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(54) Title: CATALYST AND METHODS FOR PRODUCING MULTI-WALL CARBON NANOTUBES

A Run	WT%				B Co salt	C Carbon content	D Carbon Yield (%)	E Median CNT diameter (nm)	F Mode diameter (nm)	< 10 nm
	Co	Fe	Mo	Mg						
PXE2-282	1.00	1.88	0.50	0.50	Co-Ac	49.6	100	8.24	6.00	72.9%
PXE2-283	1.00	1.00	0.50	0.50	Co-Ac	49.8	100	7.79	5.17	73.1%
PXE2-284	1.00	0.75	0.00	0.50	Co-Ac	49.2	97	9.63	11.06	54.0%
PXE2-285	1.00	0.75	0.50	0.50	Co-Nt	42.8	75	6.72	5.38	84.9%
PXE2-286	1.00	0.50	0.50	0.50	Co-Nt	43.8	78	7.35	5.19	61.6%
PXE2-288	1.00	0.00	1.00	0.50	Co-Nt	30.1	43	6.98	4.68	83.6%
PXE2-289	1.00	1.88	0.50	0.50	Co-Nt	45.2	82	7.91	5.71	69.4%
PXE2-291	0.50	1.88	0.50	0.50	Co-Nt	43.3	75	9.01	10.14	58.7%
PXE2-292	0.75	1.42	0.50	0.50	Co-Ac	44.2	79	7.58	4.97	78.1%
PXE2-293	0.75	1.42	0.40	0.50	Co-Ac	42.1	72	7.72	6.62	77.0%
PXE2-295	1.00	1.88	0.00	0.00	Co-Ac	39.2	76	7.81	8.25	78.9%
PXE2-296	0.67	1.88	0.50	0.50	Co-Ac	35.6	56	10.03	6.62	50.0%

FIGURE 1

(57) Abstract: The present invention provides a catalyst precursor and a catalyst suitable for preparing multi-wall carbon nanotubes. The resulting multi-wall carbon nanotubes have a narrow distribution as to the number of walls forming the tubes and a narrow distribution in the range of diameters for the tubes. Additionally, the present invention provides methods for producing multi-wall carbon nanotubes having narrow distributions in the number of walls and diameters. Further, the present invention provides a composition of spent catalyst carrying multi-wall nanotubes having narrow distribution ranges of walls and diameters.



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## CATALYST AND METHODS FOR PRODUCING MULTI-WALL CARBON NANOTUBES

### Background of the Invention

[001] The present application claims priority to U.S. Provisional Application Ser. No. 61/226,438 filed on July 17, 2009. The entirety of U.S. Provisional Application Ser. No. 61/226438 is incorporated herein by reference.

[002] Carbon nanotubes are known to exist in single wall and multi-wall configurations. Each configuration provides certain benefits. Single wall nanotubes are preferred for electronic applications due to the low occurrence of structural anomalies. However, multi-wall nanotubes are generally lower in cost and will provide satisfactory performance in electronic applications if the number of walls forming the nanotubes can be controlled. Unfortunately, current methods for producing multi-wall carbon nanotubes lack the ability to control the resulting number of walls in the structure in the resulting nanotubes. As a result, currently produced multi-wall carbon nanotubes generally range in diameter from about 3 to 35 nm and comprise 3 to 40 concentric graphene layers, i.e. walls. The layers are coaxially arranged cylinders of carbon atoms having an interlayer distance of about 0.37 nm. This wide distribution range in walls and external diameter size limits the value of multi-wall nanotubes for electrical conductivity applications, thermal conductivity applications and mechanical reinforcement applications.

[003] In contrast, multi-wall nanotubes, having a relatively narrow distribution range of walls and external diameters, will provide electrical conductivity characteristics approaching those of single wall nanotubes. Additionally, multi-wall nanotubes will provide such improvement at a lower cost. Further, multi-wall nanotubes batches having narrow distributions of wall numbers and external diameters will provide enhanced thermal conductivity and mechanical strength when compared to batches having wide distribution ranges.

[004] While one might consider simply isolating a narrow distribution of multi-wall carbon nanotubes from the wide distribution ranges presently manufactured, technology does not exist for carrying out this task. Thus, the currently available multi-wall nanotubes are provided solely in batches or lots having the undesirable wide distributions of walls and external diameters.

[005] As discussed in detail below, the present invention provides batches of multi-wall nanotubes having narrow distribution ranges of walls and diameters. When incorporated into thermoplastics the narrow distribution range batches provide electrical conductivity characteristics which rival single wall nanotubes and are significantly improved over currently available batches of multi-wall nanotubes. The current invention further provides catalysts and

methods for preparing batches of multi-wall carbon nanotubes having narrow distribution ranges of walls and external diameters.

### **Summary of the Current Invention**

[006] In one embodiment, the present invention provides a catalyst precursor comprising alumina ( $\text{Al}_2\text{O}_3$ ), magnesium oxide ( $\text{MgO}$ ) and magnesium aluminate ( $\text{MgAl}_2\text{O}_4$ ) as a catalyst support. The catalyst precursor further comprises metallic oxides of cobalt, iron and molybdenum. The preferred metallic oxides include, but are not necessarily limited to, one or more of the following mixed metal oxides:  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{Co}_x\text{MoO}_4$ ,  $\text{Fe}_2(\text{MoO}_4)_3$ ,  $\text{Co}_x\text{Fe}_y\text{MoO}_4$ ; where x and y represent the atomic ratios of Co and Fe relative to Mo and x is from about 1.6 to about 6.5 and y is from about 0.1 to about 10.5. Mixed metal oxides having two or more metal components are preferred, as single metal oxides produce carbon fibers and other forms of carbon.

[007] In another embodiment, the present invention provides a method for preparing a catalyst precursor and a catalyst. The method involves initially preparing a solution of mixed metallic compounds comprising two or more of the following: a cobalt compound selected from the group consisting of cobalt acetate, cobalt nitrate; an iron compound selected from the group consisting of iron acetate, iron nitrate; a molybdenum compound selected from the group consisting of ammonium heptamolybdate and ammonium dimolybdate; and magnesium nitrate. This solution is reacted with an excess of aluminum hydroxide powder and the reaction products subsequently formed into a paste. Formation of the paste causes the reaction products to agglomerate thereby yielding a particle size distribution between about 100 and 1400 microns. The reaction products are subsequently dried, reduced in size and calcined to yield a catalyst precursor. The currently preferred catalyst precursor has a particle size distribution ranging from 70  $\mu\text{m}$  to 150  $\mu\text{m}$ . Conversion of the precursor to a catalyst entails placing the catalyst precursor within a reaction chamber suitable for use as a fluidized bed reactor. The catalyst precursor is fluidized and pre-heated to the desired reaction temperature by passing an inert gas selected from the group consisting of nitrogen, argon or helium through the reaction chamber. Upon achieving steady state conditions at the desired reaction temperature, the inert gas is replaced with a blend of ethylene and inert gas. The catalyst precursor converts to the desired catalyst during the first five minutes of contact with the blend of ethylene and inert gas. During the conversion process, cobalt and iron oxides are reduced to the respective metals. Additionally, a portion of the iron oxide is reduced to iron carbide ( $\text{Fe}_3\text{C}$ ) and the molybdenum oxides are reduced to molybdenum carbide ( $\text{Mo}_2\text{C}$ ).

[008] Still further, the present invention provides a method of producing multi-wall carbon nanotubes wherein the resulting batch of multi-wall nanotubes has a narrow distribution as to the number of walls making up the nanotubes and a narrow distribution of external diameters for the resulting nanotubes. In the method of the current invention, the catalyst precursor is prepared as discussed above. Following conversion of the catalyst precursor to the reduced metal catalyst, flow of the ethylene/inert gas continues under the desired reaction conditions for a period of time sufficient to yield multi-wall carbon nanotubes. The ethylene/inert gas contains from about 10% to about 80% ethylene by volume and flows at a rate sufficient to fluidize the bed of catalyst particles. Following a reaction period of about 10 to about 30 minutes, the flow of gas to the reaction chamber is cut off and the particles carrying the multi-wall nanotubes are removed. About 95% to about 98% of the resulting carbon product carried by the spent catalyst is carbon nanotubes. From about 60% to about 90% of the resulting batch of multi-wall carbon nanotubes have from 3 to 6 walls and external diameters ranging from about 3 nm to about 7 nm. Thus, the present invention also provides a novel product comprising carbon nanotubes having 3 to 6 walls and external diameters ranging from about 3 nm to about 7 nm.

#### **Brief Description of the Figures**

[009] FIGURE 1 provides a tabular representation of the carbon yield and carbon nanotube diameter profile for various catalyst compositions on an alumina support.

[010] FIGURE 2A provides graphical representations of the carbon nanotube diameter distribution for the catalytic composition corresponding to PXE2-282 in Figure 1.

[011] FIGURE 2B provides graphical representations of the carbon nanotube diameter distribution for the catalytic composition corresponding to PXE2-285 in Figure 1.

[012] FIGURE 2C provides graphical representations of the carbon nanotube diameter distribution for the catalytic composition corresponding to PXE2-288 in Figure 1.

[013] FIGURE 2D provides graphical representations of the carbon nanotube diameter distribution for the catalytic composition corresponding to PXE2-295 in Figure 1.

[014] FIGURE 3 is a tabular representation of the effect of reaction temperature and gas composition on the carbon yield and selectivity to smaller diameter tubes.

[015] FIGURE 4A depicts the carbon nanotube diameter distribution as determined by TEM corresponding to the SMW-100 carbon nanotube product.

[016] FIGURE 4B depicts the carbon nanotube diameter distribution as determined by TEM corresponding to the MWCNT A carbon nanotube product.

[017] FIGURE 4C depicts the carbon nanotube diameter distribution as determined by TEM corresponding to the MWCNT B carbon nanotube product.

[018] FIGURE 4D depicts the carbon nanotube diameter distribution as determined by TEM corresponding to the MWCNT C carbon nanotube product.

[019] FIGURE 5 is a graphical representation of electrical volume resistivity for SMW-100 carbon nanotubes and three commercial carbon nanotube products in polycarbonate.

[020] FIGURE 6A is a graphical representation of surface resistance on the front and back of composites containing Nylon66 resin loaded with 2.5wt% SMW-100 carbon nanotubes or loaded with 2.5 wt% of commercially available multi-wall carbon nanotubes.

[021] FIGURE 6B is a graphical representation of surface resistance on the front and back of composites containing Nylon66 resin loaded with 3.5wt% SMW-100 carbon nanotubes or loaded with 3.5 wt% of commercially available multi-wall carbon nanotubes.

[022] FIGURE 7 depicts surface resistivity of thin film comprising different forms of carbon nanotubes.

#### **Detailed Description of the Preferred Embodiments**

[023] The following detailed disclosure of the current invention will describe the catalyst precursor, methods of preparing the catalyst precursor and conversion thereof to the desired catalyst. Additionally, the present invention provides methods of producing batches of desired multi-wall carbon nanotubes on the catalyst wherein the carbon nanotube product has a narrow range distribution of walls and external diameters. As used herein, "carbon content" refers the percentage of the final product (carbon nanotube + catalyst) that is carbon-based. So if 250 g of the final product is carbon and the final product is a total of 500 g, then carbon content is 50% or 50.0 (as used in figure 1). As used herein, "carbon yield" refers to the amount of carbon product produced relative to the amount of catalyst used in the reaction. It is defined by the following equation: (amount of carbon in final product (g)/amount of catalyst (g)) X 100. For example, a reaction that yields 250 g carbon product where 250 g of catalyst was used in the reaction would have a carbon yield of 100% ((250g/250g) X 100 = 100%). As used herein, (including Figures 2A-2D; 2A-4D), "frequency" refers to the number of carbon nanotubes in a sample having a specified diameter (x axis). For example, in figure 2A, there are approximately 20 carbon nanotubes that have a diameter of about 6 nm.

##### **1. The Catalyst Precursor and Catalyst**

[024] The catalyst precursor of the present invention has a surface phase of mixed metal oxides supported on a particle of alumina and magnesium aluminate. A mixed metal oxide is an oxide

having two or more metal components. Additionally, the support of alumina/magnesium aluminate carries a surface treatment of magnesium oxide. The magnesium oxide carried by the alumina/magnesium aluminate particle is not necessarily an encompassing layer. The atomic ratio of MgO to  $\text{Al}_2\text{O}_3$  is between about 0.02 and 0.04. Stated in other terms, for a ratio of 0.02:1, for every atom of MgO there are 50 atoms of  $\text{Al}_2\text{O}_3$  while at a ratio of 0.04:1, for every atom of MgO there are 25 atoms of  $\text{Al}_2\text{O}_3$ . As noted below, a portion of the MgO used in these calculations will be converted to  $\text{MgAl}_2\text{O}_4$ .

[025] The preferred surface phase of mixed metal oxides includes but is not limited to, one or more of the following:  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{Co}_x\text{MoO}_4$ ,  $\text{Co}_x\text{Fe}_y\text{MoO}_4$ ,  $\text{Fe}_2(\text{MoO}_4)_3$ . Typically, the metal oxides provide the following percent by weight concentrations of metals on the catalyst precursor: Co from about 0.5% to about 2.0%; Mo from about 0.3% to about 2.0%; and, Fe from about 0% to about 3.0%. Thus, for  $\text{Co}_x\text{Fe}_y\text{MoO}_4$ , x may range from about 1.6 to 6.5 and y may range from 0.1 to 10.5. More preferably, x will be about 3.3 and y will range from 2.6 to 6.3. In any event, a sufficient amount of the metal oxides are present on the catalyst precursor such that the resulting catalyst comprises the following percent by weights of the metal component: Co from about 0.5% to about 2.0%; Mo from about 0.3% to about 2.0%; and, Fe from about 0% to about 3.0%. In the resulting catalyst, the iron may be present as a reduced metal or a carbide ( $\text{Fe}_3\text{C}$ ), while the molybdenum is present as a carbide ( $\text{Mo}_2\text{C}$ ).

[026] Preferably, the percent by weight of each metal component based on the weight of the catalyst precursor composition is: Co, from about 0.75% to about 1.5%; Mo, from about 0.5% to about 1.0%; and, Fe, from about 0.5% to about 2.0%. Accordingly, the active metal components are present in the following atomic ratios, wherein Mo is constant: the ratio of Co to Mo ranges from about 1.6 to about 6.5, more preferably from about 2.44 to about 4.88 and most preferred about 3.3; and the ratio of Fe to Mo from about 0 to about 10.5, more preferably about 1.75 to about 6.98 and most preferred about 2.62 to about 6.28.

[027] The presence of Mg ions on the catalyst support reduces the number of strong acid sites on the surface of the Alumina support. By reducing the number of strong acid sites on the surface of the catalyst support, use of the improved catalyst will produce primarily carbon nanotubes and significantly less amorphous carbon or other carbon products. As discussed below, catalytic reactions using the improved catalyst produce at least 90% and preferably greater than 98% carbon nanotubes as the resulting carbon product.

