1: Preparation of Catalyst 1

5 A magnetite dispersion was prepared according to the method of Sugimoto and Matijevic, J. Colloid & Interfacial Sci. 74:227 (1980). Electron microscopy reveals the particle size range to be from 175 to 400 angstroms, with 260 angstroms being the approximate average (Figures 1 and 2).

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Example 2: Preparation of Catalyst 2

Into a 4 oz wide-mouth glass jar with a magnetic stirring bar was placed 10 g Davison SMR-37-1534 SRA alumina powder. 15 To the stirred powder 0.81 M $\text{Fe}(\text{NO}_3)_3$ in H_2O was added dropwise to the point of incipient wetness. 4.1 mL was required.

Example 3: Preparation of Catalyst 3

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A portion of the wet powder obtained in Example 2 was heated in the jar with stirring on a hot plate until dry. The temperature was kept below that at which NO_x evolved.

Example 4: Preparation of Catalyst 4

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A portion of Davison SMR-37-1534 SRA alumina powder was calcined in an air stream at 900°C for 90 min in a Vycor® tube. In a 4 oz wide-mouth jar with magnetic stirring bar 30 was placed 1.9977 g of the calcined Al_2O_3 . While it was being stirred, 0.81 M $\text{Fe}(\text{NO}_3)_3$ solution in H_2O was added dropwise to incipient wetness. 0.6 mL was required. The wet powder was dried with stirring on a hot plate.

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Example 5: Preparation of Catalyst 5

Into a 4 in cappable serum polymerization tube was weighed 0.44 g Degussa Aluminum Oxid C (fumed Al_2O_3). The tube was capped and argon sparged, after which 1 mL 0.5 M KOH, 1 mL 2.0 M KNO_3 , and 6 mL prefiltered deionized water were injected. The mixture was argon sparged 5 min, then 2.0 mL 0.101 M FeSO_4 was injected. The mixture was sparged with argon for 1 min. The tube was placed in a 90°C oil bath and the argon sparge continued for 5 min. Sparging was discontinued and quiescent digestion begun. (The oil bath temperature control was faulty, and temperature rose to 105°C. The bath was cooled back to 90°C.) Total digestion time was 2 h.

The system on standing separated into a white precipitate and clear supernate. It was centrifuged, the supernate decanted, the precipitate resuspended in prefiltered, deionized water. This was repeated two more times. The pH of the final supernate was approximately 8.5. The water was decanted, the precipitate blown semi-dry with argon, and resuspended in ethanol.

Example 6: Preparation of Catalyst 6

A portion of Davison SMR-37-1534 SRA alumina powder was calcined 2 h in an air stream at 900°C in a Vycor® tube. One gram of the product was placed in a cappable 4-in polymerization tube and enough 1.6 M $\text{Fe}(\text{NO}_3)_3$ solution was added to cover the alumina completely. The tube was capped and evacuated until bubbling ceased. It was vented and the excess liquid filtered off through an M glass fritted filter. The moist cake was calcined in a ceramic boat for 1 h in an air stream at 500°C.

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Example 7: Preparation of Catalyst 7

In a centrifuge bottle 6.06 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 50 mL prefiltered deionized H_2O . To the solution was
5 added 2.52 g NaHCO_3 . When foaming ceased, the solution was sparged 5 min with argon. The product Fe_2O_3 sol was a clear solution.

A portion of Cabot Sterling R V-9348 carbon powder was
10 calcined in an argon stream in a Vycor® boat in a mullite tube at 1100°C for 1 h. It was cooled to room temperature under argon. Into a 4-in polymerization tube enough carbon was placed to make about 0.25 in layer. The tube was evacuated and 2 mL Fe_2O_3 solution was added. When bubbling
15 ceased, the tube was vented and the suspension filtered on an M-glass fritted funnel. The cake was air-dried and heated for 1 h at 500°C under an argon stream in a Vycor® tube.