[028] The catalyst precursor of the present invention preferably has a particle size between about 20  $\mu\text{m}$  and about 500  $\mu\text{m}$ . Preferably, the particle size is between about 20  $\mu\text{m}$  and 250  $\mu\text{m}$ . More preferably, the catalyst precursor has a particle size between about 20  $\mu\text{m}$  and about

150  $\mu\text{m}$ . In the currently preferred method discuss below, the particles range in size from about 70  $\mu\text{m}$  to about 150  $\mu\text{m}$ .

[029] The catalyst precursor described above is converted to catalyst particles by reduction of the metal oxides to the respective metals and metal carbides, i.e.  $\text{Fe}^\circ$ ,  $\text{Fe}_3\text{C}$ ,  $\text{Co}^\circ$  and  $\text{Mo}_2\text{C}$ . The catalyst particles have the same atomic ratios of metal present as the catalyst precursor. The resulting nano-sized deposits of metallic cobalt and metallic iron will determine the interior diameter of the multi-wall nanotubes produced on the catalyst particles. Additionally, the presence of the  $\text{Mo}_2\text{C}$ , disperses or spaces the metallic cobalt, thereby precluding sintering of the cobalt and providing the desired cobalt particle size. In general, the resulting metal deposits on the support will have diameters ranging from about 1.5 nm to about 3.0 nm. Preferably, the resulting metal deposits of reduced iron and reduced cobalt will have diameters ranging from about 1.5 nm to about 2.2 nm. Additionally, as noted above, the final catalyst particles have fewer surface acid sites than catalyst particles utilizing only alumina as a support.

[030] In summary, the final catalyst particles of the present invention have particle sizes between about 20  $\mu\text{m}$  and about 500  $\mu\text{m}$ . Preferably, the particle size is between about 20  $\mu\text{m}$  and 250  $\mu\text{m}$ . More preferably, the catalyst precursor has a particle size between about 20  $\mu\text{m}$  and about 150  $\mu\text{m}$ . In the currently preferred method of making multi-wall nanotubes discussed below, the presently preferred particle size is about 70  $\mu\text{m}$  to about 150  $\mu\text{m}$ . The catalyst particles comprise:

- a. gamma alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) between about 91.0% and 97.6% by weight, preferably between about 94.8% and about 97.3% by weight;
- b. Mg (in the form of  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$ ) between about 0.5% and about 3.3% by weight, preferably between 0.5% and 1.0%;
- c. reduced Co from about 0.5% to about 2.0% by weight, preferably from about 0.75% to about 1.5% by weight;
- d. Mo, in the form of  $\text{Mo}_2\text{C}$  from about 0.3% to about 2.0% by weight, preferably from about 0.5% to about 1.0% by weight; and,
- e. Fe, in the form of reduced iron and iron carbide ( $\text{Fe}^\circ$ ,  $\text{Fe}_3\text{C}$ ) from about 0% to about 3.0% by weight, preferably from about 0.5% to about 2.0% by weight.

Typically, less than 2.0% by weight of the catalyst particle will be metal carbides. The atomic ratios of the reduced metals for catalytic production of multi-wall carbon nanotubes will not vary substantially from the catalyst precursor as the metal carbides are not produced in substantial quantities.



## 2. Method of Preparing the Catalyst Precursor Particles and Catalyst Particles

[031] The current invention provides methods for manufacturing a catalyst precursor and a catalyst suitable for the catalytic formation of multi-wall carbon nanotubes. In particular, the catalyst of the current invention enables the production of batches of multi-wall carbon nanotubes having a narrow distribution range of walls and diameters.

[032] In a preferred embodiment, the method initially involves preparing a solution of mixed metallic compounds comprising two or more of the following: a cobalt compound selected from the group consisting of cobalt acetate, cobalt nitrate; an iron compound selected from the group consisting of iron acetate, iron nitrate; a molybdenum compound selected from the group consisting of ammonium heptamolybdate and ammonium dimolybdate; and magnesium nitrate. The preferred solution comprises cobalt acetate, iron nitrate, ammonium heptamolybdate and magnesium nitrate in water.

[033] Regardless of the cobalt compound chosen, the solution contains a concentration of cobalt ion between about 20 g/L and about 50 g/L; a concentration of molybdenum ion between about 10.5 g/L and about 70.3 g/L; a concentration of iron ion between about 35 g/L and about 105 g/L; and, a concentration of Mg ion between about 6.7 g/L to about 27.0 g/L. The preferred solution contains between about 26.7 g/L and about 40.0 g/L cobalt ion; between about 17.6 g/L and about 35.2 g/L molybdenum ion; between about 52.7 g/L and about 70.1 g/L iron ion; and, between about 6.7 g/L and about 13.5 g/L magnesium ion. Most preferred is a solution of about 33.4 g/L cobalt ion; of about 17.6 g/L molybdenum ion; of about 63.1 g/L iron ion; and, about 6.7 g/L magnesium ion. Proper selection of the metal ion concentration will enhance the formation of the desired mixed metal oxides. Thus, it is desirable to provide the proper stoichiometric ratios of the metals in solution to achieve this result.

[034] The above referenced metal ions are then reacted with aluminum hydroxide to yield a mixture of metal hydroxides and other ionic compounds including, but not limited to, the following hydroxides where the stoichiometric ratios may be varied from that shown:  $\text{Mg}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{CoMoO}_4 \cdot n\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$ . Typically the foregoing reaction takes place at room temperature over a period of about two to four hours. The reaction products have a paste like consistency which promotes agglomeration of the particles. Preferably, the paste has a moisture content of about 20% to about 40% water by weight. More preferably, the paste contains from about 25% to about 30% water by weight.

[035] If necessary for agglomeration of the particles, the paste-like product is manipulated to yield agglomerated particles having particle sizes ranging from about 100  $\mu\text{m}$  to about 1400  $\mu\text{m}$ . Typically, the particles will agglomerate during the reaction. Preferably, the agglomerated

particles are between about 100  $\mu\text{m}$  to about 500  $\mu\text{m}$ . In the preferred process, the agglomerated particles are mixed in a machine which kneads or mixes the paste for about 20 to about 50 minutes. Following the kneading, the product is allowed to age for about 2 to 3 additional hours. The total time period will depend upon the batch size. For batches of about 200 to about 2000 grams, the preferred kneading period will be about 30 minutes. Larger batches will require longer mixing times. Following agglomeration, the particles are dried and sieved to isolate particles less than 1400  $\mu\text{m}$ . Preferably, the sieving step provides particles in the range of about 100  $\mu\text{m}$  to about 500  $\mu\text{m}$ .

[036] The agglomerated particles are dried to a moisture content of about 10% to about 20% water by weight. Preferably, the dried particles have less than 15% water by weight. The drying step preferably takes place at a temperature between about 30°C and 50°C.

[037] Following drying and sieving, the particles are calcined under a flowing gas at a temperature between about 400°C to about 600°C for a period of about 3 hours to about 8 hours. More preferably, the calcining step takes place at a temperature between about 400°C and 500°C for a period of about 3.5 hours to about 4.5 hours. Most preferably, the calcining step occurs at a temperature of about 440°C to about 460° for a period of about 3.5 hours to about 4.5 hours. Preferably, the calcining gas is selected from air, nitrogen, helium and mixtures thereof. Typically, the preferred calcining gas is a gas that is inert under the calcining conditions. The drying and calcining steps reduce the agglomerated particles to a particle size between about 20  $\mu\text{m}$  and 500  $\mu\text{m}$ . Alternatively, prior to calcining the particles are sieved and if necessary ground such that calcining will produce particles between 20 $\mu\text{m}$  and 250 $\mu\text{m}$ . Preferably, calcining produces particles between about 20  $\mu\text{m}$  and 200  $\mu\text{m}$ . More preferred are particles between about 20  $\mu\text{m}$  and 150  $\mu\text{m}$ . In the preferred method discussed below, the preferred particles range in size from about 70  $\mu\text{m}$  to about 150  $\mu\text{m}$ . The resulting particles are essentially free of water moisture, i.e. no greater than 3% moisture by weight.

[038] Calcining of the particles converts the metal hydroxides to the respective oxides. For example, calcining of iron hydroxide with molybdate yields iron-molybdate ( $\text{Fe}_2(\text{MoO}_4)_3$ ). Likewise, calcining cobalt hydroxide with molybdate yields cobalt-molybdate ( $\text{CoMoO}_4$ ). Further, during the calcining process  $\text{Fe}(\text{OH})_3$  and  $\text{Co}(\text{OH})_2$  combine to yield  $\text{CoFe}_2\text{O}_4$ . Finally, during calcining  $\text{Mg}(\text{OH})_2$  yields  $\text{MgO}$  and the aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) converts to gamma alumina, i.e.  $\gamma\text{-Al}_2\text{O}_3$ . During the calcining process, the oxidation of  $\text{Mg}(\text{OH})_2$  also precludes the formation of strong acid sites on the surface of the  $\gamma\text{-Al}_2\text{O}_3$ . The resulting surface configuration is believed to be a mixed oxide similar to  $\text{Mg-Al-O}$ . In any event, the surface

acidity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrying the MgO is significantly lower than the surface acidity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> when calcined without Mg(OH)<sub>2</sub> present.

[039] Further, during the calcining process, in addition to forming the respective oxides of magnesium and aluminum, a portion of the Mg<sup>+2</sup> ions adjacent to the aluminum hydroxide produces a parallel reaction. In this reaction, the solubility of the magnesium ion in the alumina allows the magnesium to displace a portion of the aluminum oxide tetrahedral structure near the surface of the particle thereby producing magnesium aluminate (MgAl<sub>2</sub>O<sub>4</sub>), a compound with a spinel like structure. The formation of magnesium aluminate is favored over the formation of CoAl<sub>2</sub>O<sub>4</sub> and FeAlO<sub>3</sub>. Thus, the favored reaction preserves the catalytic metals for reduction and conversion to catalyst sites on the surface of the resulting support particle. In particular, the reduced cobalt takes the form of nanoparticle size domains on the surface of the resulting support, the iron becomes reduced iron and iron carbide and the molybdenum becomes molybdenum carbide. The iron carbide and reduced iron disperse the cobalt on the surface of the catalyst support thereby controlling the inner diameter of the resulting nanotubes.

[040] The resulting catalyst support has a configuration wherein magnesium aluminate is incorporated into the crystalline structure of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> primarily in the outer layer of the particle. Additionally, the surface of the gamma alumina carries MgO. Without being limited by theory, the MgO on the surface is likely a mixed oxide with the alumina of the particle, i.e. a mixed oxide of Mg-Al-O. This configuration results from the reaction of the magnesium ions with the alumina during the calcining process. Finally, the preferred catalyst support is preferably free of CoAl<sub>2</sub>O<sub>4</sub> and FeAlO<sub>3</sub>. If FeAlO<sub>3</sub> is present then preferably, the catalyst support comprises less than 0.5 percent by weight FeAlO<sub>3</sub>. If CoAl<sub>2</sub>O<sub>4</sub> is present then preferably, the catalyst support comprises less than 0.5 percent by weight CoAl<sub>2</sub>O<sub>4</sub>.

[041] The presence of magnesium on the surface of the catalyst support particle reduces the surface acidity of the catalyst precursor support particle and the resulting catalyst support particle. By reducing the number acid sites on the surface of the support particle, the method of the current invention improves the production of carbon nanotubes and reduces the formation of other carbon types during the subsequent production of multi-wall carbon nanotubes. Additionally, by blocking the formation of CoAl<sub>2</sub>O<sub>4</sub> and FeAlO<sub>3</sub> the presence of the magnesium ion precludes the loss of catalytic metals.

[042] Following calcining and particle size reduction, the resulting catalyst precursor particles have a catalyst support of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/ MgAl<sub>2</sub>O<sub>4</sub> with a surface treatment of MgO. Additionally, the surface of the catalyst support carries a mixed phase of the referenced metal oxides. As noted

above the preferred mixed metal oxides include but are not necessarily limited to:  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{Co}_x\text{MoO}_4$ ,  $\text{Fe}_2(\text{MoO}_4)_3$ ,  $\text{Co}_x\text{Fe}_y\text{MoO}_4$  with  $\text{Co}_x\text{Fe}_y\text{MoO}_4$  being the most preferred.

[043] The resulting catalyst precursor is placed within a reaction chamber. Preferably, the reaction chamber is designed to produce a fluidized bed of catalyst particles when a flowing gas passes through the chamber and the particles located therein. To finally convert the catalyst precursor to a catalyst, the precursor must be heated and reacted with a carbon containing gas. In the following method for producing multi-wall nanotubes, the preferred gaseous carbon compound is ethylene. The conversion of the catalyst precursor to catalyst takes place at a temperature between about 600°C and 700°C during the first ten minutes of contact with the gaseous carbon compound. During this time period, the metal oxides are reduced to the respective metals and metal carbide discussed above. Additionally, the formation of the  $\text{Fe}_3\text{C}$  and  $\text{Mo}_2\text{C}$  preclude sintering and agglomeration of the reduced cobalt and iron on the surface of the support. Thus, the resulting nanoparticles of reduced cobalt preferably have diameters between about 1.5 nm to about 3.5 nm. More preferably, the reduced cobalt metal particles on the surface of the catalyst support have diameters between about 1.5 nm and 2.2 nm. The reduced iron particles will have similar sizes, i.e. from about 1.5 nm to about 3.5 nm preferably between about between about 1.5 nm and 2.2 nm.

[044] The resulting catalyst comprises a support of  $\gamma\text{-Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4$  with a surface treatment of  $\text{MgO}$  and nano size particles of  $\text{Fe}_3\text{C}$  and  $\text{Mo}_2\text{C}$  on the surface of the support. The reduced metallic cobalt may be carried by the  $\gamma\text{-Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4$  and may also be found on the molybdenum carbide ( $\text{Mo}_2\text{C}$ ) and iron carbide ( $\text{Fe}_3\text{C}$ ). Additionally, reduced iron may be carried by the  $\gamma\text{-Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4$  and may also be found on the molybdenum carbide ( $\text{Mo}_2\text{C}$ ) and iron carbide ( $\text{Fe}_3\text{C}$ ).

[045] As discussed above the resulting catalyst particles have particle sizes between about 20  $\mu\text{m}$  and about 500  $\mu\text{m}$ . Preferably, the particle size is between about 20  $\mu\text{m}$  and 250  $\mu\text{m}$ . More preferably, the catalyst has a particle size between about 20  $\mu\text{m}$  and about 150  $\mu\text{m}$ . In the currently preferred method of making multi-wall nanotubes, the presently preferred particle size is about 70  $\mu\text{m}$  to about 150  $\mu\text{m}$ .

[046] The catalyst particles comprise: gamma alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) between about 91.0% and 97.6% by weight, preferably between about 94.8% and about 97.3% by weight;  $\text{Mg}$  (in the form of  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$ ) between about 0.5% and about 3.3% by weight, preferably between 0.5% and 1.0%; reduced  $\text{Co}$  from about 0.5% to about 2.0% by weight, preferably from about 0.75% to about 1.5% by weight;  $\text{Mo}$ , in the form of  $\text{Mo}_2\text{C}$  from about 0.3% to about 2.0% by weight, preferably from about 0.5% to about 1.0% by weight; and,  $\text{Fe}$ , in the form of reduced iron and

iron carbide ( $\text{Fe}^\circ$ ,  $\text{Fe}_3\text{C}$ ) from about 0% to about 3.0% by weight, preferably from about 0.5% to about 2.0% by weight. Typically, less than 2.0% by weight of the catalyst particle will be metal carbides. The atomic ratios of the reduced metals for catalytic production of multi-wall carbon nanotubes will not vary substantially from the catalyst precursor as the metal carbides are not produced in substantial quantities.

[047] In an alternative method for preparing the catalyst precursor, the magnesium nitrate has been omitted from the initial solution. In this method, magnesium hydroxide powder is combined with the aluminum hydroxide powder and reacted with the solution of metallic compounds comprising a cobalt compound selected from the group consisting of cobalt acetate, cobalt nitrate, an iron compound selected from the group consisting of iron acetate, iron nitrate, a molybdenum compound selected from the group consisting of ammonium heptamolybdate and ammonium dimolybdate and mixtures thereof. The preferred solution comprises cobalt acetate, iron nitrate, ammonium heptamolybdate and magnesium nitrate in water.

[048] Regardless of the cobalt compound chosen, the solution contains a concentration of cobalt between about 20 g/L and about 50 g/L; a concentration of molybdenum ion between about 10.5 g/L and about 70.3 g/L; a concentration of iron ion between about 35 g/L and about 105 g/L; and, a concentration of Mg ion between about 6.7 g/L to about 27.0 g/L. The preferred solution contains between about 26.7 g/L and about 40.0 g/L cobalt ion; between about 17.6 g/L and about 35.2 g/L molybdenum ion; between about 52.7 g/L and about 70.1 g/L iron ion; and, between about 6.7 g/L and about 13.5 g/L magnesium ion. Most preferred is a solution of about 33.4 g/L cobalt ion; of about 17.6 g/L molybdenum ion; and about 63.1 g/L iron ion.

[049] The solution of metal ions is subsequently reacted with an excess of aluminum hydroxide powder having particles ranging in size from about 20  $\mu\text{m}$  to about 150  $\mu\text{m}$  and magnesium hydroxide powder having particles ranging in size from about 20  $\mu\text{m}$  to about 150  $\mu\text{m}$ . Following this reaction, the preparation of the catalyst precursor and the subsequent catalyst is identical to the process described above.

#### Manufacture of Multi-Wall Carbon Nanotube Batches Having Narrow Distribution Ranges of Walls and Diameters

[050] The following discussion concerning the catalytic production of multi-wall carbon nanotubes is essentially a continuation of the discussion above concerning the preparation of the catalyst precursor and the catalyst. Following placement of the calcined catalyst precursors in the reactor chamber, the particles are fluidized and converted to catalyst particles. As noted above, the catalyst may have particle sizes between about 20  $\mu\text{m}$  and about 500  $\mu\text{m}$ . Preferably, the particle size is between about 20  $\mu\text{m}$  and 250  $\mu\text{m}$ . More preferably, the catalyst precursor

has a particle size between about 20  $\mu\text{m}$  and about 150  $\mu\text{m}$ . In the currently preferred method of making multi-wall nanotubes, the presently preferred particle size is about 70  $\mu\text{m}$  to about 150  $\mu\text{m}$ . Thus, the particles are well suited for use in a fluidized bed reactor.

[051] Following placement of the catalyst precursor particles in the reaction chamber, a flowing stream of nitrogen gas passes through the reaction chamber thereby fluidizing the bed of particles. The nitrogen gas is heated to a temperature sufficient to raise the temperature within the fluidized bed to a range of about 600°C to about 700°C. Alternatively, the reaction chamber may be located in a furnace or other suitable heating device. When located within a furnace, the reaction chamber will typically be heated by both the furnace and the gas. More preferably, the fluidized bed is pre-heated to a temperature between about 600°C to about 650°C. Most preferably, the fluidized bed is pre-heated to about 610°C to about 630°C. One skilled in the art will recognize that other non-reactive gases such as argon or helium may be substituted for nitrogen. The primary requirement for the pre-heating step is fluidization and heating of the fluidized bed to the desired temperature without undesirable side reactions.

[052] Upon stabilization of the temperature within the fluidized bed, the gas flow to the bed is switched from nitrogen to a reactive gas. The reactive gas is a non-reactive carrier gas with a carbon containing gas. The preferred carrier gas is nitrogen and the preferred carbon containing gas is ethylene; however, other carrier gases such as argon or helium will perform equally well. The preferred blend of ethylene in nitrogen by volume is between about 10% and 80% by volume. More preferably, the reactive gas contains from about 20% to about 50% by volume ethylene in nitrogen. Most preferred is a reactive gas containing from about 20% to about 40% by volume ethylene in nitrogen.

[053] The flow rate of the ethylene containing gas is not dependent upon the size of the reaction chamber. Rather, the volume of gas passing through the reaction chamber depends upon the grams of catalyst precursor within the reaction chamber. The flow rate will be from about 70 L/min per kg of catalyst precursor to about 150 L/min per kg of catalyst precursor. More preferably, the flow rate will range between about 90 L/min per kg of catalyst precursor to about 120 L/min per kg of catalyst precursor.

[054] The initial reaction of the ethylene containing gas with the catalytic particles reduces the metal oxides to their respective metals ( $\text{Co}^0$  and  $\text{Fe}^0$ ) and metal carbides ( $\text{Mo}_2\text{C}$  and  $\text{Fe}_3\text{C}$ ). This reduction step generally occurs over the first five minutes of the reaction process. Preferably, the reaction temperature is 600°C to 750°C. More preferably, the reaction temperature is between 610°C and 650°C. Most preferably, the reaction temperature is 610°C. Additionally, during the first ten minutes of the reaction process, the ongoing reaction of ethylene with the catalyst

precursor and subsequent catalyst particles is an exothermic reaction. Thus, the preferred method maintains the temperature of the fluidized bed below 670°C. Temperature maintenance may be achieved by lowering the temperature of the gas entering the reaction chamber. If a furnace is used, then the temperature of the furnace may also be reduced. Preferably, the temperature is maintained below 650°C as higher temperature will lead to an increased production of amorphous carbon. As the metal oxides are reduced, the ethylene gas contacts the resulting catalytic particles and begins to grow multi-wall carbon nanotubes. Following the reduction of metal oxides to catalytic particles, the reaction process continues for about 10 to about 40 minutes. More preferably, the reaction process following the reduction of metal oxides continues for about 15 to 25 minutes.

[055] The resulting carbon product carried by the now spent catalyst particles is 98% free of amorphous carbon and other carbon forms. Thus, 98% of the carbon product is multi-wall carbon nanotubes. Further, the resulting multi-wall carbon nanotubes primarily have from 3 to 8 walls. More preferably, the resulting nanotubes carried by the spent catalyst particles primarily have from 3 to 6 walls and external diameters between about 4.0 nm to about 7.0 nm. Preferably, at least 60% of the resulting multi-wall carbon nanotubes have three to six walls and external diameters between about 4.0 nm and about 7.0 nm. More preferable, the method of the current invention yields multi-wall carbon nanotubes wherein at least 75% of the resulting multi-wall carbon nanotubes having the desired narrow distribution range of 3 to 6 walls and diameters between about 4.0 nm and 7.0 nm. More preferably, at least 85% of the resulting nanotubes carried by the spent catalyst have three to six walls and external diameters between about 4.0 nm and about 7.0 nm. Most preferably, with continuously maintained fluidization of the catalyst particles, the present invention will provide spent catalyst carrying multi-wall carbon nanotubes wherein 90% of the resulting multi-wall nanotubes will have 3 to 6 walls and diameters between about 4.0 nm and about 7.0 nm.

[056] The following examples and test data do not limit the nature of the current invention. Rather, this information will enhance the understanding of the current invention.

#### EXAMPLE 1

##### *Objective*

[057] This example demonstrates the effect of various catalyst metal compositions on carbon yield and carbon nanotube diameter.

##### *Methods*

[058] A variety of catalyst precursors were prepared to demonstrate the importance of the catalytic metals on the resulting multi-wall product. The table in Figure 1 identifies the nanotube products produced for this comparison. For these examples, 600 grams of catalyst precursor prepared as discussed above, having particles sizes of 150 to 300 microns, were placed in a fluidized bed reactor. As discussed above, the method of the current invention converts the catalyst precursor to catalyst and subsequently grows multi-wall carbon nanotubes on the resulting catalyst. For each of the examples provided in Figure 1, the final catalysts were reacted at 610 °C with 40% ethylene in nitrogen at a gas flow rate of 60 L/min (gas flow/mass of catalyst ratio of 100 L/min per Kg catalyst) for 20 minutes.

### *Results*

[059] As depicted in Figure 1, the catalytic metal composition significantly impacts the resulting multi-wall nanotube product. For example, runs PXE2-282, PXE2-285, PXE2-292 and PXE2-293, provide data regarding multi-wall carbon nanotubes prepared with catalyst precursors having Co, Mo and from about 0.75 percent weight of iron to about 1.9 percent weight of iron. The resulting batch of nanotubes have a high yield of carbon nanotubes with a median external diameter from about 6.72 nm to about 8.24 nm and a mode external diameter from about 4.97 nm to about 6 nm. Between 75% and 85% of these carbon nanotubes have external diameters of less than 10 nm. Specifically, PXE2-282 represents a batch of multi-wall nanotubes having a mode diameter of 6.0 nm, the median diameter for the batch is 8.24 nm and 73% of the batch had diameters less than 10 nm. Similarly, PXE2-285 represents a batch of multi-wall nanotubes having a mode diameter of 5.38 nm, the median diameter for the batch is 6.72 nm and 85% of the batch had diameters less than 10 nm. The values for PXE2-292 and PXE2-293 can be easily determined from Figure 1. As known to those skilled in the art, the term “mode” when used in this manner represents the value that occurs the most frequently in a data set. Thus, for PXE2-285, the most common diameter for nanotubes within the batch is 6.72 nm.

[060] These results demonstrate that catalyst precursor compositions comprising Co from about 0.75 to about 1 percent weight of total metals of catalyst precursor, Fe from about 0.75 to about 1.9 percent weight of total metals of catalyst precursor, and Mo from about 0.4 to 0.5 percent weight of total metals of catalyst precursor, result in high percentage yields of small diameter carbon nanotubes.

[061] In contrast, catalyst precursor particles lacking iron result in a significant reduction in carbon yield. For example, run PXE2-288 demonstrates a 57% loss in carbon yield when iron is removed from the precursor catalyst formulation. Interestingly, the resulting product comprises carbon nanotubes with a median external diameter of 6.98 and a mode external diameter of 4.68.



This suggests that iron is not responsible for the small diameter of the resulting carbon nanotubes. However, the results seem to suggest that molybdenum plays a role in limiting carbon nanotube diameter. For example, run PXE2-284, produced carbon nanotubes having a median and mode external diameter of 9.63 nm and 11.06 nm, respectively. Additionally, only 54% of the resulting carbon nanotubes had an external diameter less than 10 nm compared to 85% in run PXE2-285, where Mo was used in the precursor composition. Figures 2A-2D further illustrates the effect of removing either Fe or Mo from the catalyst precursor on carbon nanotube diameter distribution. Taken together, these results demonstrate that iron acts to maintain carbon yield while molybdenum promotes production of a smaller diameter carbon nanotube.

## EXAMPLE 2

### *Objective*

[062] With reference to Figure 3, this example demonstrates the effect of reaction temperature and gas composition on carbon yield and carbon nanotube diameter.

### *Methods*

[063] Catalyst compositions having the formulations of PXE2-282 and PXE2-285 in Figure 1 were used in this test as a reference. To determine the impact of reaction temperature on the resulting nanotube product, reactions were carried out at temperatures between 610-675 °C. Further, these tests determined the impact on the resulting nanotube product due to changes in ethylene concentration in the gas feed for variations of ethylene concentration between 30-40 %.

### *Results*

[064] Increasing the reaction temperature and/or lowering the gas composition from 40% to 30% ethylene decreases the carbon yield and increases the diameter of the carbon nanotubes. Thus, in order to maximize carbon yield and to produce small diameter carbon nanotubes, the catalytic reaction should occur at about 610 °C with a reactive gas mixture containing 40% ethylene.

## EXAMPLE 3

### *Objective*

[065] This example compares the electrical conductivity of composites containing primarily small diameter multi-wall carbon nanotubes having between 3-6 walls (diameters of 4-8 nm) to composites comprising larger diameter carbon nanotubes. This example and the following

examples utilize the material prepared according to the current invention and identified as PXE2-282 in Figure 1 (referred to as SMW-100).

#### *Methods*

[066] Carbon nanotubes produced by the methods and catalyst compositions of the current invention (hereinafter, SMW-100 refers to multi-wall carbon nanotubes produced by the catalyst composition described for PXE2-282 in figure 1) were compared to various commercially available carbon nanotubes having diameter distributions described in Table 1 and Figures 4A-D. The following Table 1 provides the carbon nanotube diameter distributions for various commercially available multi-wall carbon nanotubes and SMW-100. For example, with regard to SMW-100 ten percent of the nanotubes have diameters smaller than 4.2 nm, 50% of the total nanotubes have diameters smaller than 6.7 nm and 90% of the total nanotubes have diameters smaller than 12 nm.

	10%	50%	90%
<b>SMW-100</b>	4.2 nm	6.7 nm	12.0 nm
<b>MWCNT A</b>	5.5 nm	7.8 nm	13.0 nm
<b>MWCNT B</b>	7.4 nm	12.0 nm	16.5 nm
<b>MWCNT C</b>	7.1 nm	9.9 nm	13.3 nm

TABLE 1

[067] Polycarbonate Makrolon 2600 PC granules were melt mixed with the carbon nanotube sources described in Table 1. Melt mixing was performed in a DSM micro-compounder (15 cm<sup>3</sup>) under the following conditions: screw speed - 200 rpm; temperature - 280°C; time - 5 min). Pressed plates (60 mm diameter x 0.5 mm thickness) were prepared from extruded strands (temperature: 280°C, time: 1 min, pressure: 100 kN). Carbon nanotube samples were characterized by TGA and TEM analysis (Figures 4A-D).

[068] Resistivity was measured with a Keithley 6517A Electrometer in combination with a Keithley 8009 test fixture (for resistivity > 10<sup>7</sup> Ohm cm) or a strip test fixture (for resistivity < 10<sup>7</sup> Ohm cm). For the purposes of this disclosure, the term percolation threshold is that concentration of carbon loading at which there is one, and only one, continuous conducting pathway in the material.

*Results*

[069] Figure 5 demonstrates that the SMW-100 carbon nanotube material provides the lowest electrical percolation threshold. As depicted in Figure 5, a CNT loading of 0.33 wt.% satisfied the requirement for electrical percolation. As shown by Figure 5, SMW-100 provided resistivity reading of  $10^4$ - $10^2$  Ohm/cm for loadings ranging from 0.5-1.0 wt%. In contrast, the comparative carbon nanotubes having diameters between 7-9 nm (MWNT A), 10-11 nm (MWNT C), and 12-15 nm (MWNT B) respectively yielded percolation thresholds of 0.50 wt%, 0.50 wt% and 0.55-0.60 wt%.