20 Example 8: Preparation of Catalyst 8

In a 4-in polymerization tube a 0.4876 g portion of calcined Cabot Sterling R V-9348 carbon powder was evacuated and 2.0 mL 0.81 M $\text{Fe}(\text{NO}_3)_3$ solution was added. When bubbling
25 ceased, the tube was vented and the cake air-dried.

Example 9: Preparation of Catalyst 9

A pellet was made by compressing Cabot Sterling R V-9348
30 powder in a stainless die (for making KBR discs for infra-red). 0.12 g of the pellet was evacuated in a 4-in polymerization tube and 0.05 mL of a freshly-prepared Fe_2O_3 sol (prepared as in Example 7) was added. The tube was vented and the solid was air-dried.

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Example 10: Preparation of Catalyst 10

In a 4-in polymerization tube, 0.23 g of Davison SMR-37-1534 SRA alumina which had been calcined 2 h at 900°C in air was evacuated and 2.0 mL freshly prepared Fe₂O₃ sol (prepared as in Example 7) was added. The tube was vented and the solid filtered out on an M-glass fritted filter. The cake was air-dried.

Fibril Synthesis RunsExamples 11-23

Examples 11-23 describe fibril synthesis runs. Table 1 summarizes experimental conditions and results. Unless otherwise stated, the fibril precursor was benzene as an approximately 9:1 hydrogen:benzene mixture, and gas flow rates were 300 mL/min for H₂ and Ar; 300 mL/min CO and 100 mL/min H₂ for CO/H₂; 300 mL/min Ar or H₂ through benzene at 20°C for Ar/C₆H₆ or H₂/C₆H₆ (approximately 9:1 volume ratio Ar or H₂/C₆H₆). Air and hydrogen were always separated by a brief argon purge of the reactor. Experimental protocols were similar in each run, and are described in detail for Examples 11, 15 and 28.

a) Example 11

Catalyst prepared according to the method of Example 1 was ultrasonically dispersed in water and transferred to a ceramic boat. The boat was placed in the center of a 1" Vycor® tube in an electric furnace at room temperature. The catalyst was brought from room temperature to 500°C over a 15 minute period under a flow of argon. At this temperature, the gas mixture was changed to a hydrogen:benzene (9:1) mixture. This composition was fed into the reactor for 60 minutes.

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The hydrocarbon flow was terminated and replaced by argon, and the reactor cooled to room temperature. The boat was removed from the tube and a quantity of carbon was scraped from it. This carbon was ultrasonically dispersed in ethanol and a 10 microliter sample was examined by electron microscopy. The micrographs revealed that most of the iron particles were encapsulated in 50 to 150 angstrom carbon sheaths (Figure 3).

b) Example 15

Catalyst prepared as in Example 2 was dispersed in a ceramic boat. The boat was placed in a 1" Vycor® tube in the same electric furnace as used in Example 11.

The furnace temperature was raised from room temperature to 500°C and maintained at 500°C for 60 minutes under air. The reactor was briefly purged with argon. The temperature was then raised from 500°C to 900°C over a 15 minute period under hydrogen and maintained at 900°C for 60 minutes under that hydrogen flow.

Gas flow was then switched to benzene-saturated hydrogen for 180 minutes at 900°C. After cooling to room temperature under argon a sample was prepared according to the procedure of Example 11, and examined by electron microscopy. Electron micrographs revealed numerous 100-450 angstrom diameter fibrils (Figure 4).

c) Example 28

Catalyst prepared as in Example 3 was dispersed in a ceramic boat. The boat was placed in a 1" mullite tube in the same electric furnace as used in Example 11.

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The furnace temperature was raised from room temperature to 500°C over 15 minutes and maintained at 500°C for 60 minutes under air. The reactor was briefly purged with argon. The temperature was then raised from 500°C to 900°C over a 20 minute period under hydrogen and maintained at 900°C for 60 minutes under that hydrogen flow. The temperature was then raised still further to 1100°C over a 20 minute period maintaining the same hydrogen flow.