[070] Based on the above, results, the use of a batch of straight multi-wall carbon nanotubes having the characteristics of SMW-100 provided by Table 1 and Figure 1 will provide higher conductivity properties at lower loading levels than other commercially available sources of multi-wall carbon nanotubes.

**EXAMPLE 4***Objective*

[071] This study compares the performance of composites based on commercially available multi-wall carbon nanotubes dispersed in Nylon 66 resin to composites prepared from SMW-100 carbon nanotubes dispersed in Nylon66 resin.

*Methods*

[072] CNT-Nylon 6,6 compounding was performed via twin screw extrusion. The resulting composites were then injection-molded into standard ASTM test bars and plaque (4in by 4in by 3.2mm). Conductivity measurements were then performed on the injection-molded plaques using a standard ProStat resistance meter as per ASTM D-257 for Volume and Surface resistance. Surface resistance was determined using PRF-912B probe at 25 predetermined locations on each surface of the injection molded plaques – i.e. 25 points on the front surface and 25 points on the back surface of the plaques. This rigorous testing is designed to bring out any minor variations in electrical performance due to non-uniformity in material and/or processing. The front surface of the plaques corresponds to where the ejector pins are located. The back surface of the plaques corresponds to the fixed part of the tool (closer to Nozzle). Volume resistances of the plaques were tested using a PRF-911 concentric ring at five locations per sample and averaged for both the front and back of the plaques.

*Results*

[073] The surface resistance data is depicted in Figures 6A and 6B. SMW-100 composites exhibited lower and more uniform electrical resistance properties after molding compared to the commercially available multi-wall carbon nanotube (MWCNT). The surface resistance, of the MWCNT and SMW-100 filled samples are fairly uniform and consistent with very good agreement on the front and back surfaces of the plaques.

[074] Furthermore, Nylon 6,6 based composite with SMW-100 showed higher conductivity values than Nylon 6,6 based composite with commercially available grades of MWCNT. The SMW-100 composites also showed more uniform resistance values, with a narrower range of standard deviation between the tested points and between the front and back surfaces of the plaques. As reflected by Figures 6A and 6B, composites prepared from the inventive carbon nanotube material, i.e. a batch of nanotubes having a narrow distribution of diameters and number of walls, have improved conductivity when compared to currently available materials.

#### EXAMPLE 5

##### *Objective*

[075] This example compares the surface resistivity of thin films containing respectively: SMW-100; single-wall carbon nanotubes (SWNT); double-wall carbon nanotubes (DWNT); and, commercially available multi-wall carbon nanotubes (MWCNT B - from Example 3).

##### *Methods*

[076] Carbon nanotube-based thin films having different degrees of transparencies (80-95% transmittance) were prepared using solutions containing 1 g carbon nanotube /liter in 1% Triton-X 100 surfactant. The solutions were then sonicated and centrifuged. The various carbon nanotube inks were deposited on a PET 505 substrate employing the rod coating technique.

##### *Results*

[077] As depicted in Figure 7, films having 80-90 % transparency prepared with SWNTs demonstrate higher electrical conductivity than the other type of carbon nanotube materials in thin film. However, films prepared using the novel batch material of the current invention, i.e. the SMW-100, had better conductivity performance than films incorporating conventional DWNT and MWNT.

[078] Other embodiments of the current invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. Thus, the foregoing specification is considered merely exemplary of the current invention with the true scope and spirit of the invention being defined by the following claims.

We claim:

1. A catalyst precursor composition comprising:  
a support; and  
mixed metal oxides on a surface of the support, wherein the mixed metal oxides are selected from the group consisting of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{Co}_x\text{Fe}_y\text{MoO}_4$ ,  $\text{Fe}_2(\text{MoO}_4)_3$  and blends thereof,  
wherein x and y each represent the atomic ratio of the corresponding metal oxide, wherein x is from about 1.6 to 6.5, and y is from about 0 to 10.5.
2. The catalyst precursor composition of claim 1, wherein x is from about 2.44 to 4.88 and y is from about 1.75 to 6.98.
3. The catalyst precursor composition of claim 1, wherein the mixed metal oxide is selected from the group consisting of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{Co}_{3.3}\text{Fe}_{2.62}\text{MoO}_4$  and blends thereof.
4. The catalyst precursor composition of claim 1, wherein the mixed metal oxide is selected from the group consisting of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{Co}_{3.3}\text{Fe}_y\text{MoO}_4$  and blends thereof, where y may range from 2.6 to 6.3.
5. The catalyst precursor composition of any of claims 1 to 4, wherein the support comprises alumina and magnesium aluminate.
6. The catalyst precursor composition of claim 5 wherein magnesium oxide is located on the surface of the support.
7. The catalyst precursor composition of claim 6 wherein the alumina is gamma-alumina.
8. A catalyst precursor composition comprising:  
a support comprising alumina and a magnesium compound; and  
mixed metal oxides on a surface of the support, wherein the metal components of the mixed metal oxides are selected from the group consisting of cobalt, molybdenum and iron,  
wherein said cobalt is from about 0.5 to about 2.0 percent by weight concentration of the total metals of said catalyst precursor composition, said molybdenum is from about 0.3 to about 2.0 percent by weight concentration of the total metals of said catalyst precursor composition, said iron is from about 0 to about 3.0 percent by weight concentration of the total metals of said catalyst precursor composition, said magnesium is from about 0.5 to about 3.3 percent by weight concentration of the total metals of said catalyst precursor composition.
9. The catalyst precursor composition of claim 8, wherein the alumina is gamma-alumina.
10. The catalyst precursor composition of claim 8, wherein the magnesium compound is magnesium aluminate.

11. The catalyst precursor composition of claim 8, wherein magnesium oxide is present on the surface of the support.
12. The catalyst precursor composition of claim 8, wherein said catalyst precursor composition has a particle size between about 20 and about 500 microns.
13. The catalyst precursor composition of claim 8, wherein said catalyst precursor composition has a particle size between about 20 and about 250 microns.
14. The catalyst precursor composition of claim 8, wherein said catalyst precursor composition has a particle size between about 20 and about 150 microns.
15. The catalyst precursor composition of claim 8, wherein said catalyst precursor composition is substantially free of  $\text{FeAlO}_3$  and  $\text{CoAl}_2\text{O}_4$ .
16. The catalyst precursor composition of claim 8, wherein said catalyst precursor composition has less than 0.5 percent by weight of  $\text{FeAlO}_3$  and less than 0.5 percent by weight of  $\text{CoAl}_2\text{O}_4$ .
17. The catalyst precursor composition of claim 8, wherein said cobalt is about 0.75 to about 1.5 percent by weight concentration of the total metals of said catalyst precursor composition, said molybdenum is from about 0.5 to about 1.0 percent by weight concentration of the total metals of said catalyst precursor composition, said iron is from about 0.5 to about 2.0 percent by weight concentration of the total metals of said catalyst precursor composition, and said magnesium is from about 0.5 to about 1.0 percent by weight concentration of the total metals of said catalyst precursor composition
18. A catalyst composition comprising:
  - a support comprising gamma-alumina and magnesium aluminate; and
  - the surface of said support carrying cobalt, molybdenum and iron, wherein said cobalt is in the form of metallic cobalt and is from about 0.5 to about 2.0 percent by weight of said catalyst composition, wherein said molybdenum is in the form of molybdenum carbide and is from about 0.3 to about 2.0 percent by weight concentration of said catalyst composition, and wherein said iron is in the form of metallic iron and iron carbide and the total iron component is from about 0 to about 3.0 percent by weight concentration of said catalyst composition.
19. The catalyst composition of claim 18, wherein the gamma-alumina is from about 91.0 to about 97.6 percent by weight of said catalyst composition and wherein the magnesium, in the form of  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$ , is from about 0.5 to about 3.3 percent by weight of said catalyst composition.
20. The catalyst composition of claim 18, wherein the gamma-alumina is from about

94.8 to about 97.6 percent by weight concentration of said catalyst composition and wherein the magnesium is from about 0.5 to about 1.0 percent by weight concentration of said catalyst composition.

21. The catalyst composition of claim 18, wherein said cobalt is in the form of metallic cobalt and is from about 0.75 to about 1.5 percent by weight concentration of said catalyst composition, wherein said molybdenum is in the form of molybdenum carbide and is from about 0.5 to about 1.0 percent by weight concentration of said catalyst composition, and wherein said iron is in the form of metallic iron and iron carbide and the total iron component is from about 0.5 to about 2.0 percent by weight concentration of said catalyst composition.

22. The catalyst composition of claim 18, wherein the molybdenum carbide and iron carbide comprise from zero to less than 2.0 percent by weight of said catalyst composition.

23. The catalyst composition of claim 18, wherein said metallic cobalt is on the surface of said support as particles having sizes between about 1.5 nm to about 3.0 nm.

24. The catalyst composition of claim 18, wherein said metallic cobalt is on the surface of said support as particles having sizes between about 1.5 nm to about 2.2 nm.

25. The catalyst composition of claim 18, wherein magnesium oxide is present on the surface of the support.

26. The catalyst composition of claim 18, wherein said catalyst composition has a particle size between about 20 and about 500 microns.

27. The catalyst composition of claim 18, wherein said catalyst composition has a particle size between about 20 and about 250 microns.

28. The catalyst composition of claim 18, wherein said catalyst composition has a particle size between about 20 and about 150 microns.

29. A composition of matter comprising:

a plurality of spent catalyst particles, said spent catalyst particles carrying catalytically formed carbon products, wherein at least 70% of the carbon products carried by said spent catalyst particles are multi-wall carbon nanotubes and wherein at least 60% of the multi-wall carbon nanotubes have between about 3 and about 8 walls.

30. The composition of matter of claim 29, wherein at least 98% of the carbon products are multi-wall carbon nanotubes.

31. The composition of matter of claim 29, wherein at least 60% of said multi-wall carbon nanotubes have between 3 and 6 walls.

32. The composition of matter of claim 29, wherein at least 75% of said multi-wall carbon nanotubes have between about 3 and about 8 walls.

33. The composition of matter of claim 29, wherein at least 75% of said multi-wall carbon nanotubes have between 3 and 6 walls.
34. The composition of matter of claim 29, wherein at least 85% of said multi-wall carbon nanotubes have between about 3 and about 8 walls.
35. The composition of matter of claim 29, wherein at least 85% of said multi-wall carbon nanotubes have between 3 and 6 walls.
36. The composition of matter of claim 29, wherein at least 90% of said multi-wall carbon nanotubes have between about 3 and about 8 walls.
37. The composition of matter of claim 29, wherein at least 90% of said multi-wall carbon nanotubes have between 3 and 6 walls.
38. The composition of matter of claim 29, wherein at least 60% of said multi-wall carbon nanotubes have external diameters less than about 7 nm.
39. The composition of matter of claim 29, wherein at least 75% of said multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
40. The composition of matter of claim 29, wherein at least 85% of said multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
41. The composition of matter of claim 29, wherein at least 90% of said multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
42. A method of preparing a catalyst precursor composition comprising:  
preparing a solution comprising two or more metallic compounds, wherein the metallic portions of the compounds are selected from the group consisting of cobalt, iron, molybdenum, magnesium and mixtures thereof;  
reacting the solution of metallic compounds with aluminum hydroxide to yield a product comprising reacted particles;  
drying the particles;  
calcining the particles under a flowing gas; and  
reducing the size of the particles.
43. The method of claim 42, wherein the cobalt-containing compound is selected from the group consisting of cobalt acetate and cobalt nitrate; the iron-containing compound is selected from the group consisting of iron acetate and iron nitrate; the molybdenum-containing compound is selected from the group consisting of ammonium heptamolybdate and ammonium dimolybdate; and the magnesium-containing compound is magnesium nitrate.
44. The method of claim 42, wherein the solution comprises cobalt acetate, iron nitrate, ammonium heptamolybdate, and magnesium nitrate.



45. The method of claim 42, wherein the reaction between the solution of metallic compounds and the aluminum hydroxide is performed at room temperature for a period of about two to four hours.
46. The method of claim 42, wherein the product of reacted particles has a paste-like consistency.
47. The method of claim 42, wherein prior to drying, said product comprising reacted particles has a moisture content between about 20% and 40% by weight.
48. The method of claim 42, wherein prior to drying, said product comprising reacted particles has a moisture content between about 25% and 30% by weight.
49. The method of claim 42, further comprising the step of manipulating the reacted particles by kneading said particles for a period between about 20 minutes to about 50 minutes.
50. The method of claim 42, wherein the drying step is performed at a temperature between about 30°C and about 50°C.
51. The method of claim 42, wherein the drying step results in a moisture content from about 10% to about 20% water by weight.
52. The method of claim 42, wherein the drying step results in a moisture content of less than 15% water by weight.
53. The method of claim 42, wherein the calcining step is performed at a temperature between about 400° and 600°C for a period of time of about three hours to about five hours.
54. The method of claim 42, wherein the calcining step is performed at a temperature between about 400° and about 500°C for a period of time between about 3.5 hours and 4.5 hours.
55. The method of claim 42, wherein the calcining step is performed at a temperature between about 440° and about 460°C for a period of time between about 3.5 hours and 4.5 hours.
56. The method of claim 42, wherein the step of reducing particle size produces particles between about 20  $\mu\text{m}$  and about 500  $\mu\text{m}$ .
57. The method of claim 42, wherein the step of reducing particle size produces particles between about 20  $\mu\text{m}$  and about 250  $\mu\text{m}$ .
58. The method of claim 42, wherein the step of reducing particle size produces particles between about 20  $\mu\text{m}$  and about 150  $\mu\text{m}$ .
59. A method of preparing a catalyst precursor composition comprising:  
preparing a solution comprising two or more metallic compounds, wherein the metallic portions of the compounds are selected from the group consisting of cobalt, iron, molybdenum, and mixtures thereof;  
preparing a mixture of aluminum hydroxide and magnesium hydroxide;

reacting the mixture of aluminum hydroxide and magnesium hydroxide with the solution of compounds to yield a product comprising reacted particles;

drying the particles;

calcining the particles under a flowing gas; and

reducing the size of the particles.

60. The method of claim 59, wherein the calcining step is performed at a temperature between about 400° and about 500°C over a period of time between about three hours to about five hours.

61. The method of claim 59, wherein the calcining step is performed at a temperature between about 425° and about 475°C for a period of time between about 3.5 hours and 4.5 hours.

62. The method of claim 59, wherein calcining step is performed at a temperature between about 440° and about 460°C for a period of time between about 3.5 hours and 4.5 hours.

63. A method of preparing multi-wall carbon nanotubes comprising:

placing catalyst precursor particles having a particle size between about 20 microns and 500 microns in a reactor chamber, said catalyst precursor composition comprising:

a support; and

a phase of mixed metal oxides on a surface of the support, wherein the metals of said mixed metal oxides are selected from the group consisting of cobalt, molybdenum and iron;

flowing a stream of non-reactive gas through the reaction chamber at a flow rate sufficient to fluidize the catalyst precursor particles thereby forming a fluidized bed;

heating said fluidized bed to a temperature between about 600°C and about 750°C;

flowing a reactive gas mixture through the reaction chamber while maintaining the temperature of said fluidized bed between about 600°C and about 750°C, wherein said flow of reactive gas reduces the metals oxides of said catalytic precursor composition to yield a composition comprising catalyst particles; and,

continuing to flow said reactive gas mixture through the reaction chamber thereby producing multi-wall carbon nanotubes on the catalyst particles.