Gas flow was then switched to benzene saturated hydrogen for 5 minutes at 1100°C. After cooling to room temperature under argon a sample was prepared according to the procedure of Example 11, and examined by electron microscopy. Electron micrographs revealed fibrils ranging in diameter from 30 to 300 angstroms (Figure 5).

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Table 1: Fibril Synthesis Runs

Example No.	Growth Temp. (°C)	Catalyst No.	Growth Time (min)	Pretreatment Conditions	Fibrils	
					Yes	No
11	500	1	60	25-500° in 15 min (Ar)		N
12	750	1 ¹	420	23-750° in 40 min (Ar)		N
13	800	3	15	22-500° in 15 min (air) 500° for 60 min (air) 500-900° in 15 min (H ₂) 900° for 60 min (H ₂) 900-800° in 11 min (H ₂)		N
14	900	12	180	26-350° in 20 min (H ₂) 350° for 15 min (H ₂) 350-400° in 10 min (CO/H ₂) 400° for 210 min (CO/H ₂) 400-900° in 26 min (Ar)	Y	
15	900	2	180	500° for 60 min (air) 500-900° in 15 min (H ₂) 900° for 60 min (H ₂)	Y	
16	900	4	180	24-900° in 35 min (Ar) 900° for 60 min (H ₂)	Y	

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Example No.	Growth Temp. (°C)	Catalyst No.	Growth Time (min)	Pretreatment Conditions	Fibrils	
					Yes	No
17	900	3	15	80-500° in 15 min (air) 500° for 60 min (air) 500-900° in 15 min (H ₂) 900 for 60 min (H ₂)		N
18	900	3	60	22-500° in 15 min (air) 500° for 60 min (air) 500-750° in 10 min (H ₂) 750° for 70 min (H ₂) 750-500° in 15 min (H ₂) 500° for 60 min (Ar/C ₆ H ₆) 500° for 90 min (H ₂) 500-900° in 20 min (H ₂)		N
19	900	9	60	90-900° in 30 min (H ₂) 900° for 60 min (H ₂) 900° for 25 min (Ar)		N
20	900	1	60	26-900° in 25 min (Ar)		N
21	900	1	5	220-900° in 20 min (Ar)		N
22	1000	1	5	252-1000° in 30 min (Ar)		N
23	1000	1	120	31-1000° in 85 min (H ₂ /C ₆ H ₆)		N

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Example No.	Growth Temp. (°C)	Catalyst No.	Growth Time (min)	Pretreatment Conditions	Fibrils	
					Yes	No
24	1100	5	5	24-500° in 15 min (Ar) 500-900° in 15 min (H ₂) 900° for 60 min (H ₂) 900-1100° in 15 min (H ₂)		N
25	1100	10	1	24-500° in 55 min (air) 500° for 60 min (air) 500-1100° in 30 min (H ₂) 100° for 30 min (H ₂)		N
26	1100	9	1	140-500° in 10 min (Ar) 500° for 60 min (Ar) 500-1100° in 26 min (H ₂) 1100° for 60 min (H ₂)		N
273	1100	5	5	25-500° in 20 min (Ar) 500-900° in 20 min (H ₂) 900° for 60 min (H ₂) 900-1100° in 15 min (H ₂)		N
28	1100	3	5	25-500° in 15 min (air) 500° for 60 min (air) 500-900° in 20 min (H ₂) 900° for 60 min (H ₂) 900-1100° in 20 min (H ₂)	Y	

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Example No.	Growth Temp. (°C)	Catalyst No.	Growth Time (min)	Pretreatment Conditions	Fibrils	
					Yes	No
29	1100	3	1	85-500° in 10 min (air) 500° for 60 min (air) 500-900° in 20 min (H ₂) 900° for 60 min (H ₂) 900-1100° in 10 min (H ₂)	Y	
30	1100	6	5	42-500° in 15 min (Ar) 500-900° in 15 min (H ₂) 900° for 60 min (H ₂) 900-1100° in 15 min (H ₂)	Y	
31	1100	3	5	26-500° in 20 min (air) 500° for 60 min (air) 500-750° in 10 min (H ₂) 750° for 60 min (H ₂) 750-500° in 10 min (H ₂) 500° for 60 min (Ar/C ₆ H ₆) 500° for 90 min (H ₂) 500-1100° in 30 min (Ar)	Y	
32	1150	8	1	98-500° in 20 min (Ar) 500° for 60 min (Ar) 500-750° in 10 min (H ₂) 750° for 30 min (H ₂) 750-1150° in 20 min (Ar) 1150° for 15 min (Ar)		N

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35	30	25	20	15	10	5	
Example No.	Growth Temp. (°C)	Catalyst No.	Growth Time (min)	Pretreatment Conditions	Fibrils		
					Yes	No	
33	1150	7	1	30-1150° in 45 min (H ₂) 1150° for 15 min (H ₂)		N	

Footnotes to Table 1

1. Catalyst 1 was heated from 27° to 350° in 10 min under H₂, from 350° to 500° in 30 min under CO/H₂, held at 500° for 240 min under CO/H₂, and cooled to room temperature prior to use.
2. Catalyst 1 was supported on a carbon fiber.
3. Feed was approximately 18:1 H₂:C₆H₆.

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WHAT IS CLAIMED IS:

1. An essentially cylindrical discrete carbon fibril characterized by a substantially constant diameter between
5 about 3.5 and about 70 nanometers, length greater than about 10^2 times the diameter, an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core region, each of the layers and core
10 disposed substantially concentrically about the cylindrical axis of the fibril.
2. A fibril of claim 1, wherein the core is hollow.
3. A fibril of claim 1, wherein the inner core region
15 comprises carbon atoms which are less ordered than the ordered carbon atoms of the outer region.
4. A fibril of claim 1, wherein the ordered carbon atoms are
20 graphitic.
5. A fibril of claim 1, wherein the length is greater than about 10^3 times the diameter.
6. A fibril of claim 1, wherein the length is greater than
25 about 10^4 times the diameter.
7. A fibril of claim 1, wherein the diameter is between about 7 and 25 nanometers.
8. A fibril of claim 1, wherein the inner core region has
30 a diameter greater than about 2 nanometers.
9. A plurality of essentially discrete carbon fibrils
35 characterized by a substantially constant diameter between about 3.5 and about 70 nanometers, length greater than

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about 10^2 times the diameter, an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core region, each of the layers and core disposed substantially concentrically about the cylindrical axis of the fibrils.

10. A method for producing an essentially cylindrical, carbon fibril which comprises contacting for an appropriate period of time and at a suitable pressure a suitable metal-containing particle with a suitable gaseous, carbon-containing compound, at a temperature between about 850°C and about 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal-containing particle being at least about 100:1.

11. A method according to claim 10, wherein the contacting of metal-containing particle with carbon-containing compound is carried out in the presence of a compound capable of reaction with carbon to produce gaseous products.

12. A method according to claim 11, wherein the compound capable of reacting with carbon is CO_2 , H_2 or H_2O .

13. A method according to claim 10, wherein the carbon-containing compound is carbon monoxide.

14. A method according to claim 10, wherein the carbon-containing compound is a hydrocarbon.

15. A method according to claim 14, wherein the hydrocarbon contains oxygen.

16. A method according to claim 15, wherein the oxygen containing hydrocarbon is formaldehyde, acetaldehyde, acetone, methanol, ethanol, or mixtures thereof.

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17. A method according to claim 14, wherein the hydrocarbon is aromatic.

5 18. A method according to claim 17, wherein the aromatic hydrocarbon is benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene or mixtures thereof.