64. The method of claim 63, wherein between about 60% and about 95% percent of the resulting multi-wall carbon nanotubes have between three and seven walls.

65. The method of claim 63, wherein the temperature of the fluidized bed is maintained below 650 °C during passage of gases through the fluidized bed.

66. The method of claim 63, wherein said reactive gas mixture comprises nitrogen and ethylene.

67. The method of claim 66, wherein said reactive gas mixture contains between about 10% and 50% by volume ethylene.
68. The method of claim 66, wherein said reactive gas mixture contains between about 20% and 30% by volume ethylene.
69. The method of claim 63, wherein said gases pass through said bed at a rate of about 70 liters/min per kg of catalyst precursor to about 150 liters/min per kg of catalyst precursor.
70. The method of claim 63, wherein said gases pass through said bed at a rate of about 90 liters/min per kg of catalyst precursor to about 120 liters/min per kg of catalyst precursor.
71. The method of claim 63, wherein said gases pass through said bed at a rate of about 100 liters/min per kg of catalyst precursor.
72. The method of claim 63, wherein following reduction of said metal oxides the reactive gas mixture is flowed through the reaction chamber for a period of time between about 15 and to about 30 minutes.
73. The method of claim 63, wherein following the catalytic reaction said catalyst particles are spent catalyst particles carrying said multi-wall carbon nanotubes and further comprising the step of removing the spent catalyst particles carrying said multi-wall carbon nanotubes.
74. The method of claim 63, wherein said cobalt is from about 0.5 to about 2.0 percent by weight concentration of metals of said catalyst precursor composition, said molybdenum is from about 0.3 to about 2.0 percent by weight concentration of the total metals of said catalyst precursor composition, said iron is from about 0 to about 3.0 percent by weight concentration of the total metals of said catalyst precursor composition.
75. The method of claim 63, wherein the support comprises alumina and magnesium aluminate.
76. A batch of carbon nanotubes comprising:  
multi-wall carbon nanotubes, wherein said multi-wall carbon nanotubes comprise from about 60% to about 100% of said batch by weight and wherein at least 60% of the multi-wall carbon nanotubes have between about 3 and about 7 walls.
77. The batch of carbon nanotubes of claim 76, wherein at least 75% of the multi-wall carbon nanotubes have between about 3 and about 7 walls.
78. The batch of carbon nanotubes of claim 76, wherein at least 85% of the multi-wall carbon nanotubes have between about 3 and about 7 walls.
79. The batch of carbon nanotubes of claim 76, wherein at least 90% of the multi-wall carbon nanotubes have between about 3 and about 7 walls.

80. The batch of carbon nanotubes of claim 76, wherein at least 60% of the multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
81. The batch of carbon nanotubes of claim 76, wherein at least 75% of the multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
82. The batch of carbon nanotubes of claim 76, wherein at least 85% of the multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
83. The batch of carbon nanotubes of claim 76, wherein at least 90% of the multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
84. The batch of carbon nanotubes of any of claims 76 to 83, wherein said multi-wall carbon nanotubes comprise from about 80% to about 98% of said batch by weight
85. A composition comprising multi-wall carbon nanotubes, wherein from about 60% to about 90% by weight of said multi-wall carbon nanotubes have 3 to 7 walls.
86. The composition of matter of claim 85, wherein at least 75% of said multi-wall carbon nanotubes have between about 3 and about 7 walls.
87. The composition of matter of claim 85, wherein at least 85% of said multi-wall carbon nanotubes have between about 3 and about 7 walls.
88. The composition of matter of claim 85, wherein at least 90% of said multi-wall carbon nanotubes have between about 3 and about 7 walls.
89. The composition of matter of claim 85, wherein at least 60% of said multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
90. The composition of matter of claim 85, wherein at least 75% of said multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
91. The composition of matter of claim 85, wherein at least 85% of said multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
92. The composition of matter of claim 85, wherein at least 90% of said multi-wall carbon nanotubes have external diameters between about 4 nm and about 7 nm.
93. A batch of carbon nanotubes comprising:  
wherein from about 60% to about 100% of said batch by weight of said carbon nanotubes are multi-wall carbon nanotubes and wherein between 50% to about 90% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.
94. The batch of carbon nanotubes of claim 93, wherein between 54% and 85% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.
95. The batch of carbon nanotubes of claim 93, wherein between 60% and 75% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.

96. The batch of carbon nanotubes of claim 93, wherein said multi-wall carbon nanotubes have a median external diameter from about 6.5 nm to about 8.5 nm.
97. The batch of carbon nanotubes of claim 93, wherein said multi-wall carbon nanotubes have a median external diameter from about 7 nm to about 8 nm.
98. The batch of carbon nanotubes of claim 93, wherein said multi-wall carbon nanotubes have a mode external diameter from about 4 nm to about 7 nm.
99. The batch of carbon nanotubes of claim 93, wherein said multi-wall carbon nanotubes have a mode external diameter from about 4.5 nm to about 6.7 nm.
100. The batch of carbon nanotubes of claim 93, wherein said multi-wall carbon nanotubes have a mode external diameter from about 5.1 nm to about 6.2 nm.
101. The batch of carbon nanotubes of any of claims 93-100, wherein said multi-wall carbon nanotubes comprise at least 90% of said batch by weight.
102. The batch of carbon nanotubes of any of claims 93-100, wherein said multi-wall carbon nanotubes comprise at least 98% of said batch by weight.
103. A composition comprising multi-wall carbon nanotubes, wherein between 50% and 90% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.
104. The composition of claim 103, wherein between 54% and 85% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.
105. The composition of claim 103, wherein between 60% and 75% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.
106. The composition of claim 103, wherein said multi-wall carbon nanotubes have a median external diameter from about 6.5 nm to about 8.5 nm.
107. The composition of claim 103, wherein said multi-wall carbon nanotubes have a median external diameter from about 6.5 nm to about 8.5 nm.
108. The composition of claim 103, wherein said multi-wall carbon nanotubes have a mode external diameter from about 4 nm to about 7 nm.
109. The composition of claim 103, wherein said multi-wall carbon nanotubes have a mode external diameter from about 5.1 nm to about 6.2 nm.

Run	WT%				Co salt	Carbon content	Carbon Yield (%)	Median CNT diameter (nm)	Mode diameter (nm)	< 10 nm
	Co	Fe	Mo	Mg						
PXE2-282	1.00	1.88	0.50	0.50	Co-Ac	49.6	100	8.24	6.00	72.9%
PXE2-283	1.00	1.00	0.50	0.50	Co-Ac	49.8	100	7.79	6.17	73.1%
PXE2-284	1.00	0.75	0.00	0.50	Co-Ac	49.2	97	9.63	11.06	54.0%
PXE2-285	1.00	0.75	0.50	0.50	Co-Nt	42.8	75	6.72	5.38	84.9%
PXE2-286	1.00	0.50	0.50	0.50	Co-Nt	43.8	78	7.35	5.19	61.6%
PXE2-288	1.00	0.00	1.00	0.50	Co-Nt	30.1	43	6.98	4.68	83.6%
PXE2-289	1.00	1.88	0.50	0.50	Co-Nt	45.2	82	7.91	5.71	69.4%
PXE2-291	0.50	1.88	0.50	0.50	Co-Nt	43.3	75	9.01	10.14	58.7%
PXE2-292	0.75	1.42	0.50	0.50	Co-Ac	44.2	79	7.58	4.97	78.1%
PXE2-293	0.75	1.42	0.40	0.50	Co-Ac	42.1	72	7.72	6.62	77.0%
PXE2-295	1.00	1.88	0.00	0.00	Co-Ac	39.2	76	7.81	8.25	78.9%
PXE2-296	0.67	1.88	0.50	0.50	Co-Ac	35.6	56	10.03	6.62	50.0%