10 19. A method according to claim 14, wherein the hydrocarbon is non-aromatic.

15 20. A method according to claim 19, wherein the hydrocarbon is methane, ethane, propane, ethylene, propylene or acetylene or mixtures thereof.

20 21. A method according to claim 10, wherein the metal-containing particle comprises an iron-, cobalt-, or nickel-containing particle having a diameter between about 3.5 and about 70 nanometers.

22. A method according to claim 10, wherein the metal-containing particle is supported on a chemically compatible, refractory support.

25 23. A method according to claim 22, wherein the support is alumina.

30 24. A method according to claim 22, wherein the support is carbon.

25. A method according to claim 22, wherein the support is a silicate.

35 26. A method according to claim 25, wherein the silicate is an aluminum silicate.

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27. A method according to claim 10, wherein the period of time is from about 10 seconds to about 180 minutes, the pressure is from about one-tenth atmosphere to about ten atmospheres, ~~the~~ metal-containing particle is an iron-containing particle, the carbon-containing compound is benzene, the temperature is from about 900°C to about 1150°C, and the ratio on a dry weight basis of benzene to iron-containing particle is at least about 1000:1.
28. A method according to claim 27, wherein the period of time is about 180 minutes, the pressure is about one atmosphere, the carbon-containing compound is benzene in an approximately 9:1 volume mixture of hydrogen:benzene, and the temperature is about 900°C.
29. A method according to claim 27, wherein the period of time is from about one to about five minutes, the pressure is about one atmosphere, the carbon-containing compound is benzene in an approximately 9:1 volume mixture of hydrogen:benzene, and the temperature is about 1100°C.
30. A method according to claim 27, wherein the iron-containing particle is supported on a chemically compatible, refractory support.
31. A method according to claim 30, wherein the refractory support is alumina or carbon.
32. A method for producing an essentially cylindrical carbon fibril which comprises contacting for a period of time from about 10 seconds to about 180 minutes and at a pressure of from about one-tenth atmosphere to about ten atmospheres a suitable iron-containing particle with gaseous benzene at a temperature between about 900°C and about 1150°C, the ratio on a dry weight basis of benzene to iron-containing particle being at least about 1000:1.

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33. A method according to claim 32, wherein the period of time is about 180 minutes, the pressure is about one atmosphere, the benzene is in an approximately 9:1 volume mixture of hydrogen:benzene, and the temperature is about 900°C.

34. A method according to claim 32, wherein the period of time is from about one to about five minutes, the pressure is about one atmosphere, the benzene is in an approximately 9:1 volume mixture of hydrogen:benzene, and the temperature is about 1100°C.

35. A method according to claim 32, wherein the iron-containing particle is supported on a chemically compatible, refractory support.

36. A method according to claim 35, wherein the refractory support is alumina or carbon.

37. A method for producing an essentially cylindrical carbon fibril which comprises contacting for an appropriate period of time and at a suitable pressure a suitable metal-containing particle with a suitable gaseous, carbon-containing compound, wherein the metal-containing particle is independently heated to a temperature between about 850°C and about 1800°C, the temperature of the particle being higher than the temperature of the gaseous, carbon-containing compound.

38. A method according to claim 37, wherein the particle is heated with electromagnetic radiation.

39. A carbon fibril produced according to the method of claim 10.

40. A method for producing a substantially uniform plu-

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5 rality of essentially cylindrical, discrete carbon fibrils which comprises contacting for an appropriate period of time and at a suitable pressure, suitable metal-containing particles with a suitable gaseous carbon-containing compound, at a temperature between about 850°C and 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal-containing particles being at least about 100:1.

10 41. A method of claim 40, wherein each of the fibrils has a diameter substantially equal to the diameter of each other fibril.

42. A method of claim 40, wherein the metal-containing particles are pre-formed.

15 43. A substantially uniform plurality of carbon fibrils produced according to the method of claim 40.