FIGURE 1

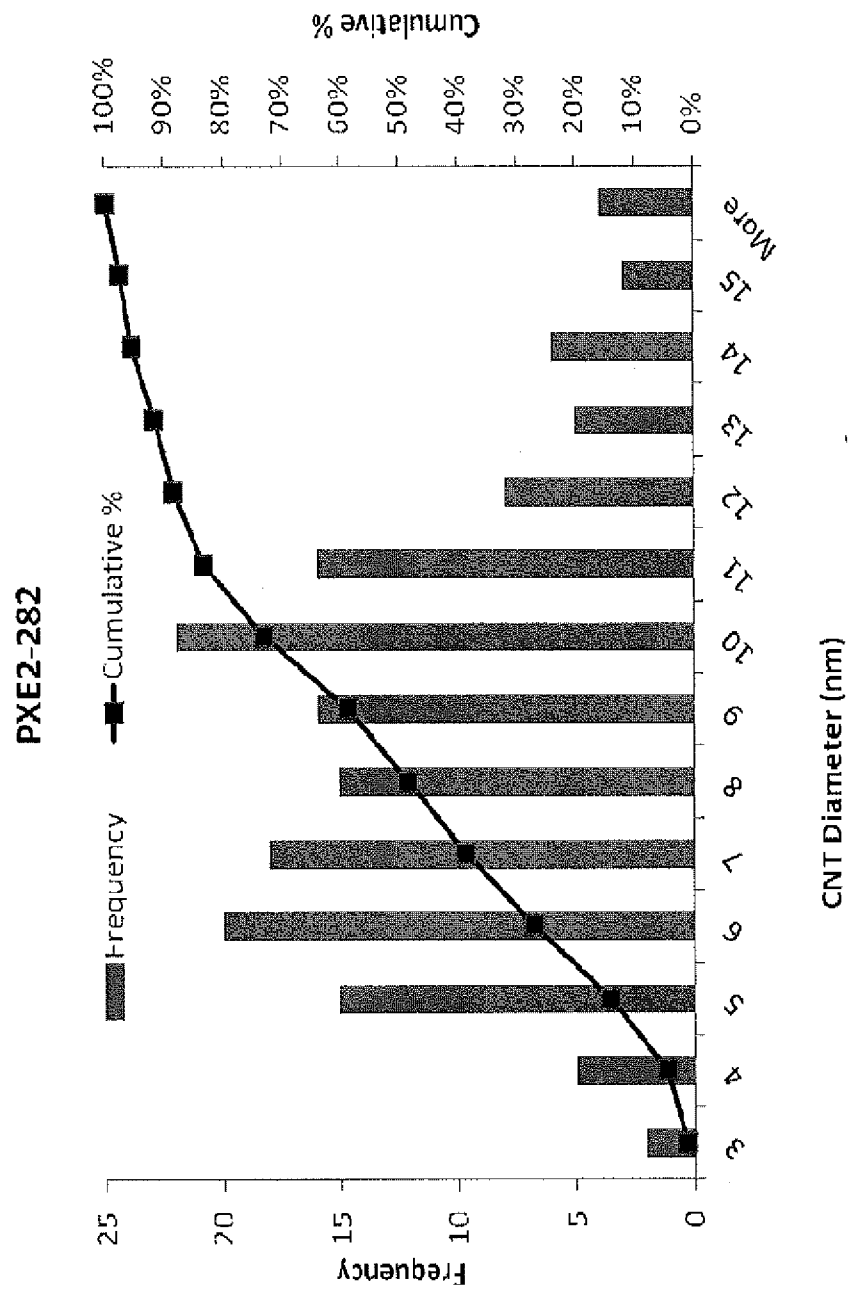


FIGURE 2A

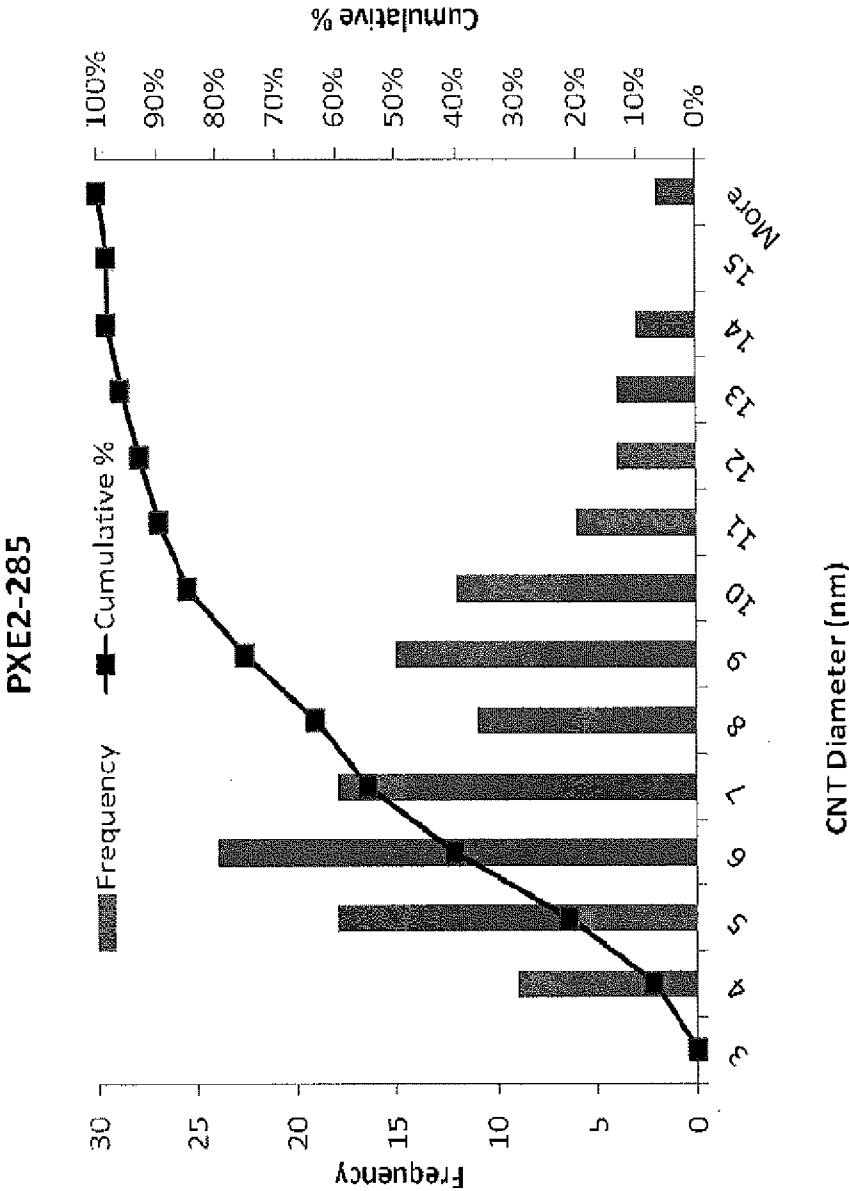


FIGURE 2B



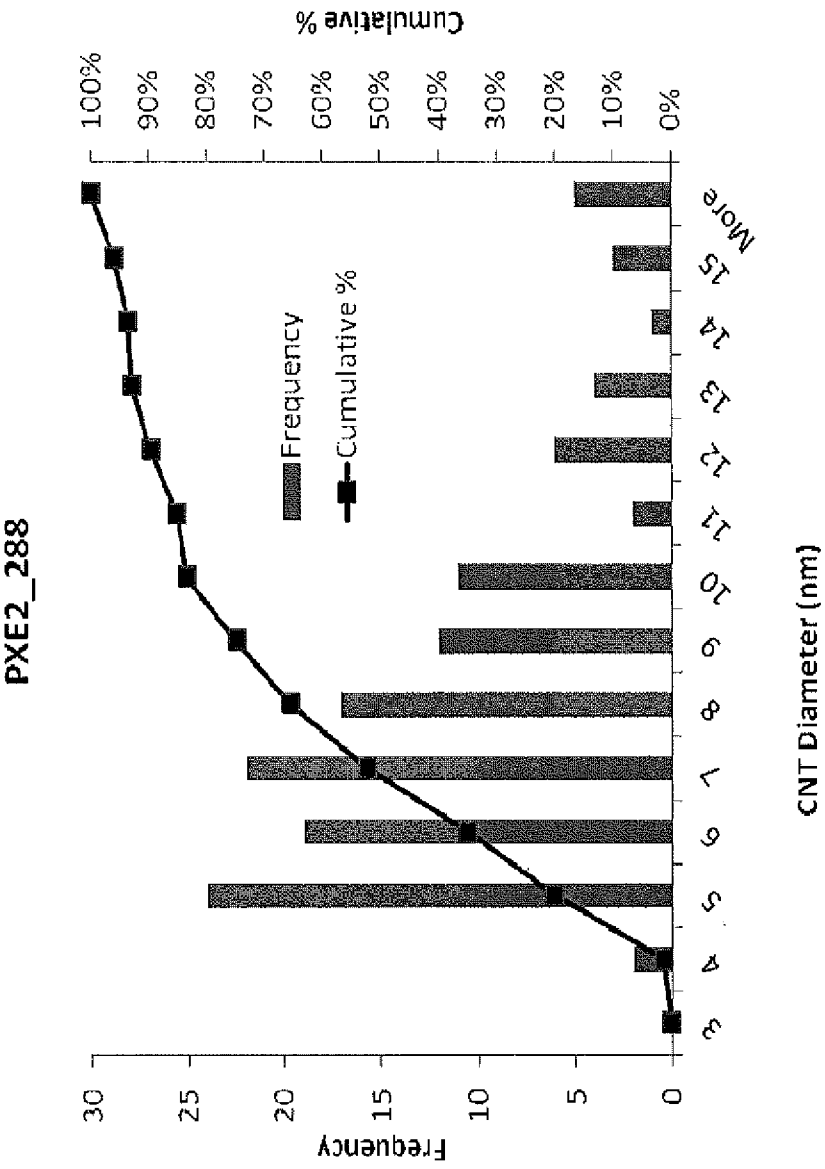


FIGURE 2C

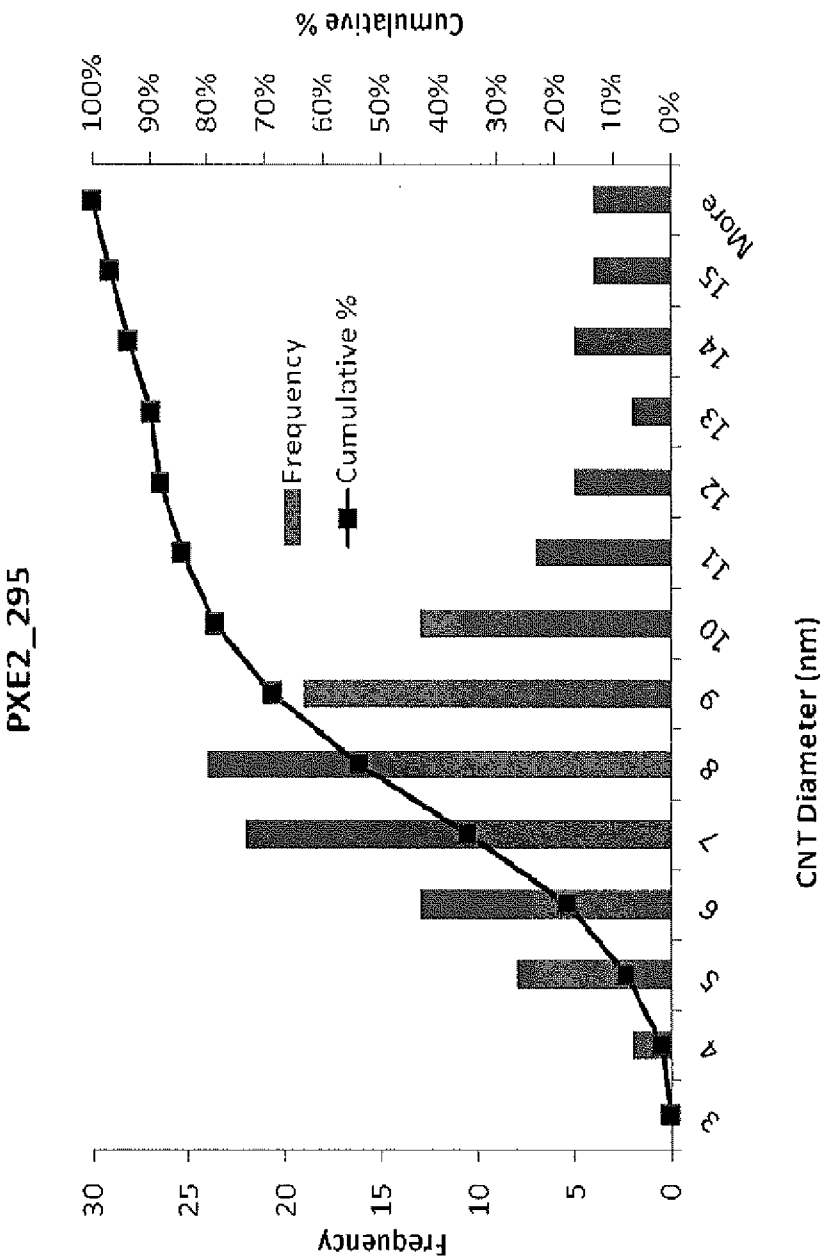


FIGURE 2D

Run	WT %				T(C)	% C <sub>2</sub> H <sub>4</sub>	Carbon content	Carbon Yield (%)	Median CNT diameter (nm)	Mode diameter (nm)	< 10 nm
	Co	Fe	Mo	Mg							
E2-282	1.00	1.88	0.50	0.50	610	40	50	100	8.24	6.00	73%
E2-297	1.00	1.88	0.50	0.50	650	30	39	64	12.09	12.88	35%
E2-298	1.00	1.88	0.50	0.50	675	30	38	61	13.78	15.94	22%
E2-285	1.00	0.75	0.50	0.50	610	40	43	75	6.72	5.38	85%
E2-301	1.00	0.75	0.50	0.50	675	30	34	52	9.80	11.45	53%

FIGURE 3

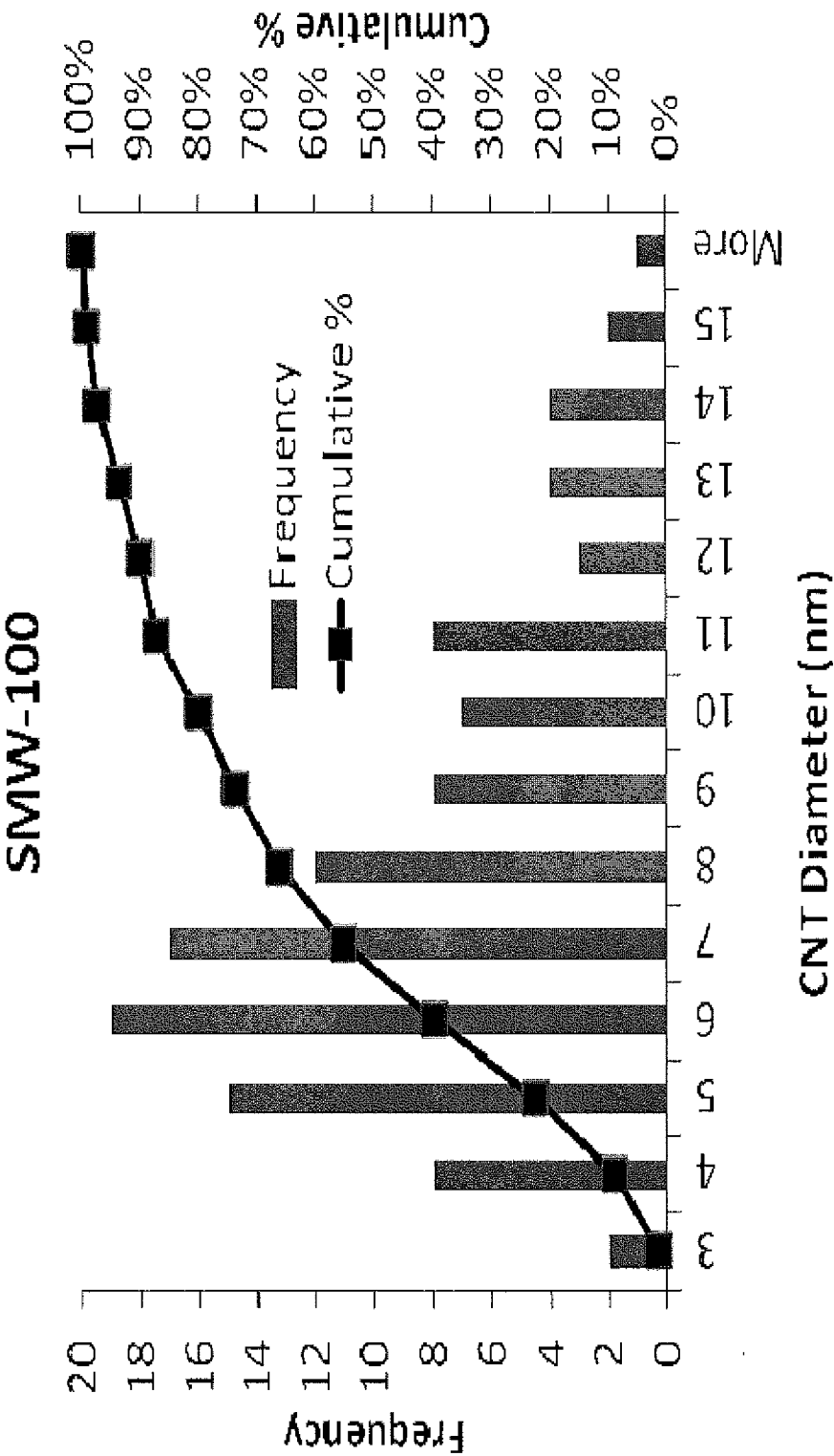


FIGURE 4A

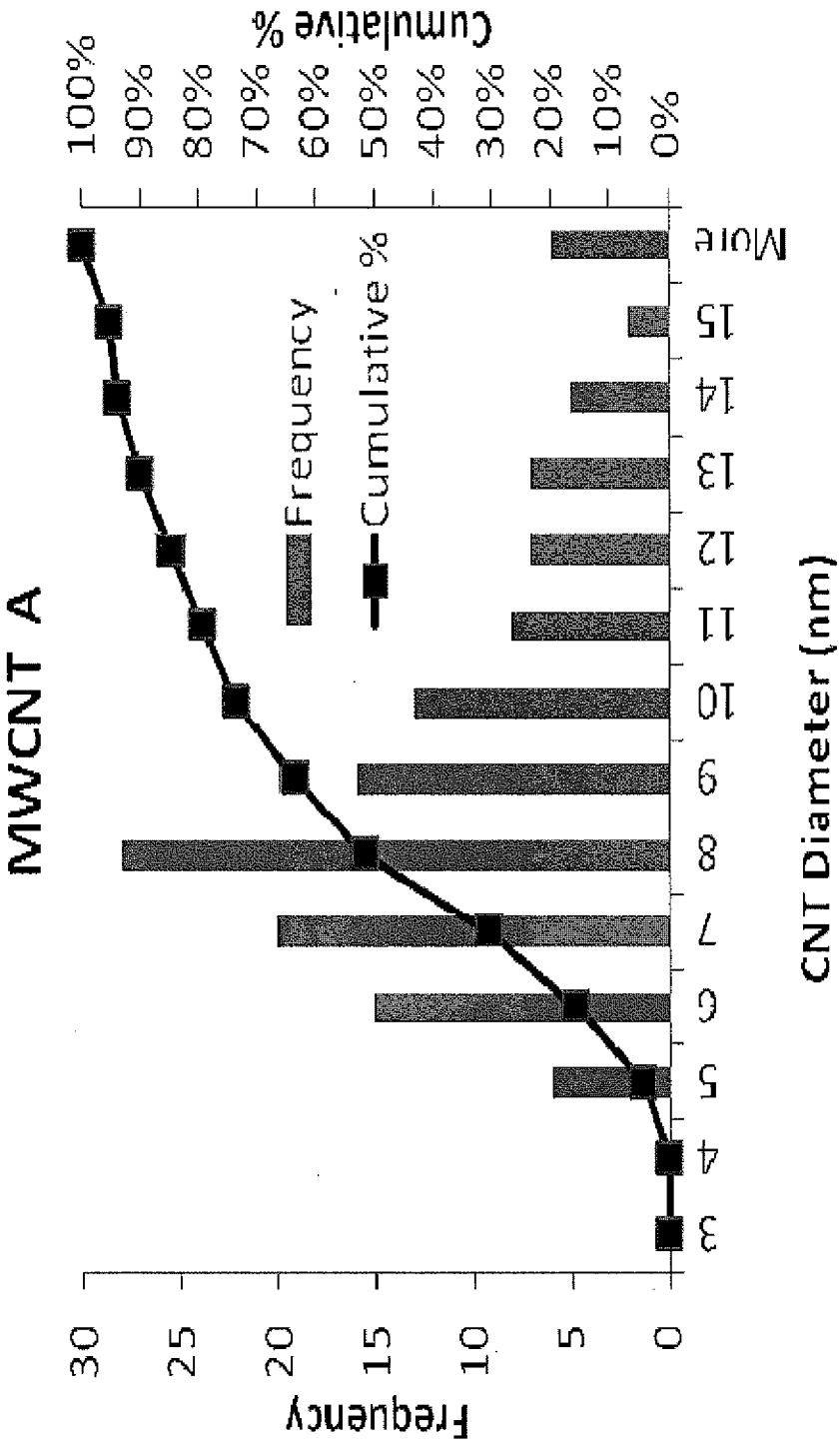


FIGURE 4B

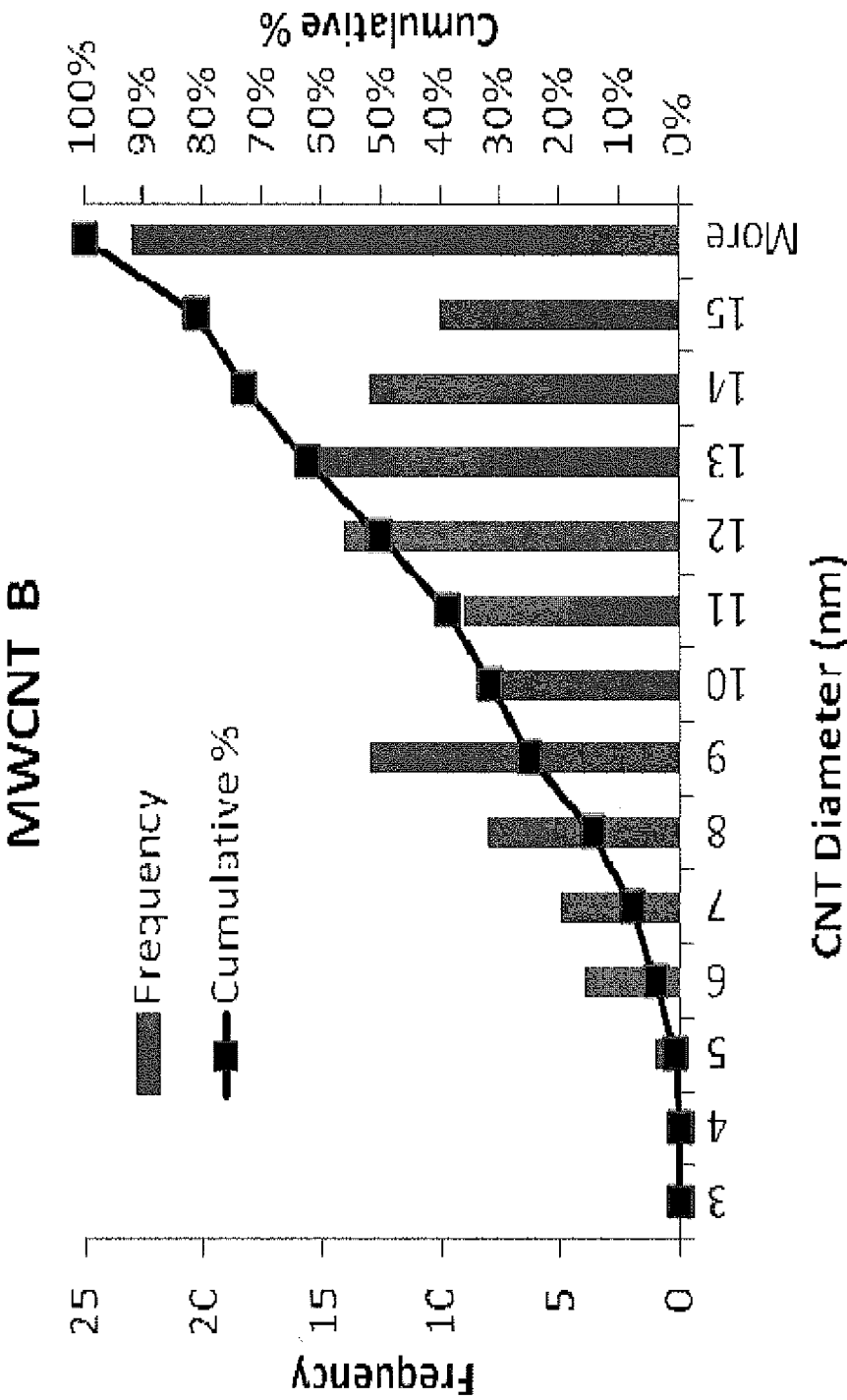


FIGURE 4C

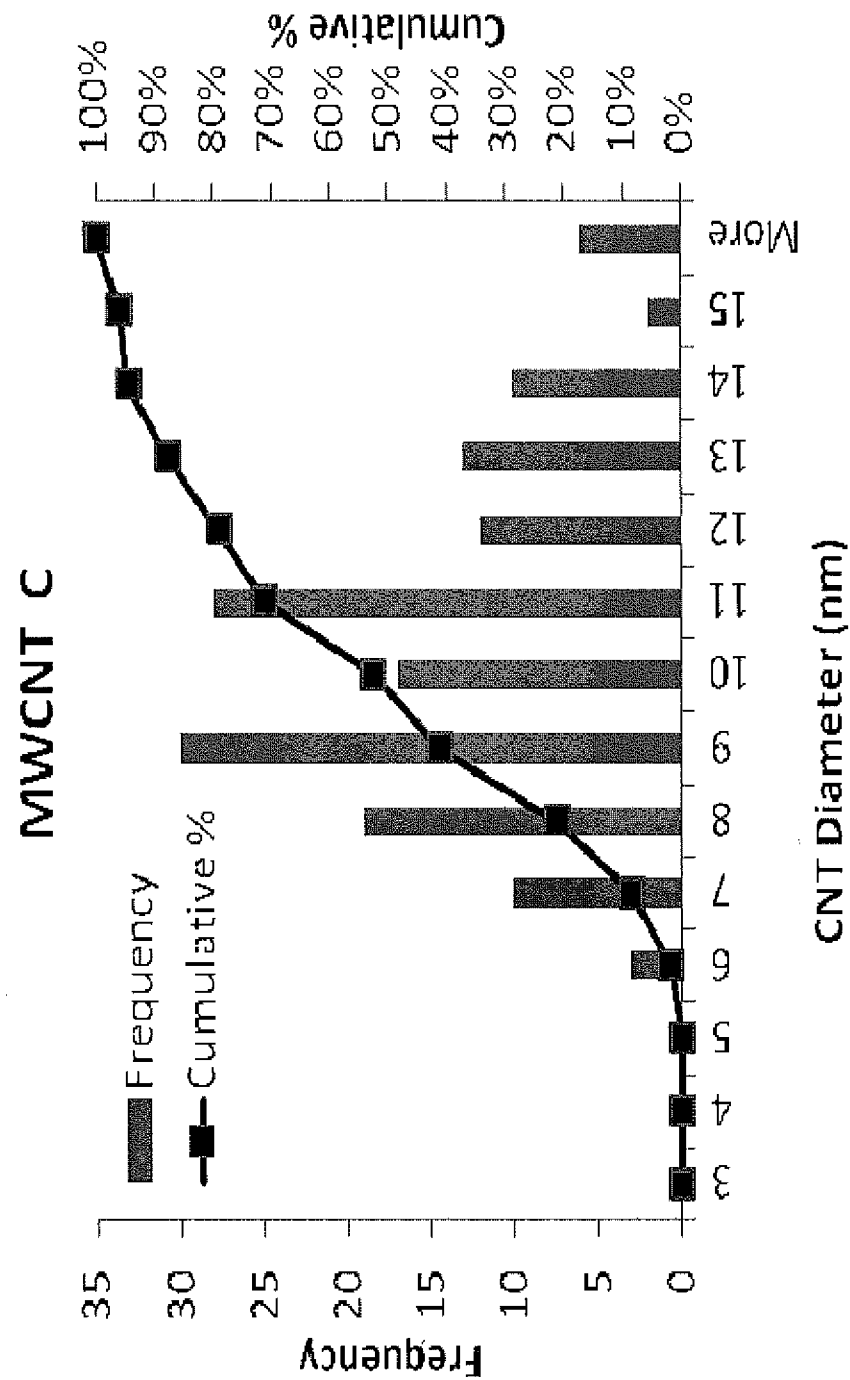


FIGURE 4D

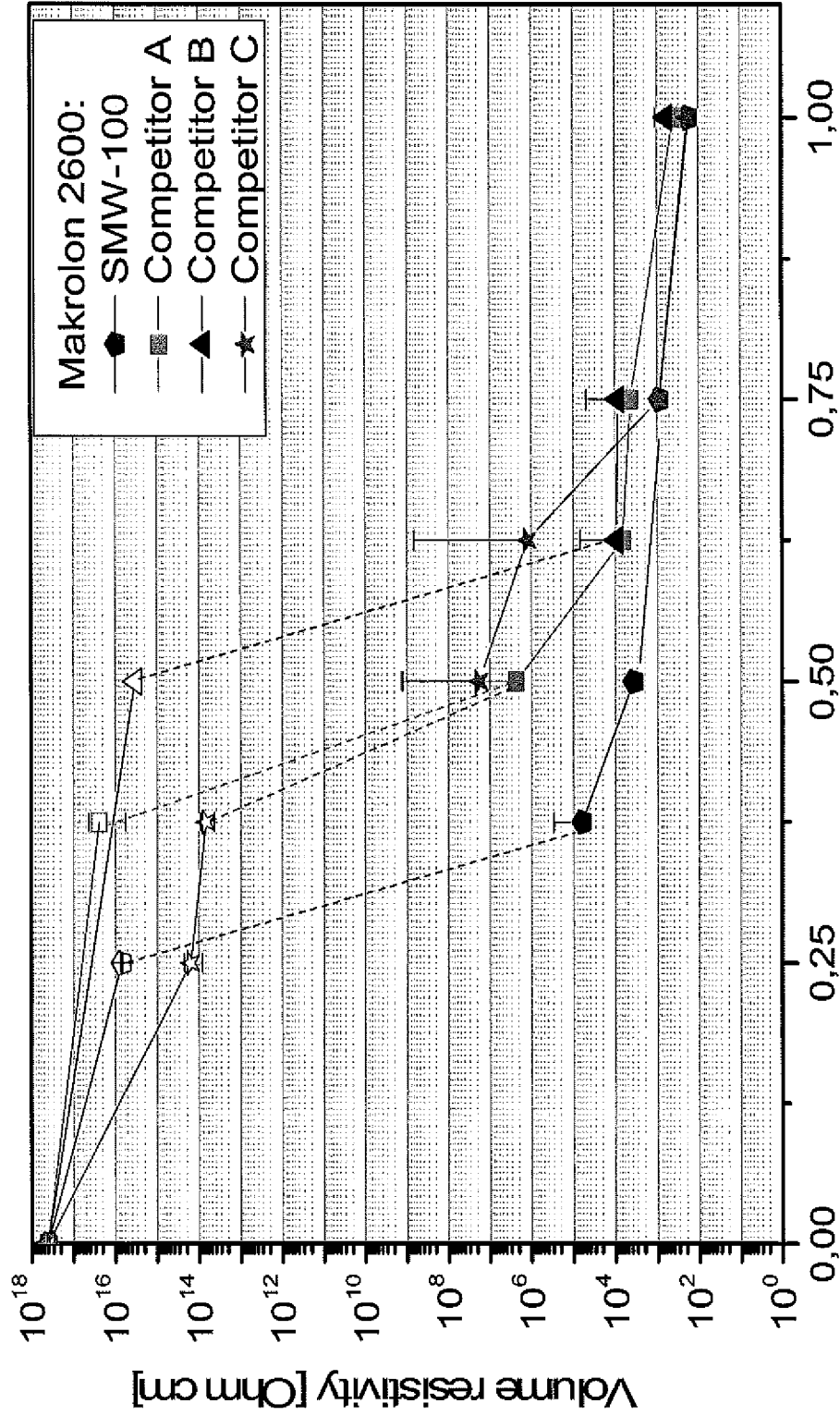


FIGURE 5



FIGURE 6A

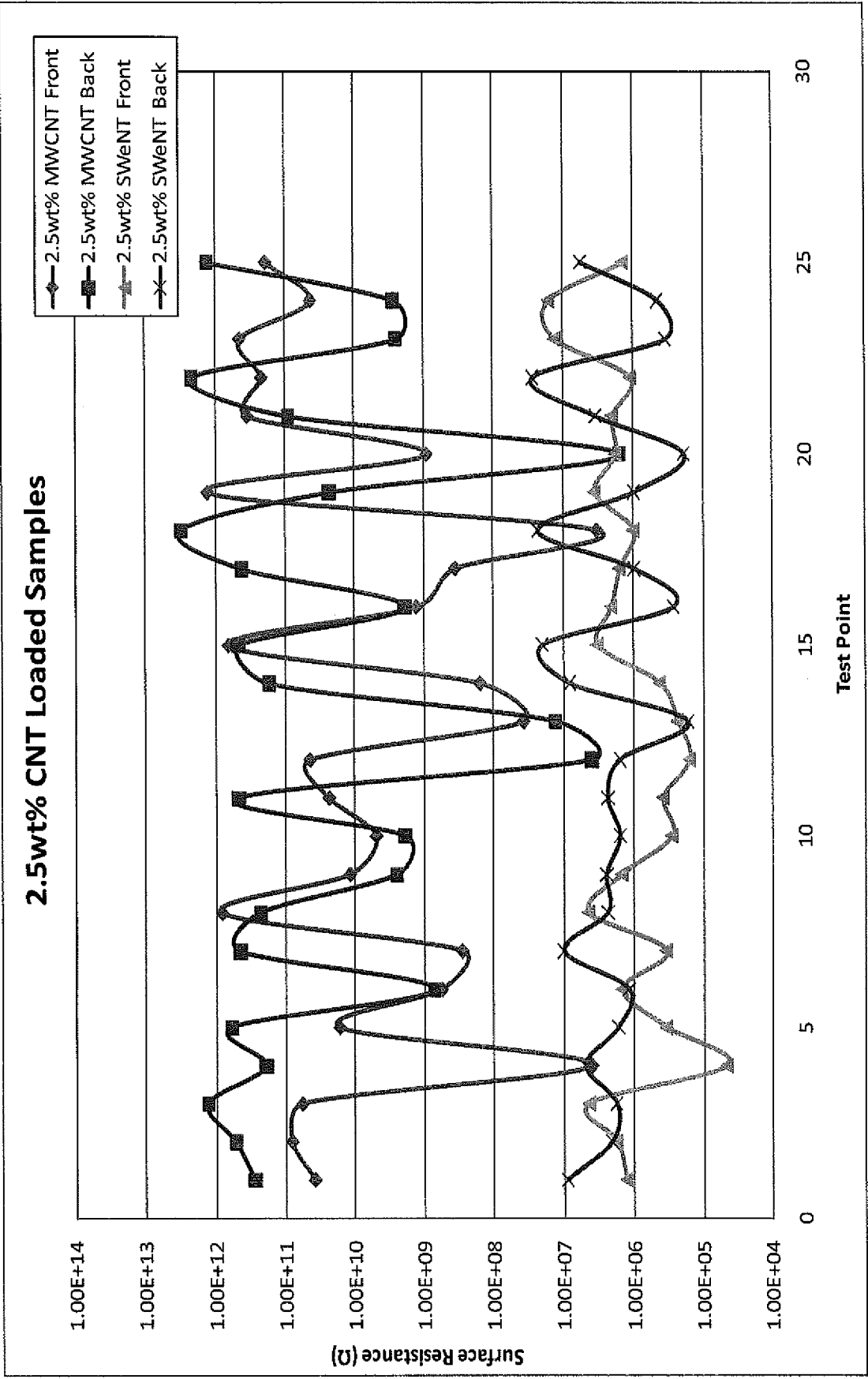
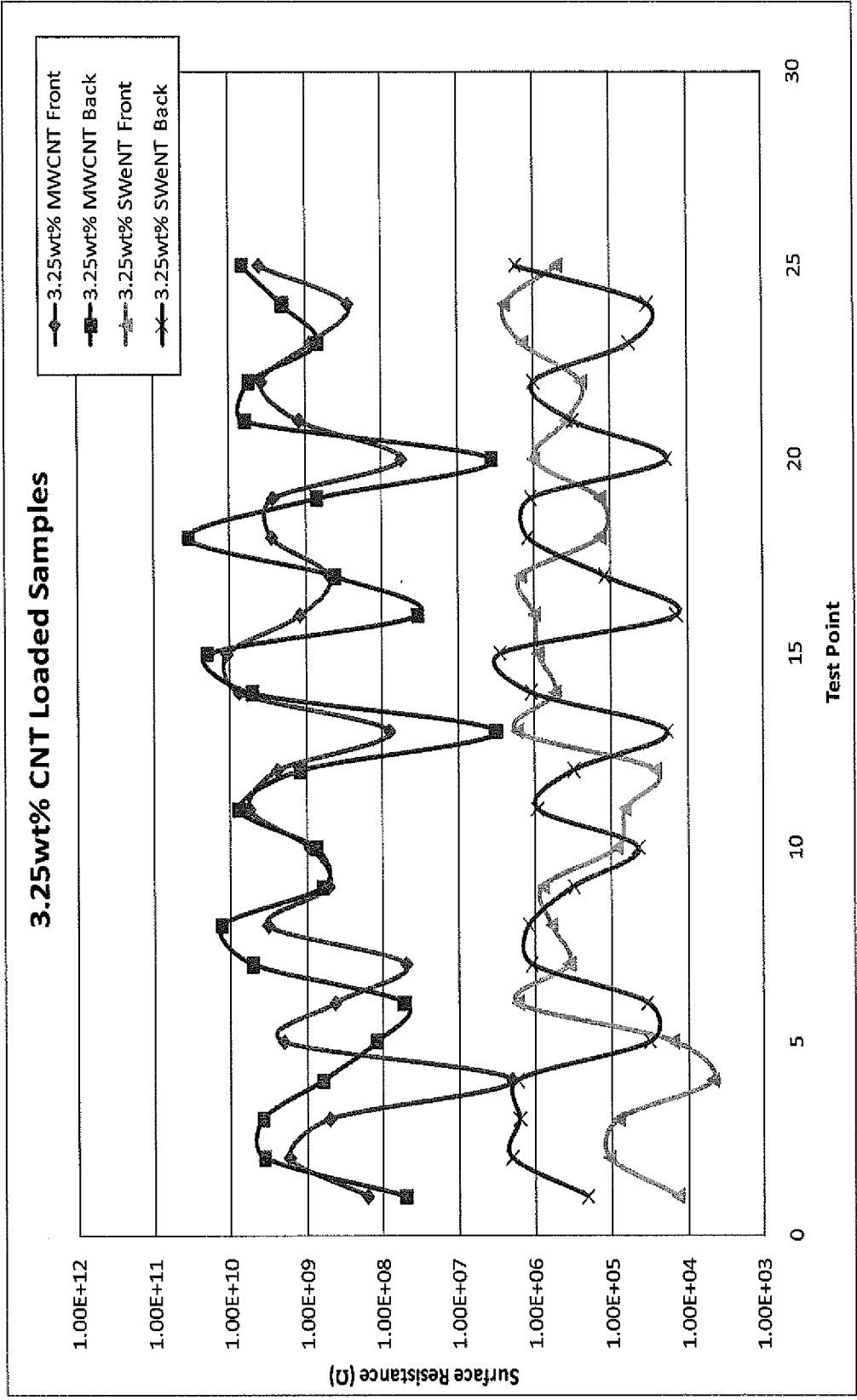