20 44. A composite which comprises a plurality of carbon fibrils according to claim 1, 9, 39 or 43.

45. A composite according to claim 44 which comprises a matrix of an organic polymer.

25 46. A composite according to claim 44 which comprises a matrix of an inorganic polymer.

47. A composite according to claim 44 which comprises a matrix of a metal.

30 48. A method of reinforcing a structural material which comprises incorporating therein an effective reinforcing amount of carbon fibrils according to claim 1, 9, 39 or 43.

35 49. A method of enhancing the electrical conductivity of a material which comprises incorporating therein an effec-

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tive electrical conductivity-enhancing amount of carbon fibrils according to claim 1, 9, 39 or 43.

5 50. A method of enhancing the thermal conductivity of a material which comprises incorporating therein an effective thermal conductivity-enhancing amount of carbon fibrils according to claim 1, 9, 39 or 43.

10 51. A method of increasing the surface area of an electrode or an electrolytic capacitor plate which comprises attaching thereto one or more fibrils according to claim 1, 9, 39 or 43.

15 52. A method of supporting a catalyst which comprises attaching a catalyst to a fibril according to claim 1, 9, 39 or 43.

20 53. A method according to claim 52, wherein the catalyst is an electrochemical catalyst.

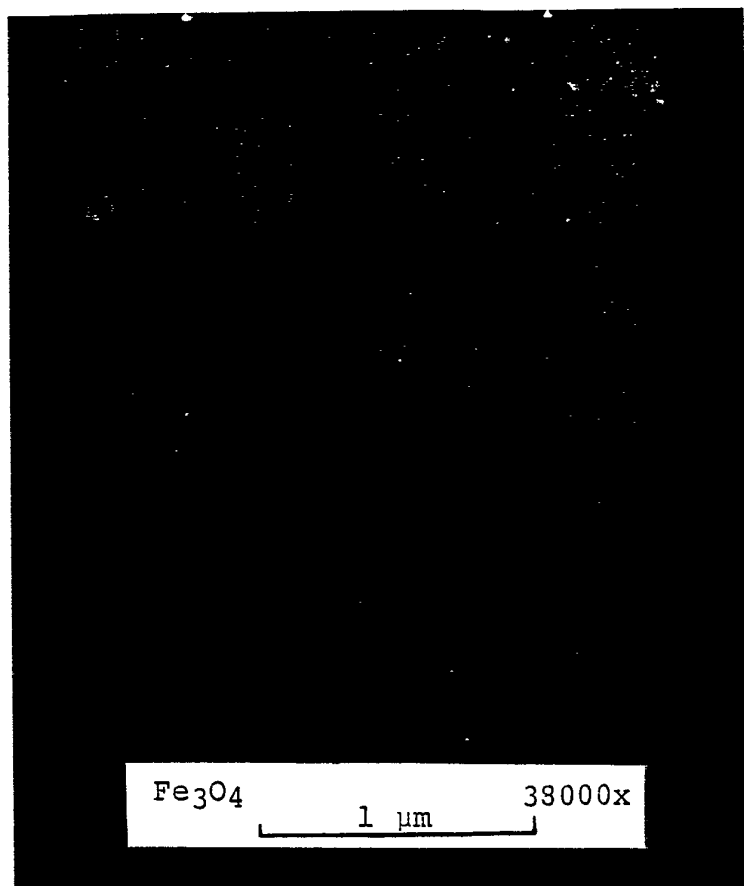
25 54. A method of shielding an object from electromagnetic radiation which comprises incorporating therein an effective shielding amount of carbon fibrils according to claim 1, 9, 39 or 43.

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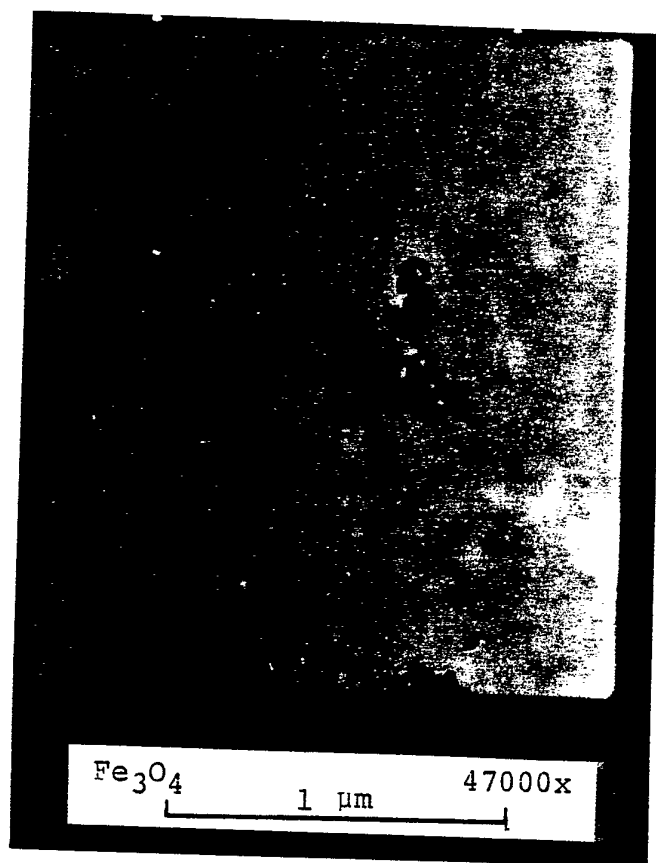
FIG. 1



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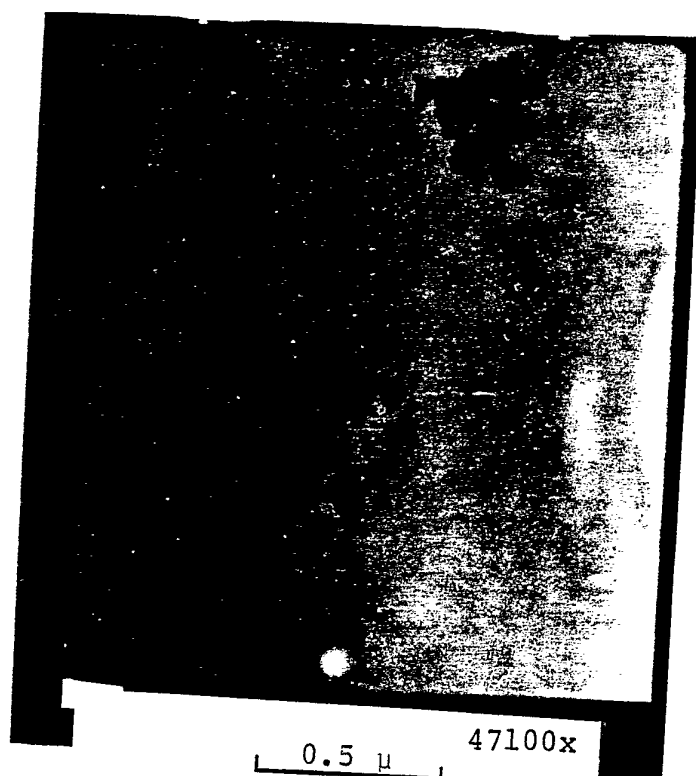
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FIG. 2