FIGURE 6B



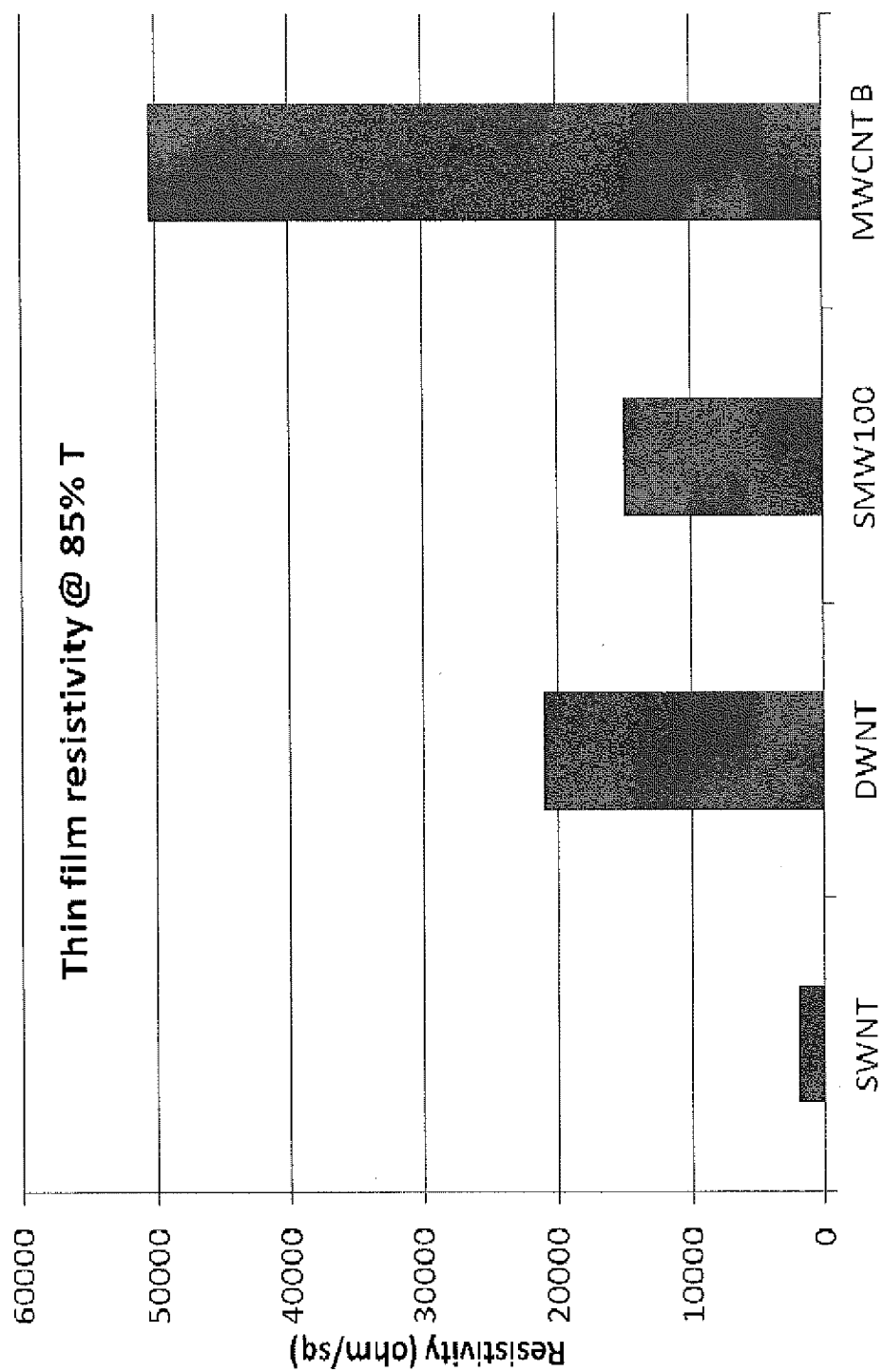


FIGURE 7

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/42321

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 23/00; B01J 23/84

USPC - 502/313; 502/316; 502/326

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)

USPC - 502/313; 502/316; 502/326

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 502/313,316,326;423/447.3;977/843

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWest: PGPB,USPT,USOC,EPAB,JPAB; Google; catalyst, support, substrate, CoFe<sub>2</sub>O<sub>4</sub>, CoMoO<sub>4</sub>, cobalt ferrite, cobalt molybdate, ferric molybdate, alumina, magnesium aluminate, magnesium oxide, spinel

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X - Y	US 7,304,012 B2 (GREEN et al.) 04 December 2007 (04.12.2007) col 1, ln 9-13, col 3, ln 14-19 and ln 46-54, col 4, ln 18-25, col 6, ln 56-59, col 13, ln 21-23 and col 14, ln 1-8.	1, 3-4, 5/1, 3 and 4, 6/1, 3 and 4, 7/1, 3 and 4, 8-11 and 15-17 ----- 2, 5/2, 6/2, 7/2, 12-14 and 18-28
X - Y	US 2003/0091496 A1 (RESASCO et al.) 15 May 2003 (15.05.2003) para [0031] and para [0068].	1 and 3-4 ----- 18-28
X	US 2008/0206125 A1 (SILVY et al.) 28 August 2008 (28.08.2008) para [0096]-[0097] and para [0136].	1 and 3-4
Y	US 2006/0024227 A1 (MARUYAMA et al.) 02 February 2006 (02.02.2006) para [0038].	2, 4, 5/2, 6/2 and 7/2
Y	US 2005/0002851 A1 (McELRATH et al.) 06 January 2005 (06.01.2005) para [0063].	12-14 and 26-28

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

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

06 December 2010 (06.12.2010)

Date of mailing of the international search report

17 DEC 2010

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300  
PCT OSP: 571-272-7774

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/42321

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:  
See Attached Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:  
1-28
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/42321

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-7 directed to a catalyst precursor composition comprising:

a support; and

mixed metal oxides on a surface of the support, wherein the mixed metal oxides are selected from the group consisting of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{CoxFeyMoO}_4$ ,  $\text{Fe}_2(\text{MoO}_4)_3$  and blends thereof,

wherein x and y each represent the atomic ratio of the corresponding metal oxide, wherein x is from about 1.6 to 6.5, and y is from about 0 to 10.5.

Group II: claims 8-28 directed to a catalyst precursor composition comprising:

a support comprising alumina and a magnesium compound; and

mixed metal oxides on a surface of the support, wherein the metal components of the mixed metal oxides are selected from the group consisting of cobalt, molybdenum and iron, wherein said cobalt is from about 0.5 to about 2.0 percent by weight concentration of the total metals of said catalyst precursor composition, said molybdenum is from about 0.3 to about 2.0 percent by weight concentration of the total metals of said catalyst precursor composition, said iron is from about 0 to about 3.0 percent by weight concentration of the total metals of said catalyst precursor composition, said magnesium is from about 0.5 to about 3.3 percent by weight concentration of the total metals of said catalyst precursor composition.

Group III: claims 29-41 directed to a composition of matter comprising:

a plurality of spent catalyst particles, said spent catalyst particles carrying catalytically formed carbon products, wherein at least 70% of the carbon products carried by said spent catalyst particles are multi-wall carbon nanotubes and wherein at least 60% of the multi-wall carbon nanotubes have between about 3 and about 8 walls.

Group IV: claims 42-62 directed to a method of preparing a catalyst precursor composition comprising:

preparing a solution comprising two or more metallic compounds, wherein the metallic portions of the compounds are selected from the group consisting of cobalt, iron, molybdenum, magnesium and mixtures thereof;

reacting the solution of metallic compounds with aluminum hydroxide to yield a product comprising reacted particles;

drying the particles;

calcining the particles under a flowing gas; and

reducing the size of the particles.

Group V: claims 63-75 directed to a method of preparing multi-wall carbon nanotubes comprising:

placing catalyst precursor particles having a particle size between about 20 microns and 500 microns in a reactor chamber, said catalyst precursor composition comprising:

a support; and

a phase of mixed metal oxides on a surface of the support, wherein the metals of said mixed metal oxides are selected from the group consisting of cobalt, molybdenum and iron;

flowing a stream of non-reactive gas through the reaction chamber at a flow rate sufficient to fluidize the catalyst precursor particles thereby forming a fluidized bed;

heating said fluidized bed to a temperature between about 600°C and about 750°C;

flowing a reactive gas mixture through the reaction chamber while maintaining the temperature of said fluidized bed between about 600°C and about 750°C, wherein said flow of reactive gas reduces the metal oxides of said catalytic precursor composition to yield a composition comprising catalyst particles; and,

continuing to flow said reactive gas mixture through the reaction chamber thereby producing multi-wall carbon nanotubes on the catalyst particles.

Group VI: claims 76-92 directed to a batch of carbon nanotubes comprising:

multi-wall carbon nanotubes, wherein said multi-wall carbon nanotubes comprise from about 60% to about 100% of said batch by weight and wherein at least 60% of the multi-wall carbon nanotubes have between about 3 and about 7 walls.

Group VII: claims 93-102 directed to a batch of carbon nanotubes comprising:

wherein from about 60% to about 100% of said batch by weight of said carbon nanotubes are multi-wall carbon nanotubes and wherein between 50% to about 90% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.

Group VIII: claims 103-109 directed to a composition comprising multi-wall carbon nanotubes, wherein between 50% and 90% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm.

The inventions listed as Groups I-VIII do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Groups II, III, IV, V, VI, VII and VIII do not include the  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoMoO}_4$ ,  $\text{CoxFeyMoO}_4$ ,  $\text{Fe}_2(\text{MoO}_4)_3$  and blends thereof, wherein x and y each represent the atomic ratio of the corresponding metal oxide, wherein x is from about 1.6 to 6.5, and y is from about 0 to 10.5 of group I.

Groups I, III, IV, V, VI, VII and VIII do not include the alumina and a magnesium compound; and the mixed metal oxides in the claimed weight percents of group II.

Groups I, II, IV, V, VI, VII and VIII do not include the spent catalyst of group III.

Groups I, II and IV do not include the multi-walled carbon nanotubes of groups III, V, VI, VII and VIII.

Groups I, II, III, V, VI, VII and VIII do not include the aluminum hydroxide, drying, calcining and reducing of group IV.

---See Continuation Sheet---

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/42321

## Lack of Unity Continued---

Groups I, II, III, IV, VI, VII and VIII do not include the preparing multi-walled carbon nanotubes with a phase of mixed metal oxides on a surface of the support of group V.

Groups I, II, IV, V and VIII do not include the multi-wall carbon nanotubes have between about 3 and about 7 walls of groups III, VI and VII.

Groups I, II, IV, V, VII and VIII do not include the multi-wall carbon nanotubes comprise from about 60% to about 100% of said batch by weight of groups III, and VII.

Groups I, II, III, IV, V and VI do not include the between 50% and 90% of the multi-wall carbon nanotubes have an external diameter of less than 10 nm of groups VII and VIII.

The common feature of a catalyst comprising a support and mixed metal oxides of iron, molybdenum and cobalt of Groups I, II and V is taught by US 7,250,148 B2 issued to Yang et al. 31 July 2007 (col 5, ln 46 to col 6, ln 14).

The common feature of multi-walled carbon nanotubes of groups III, V, VI, VII and VIII and the common feature of 70% to about 100% of said batch by weight of said carbon nanotubes are multi-wall carbon nanotubes of groups III, VI and VII and the common feature of at least 60% of the multi-wall carbon nanotubes having greater than 3 walls of groups III and VI are taught by US 2006/0099136 A1 by Dillon et al. published 11 May 2006 (para [0063]; [0077]-[0078]).

The common feature of the multi-wall carbon nanotubes having an external diameter of less than 10 nm groups VII and VIII is taught by US 2004/0150312 A1 by McElrath et al. published 05 August 2004 (para [0111]; [0079]); therefore the common feature is not an improvement over the prior art.

None of these technical features are common to the other groups, nor do they correspond to a special technical feature in the other groups. Therefore, unity of invention is lacking.