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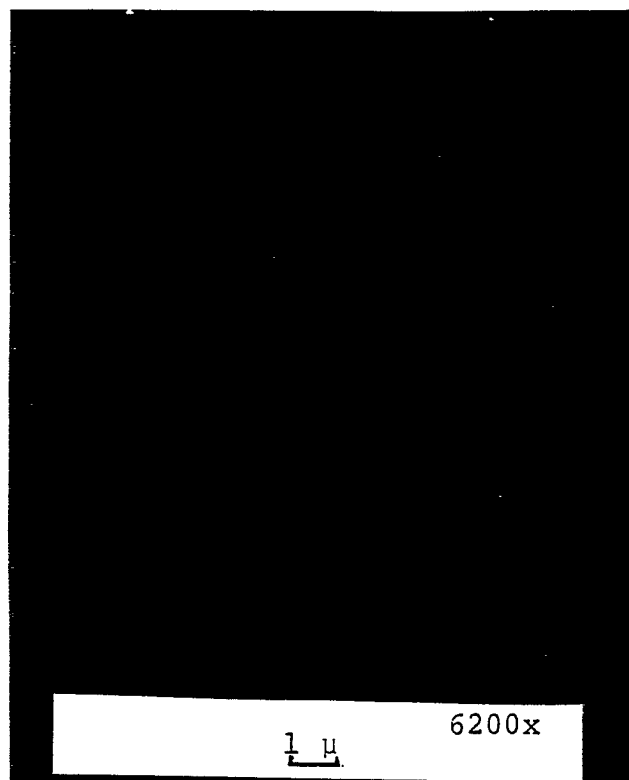
FIG. 3



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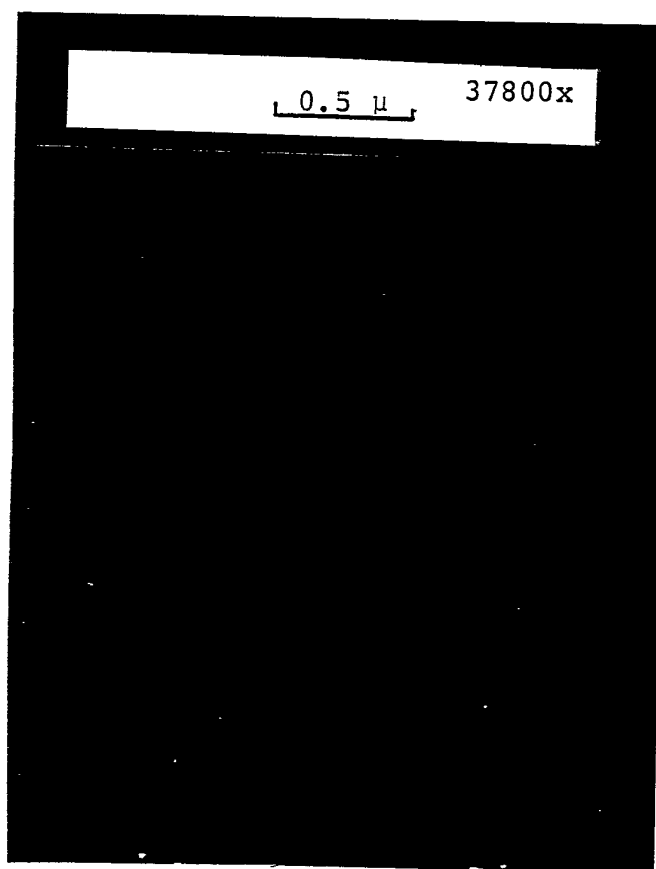
FIG. 4



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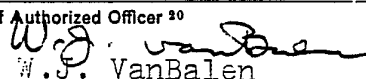
FIG. 5



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INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/02390

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. <u>4 B32B 9/00</u> U.S. CL. <u>427/249, 255.1; 428/367, 376, 398, 408</u>		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	427/216, 249, 255.1; 428/367, 376, 398, 408	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 4,397,901 (JAMES W. WARREN) 09 AUGUST 1983	
A	US, A, 4,472,454 (COMMISSARIAT a l'ENERGIE ATOMIQUE) 18 SEPTEMBER 1984	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
27 FEBRUARY 1986	03 MAR 1986	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 W.J. VanBalen	