Inconsistencies in the Carbon Nanotube Patent Space: A Scientific Perspective

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ABSTRACT

Carbon nanotubes (CNTs) are tubular, crystalline, carbon structures with extraordinary physical, chemical, mechanical, optical, and electrical properties. These properties make CNTs valuable in a large number of end-use applications, the market for which is forecast to reach multi-billion dollar value within a decade. This in turn has lead to aggressive patenting practices; however, a lack of scientific guidance on the requirements for carbon nanotube patenting has resulted in patents that do not unambiguously describe many aspects of the "product and process" of CNTs. In this article, the authors—as engineers rather than lawyers—discuss critical issues related to the patenting of nanotube inventions. These include: 1) adequately defining the CNT material, 2) structural patentability, and 3) characterizing the detailed morphology and CNT properties. This is followed by a brief discussion on the relationship between the CNT product, synthesis conditions and growth apparatus, and the impact this will have on the level of detail required for future patent applications.

I. INTRODUCTION

Carbon nanotubes (CNTs) are a form of crystalline carbon with extraordinary physical, chemical, mechanical, and electrical properties. These properties make CNTs one of the most advanced materials yet discovered, with applications in composite materials,[1] electronics,[2] medicine,[3]

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[1] *See* Rodney S. Ruoff, Dong Qian, & Wing K. Liu, *Mechanical Properties of Carbon Nanotubes:Theoretical Predictions and Experimental Measurements*, 4 COMPTES RENDUS PHYSIQUE 993, 993-1008 (2003).

energy storage,[4] aeronautics[5] and many others.

The vast range of CNT applications has resulted in astonishing CNT market growth predictions. A 2007 market report by BCC Research[6] estimated the global market to be U.S. $79.1 million by the end of 2007, and upwards of U.S. $807.3 million by 2011. A 2006 study from the Freedonia Group[7] is even more optimistic, expecting the CNT market to increase from U.S. $200 million in 2009 to U.S. $9 billion by 2020.

Because of this predicted market value growth, companies and institutions developing carbon nanotube technology have been aggressively pursuing intellectual property protection. A 2007 report by Oliver[8] estimates the number of U.S.-based CNT related patents issued between 1994 and 2006 was 1,865, however "*in the past 3 years the number of CNT-related issued patents has almost tripled, reaching close to 600 patents in 2006 alone. For patents pending, the situation is even more dramatic, approaching a cumulative backlog [of] close to 4500 patents applications*."[9]

This substantial increase in the number of CNT patents filed has resulted in an increase in related publications in legal journals where justifiably, the focus has been on legal aspects. However we feel that a number of outstanding scientific issues are equally relevant and must also be considered. We believe these greatly increase the complexity of patenting CNT inventions and will have a material impact on the level of information required for patents, the way patents are constructed, and ultimately on their validity. We have previously reported on many of these issues[10] in an engineering context. However, we feel it necessary to reproduce a revised version of this work to stimulate discussion amongst a legal audience. We fear that the apparent segregation between engineering/science and law may result in legal rulings that are not truly representative of the carbon nanotechnology field.

II. OUTSTANDING ISSUES RELATED TO PATENTING CARBON NANOTECHNOLOGIES

The sections of the U.S. Patent Act most relevant to CNT patenting are generally perceived to be §§ 101,102, 103 and 112. However, due to the immaturity of the field and the absence of litigation to provide guidance, it is not clear what level of detail, evidence, and prior art investigation is required to satisfy these sections. Worryingly, there is also mounting, and seemingly well-founded, concern regarding the competence of the USPTO (and other patent offices) in regard to nanotechnology patents.[11]

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[2] *See* Yahachi Saito et al., *Field Emission of Carbon Nanotubes and its Application as Electron Sources of Ultra-High Luminance Light-Source Devices*, 323 PHYSICA B: CONDENSED MATTER 30, 30-37 (2002).

[3] *See* Feng Yang et al., *Magnetic Lymphatic Targeting Drug Delivery System Using Carbon Nanotubes*, MED. HYPOTHESES (forthcoming 2008)).

[4] *See* Yongmin Liang et al., *Preparation and Characterization of Multi-Walled Carbon Nanotubes Supported PtRu Catalysts for Proton Exchange Membrane Fuel Cells*, 43 CARBON 3144, 3144-52 (2005).

[5] *See* Ki-Yeon Park et al., *Application of MWNT-Added Glass Fabric/Epoxy Composites to Electromagnetic Wave Shielding Enclosures*, 81 COMPOSITE STRUCTURES 401, 401-06 (2007).

[6] BCC Res., *Carbon Nanotube Use in Composites Predicted to Soar*, 2007 ADDITIVES FOR POLYMERS 9 (2007).

[7] The Freedonia Group. World Nanotubes to 2009, http://www.freedoniagroup.com (last visited Fed. 23, 2008).

[8] BBC RES., CARBON NANOTUBES: TECHNOLOGIES AND COMMERCIAL PROSPECTS 44, 44-66 (2007), *available at* http://www.bccresearch.com/RepTemplate.cfm?reportID=406&RepDet=HLT&cat=nan&target=repdetail.cfm (analyst: John Oliver).

[9] *Id.*

[10] *See* Kieran MacKenzie et al., *Large-Scale Carbon Nanotube Synthesis*, 2 RECENT PATENTS IN NANOTECH. 25, 25-40 (2008).

[11] *See, e.g.*, Raj Bawa, *Nanotechnology Patenting in the US*, 1 NANOTECH. L. & BUS. 31, 31-50 (2004); John C. Miller & Drew L. Harris, *The Carbon Nanotube Patent Landscape*, 3 NANOTECH. L. & BUS. 427, 427-54 (2006); Ruben Serrato et. al., *The Nanotech Intellectual Property Landscape,* 2 NANOTECH. L. & BUS. 150, 150-55 (2005).

We foresee the CNT patent landscape becoming significantly more complex than current discussions anticipate and that the issues described in Sections II, III, and IV below may become absolutely critical in future intellectual property disputes. As engineers rather than lawyers, we note that our analysis is based upon science and engineering rather than procedure or law. Therefore, this article cannot be considered to be a legal opinion, and readers should seek patent counsel regarding the validity of individual patents.

A further general issue with the CNT field, and indeed all nanotechnology, is the dimension of the subject matter. In particular, the nanometer scale makes it problematic to produce high-resolution images of CNTs and to accurately test their properties. This has significant implications for the interpretation of CNT patents and adds a layer of complexity that is absent from traditional "macro" scale products.

1. Properly Defining Carbon Nanotubes and the Correct Use of Nomenclature

A major issue patent reviewers face when conducting prior art searches is the numerous terms used to describe "hollow cylindrical carbon nanostructures." For example, the terminology used to describe multi-walled carbon nanotubes (MWCNTs) has included "fibrils," "nanofibers," "carbon nanotubes" and "nanotubes." Terms for single-walled carbon nanotubes (SWCNTs) have included "buckytubes," "single shell nanocylinders," "carbon nanotubes" and "nanotubes."[12] The multitude of terms for carbon nanotubes has arisen, in part, because patent applicants act as their own lexicographer.[13]

We believe, in relation to carbon nanotubes, that on this point law and science are at odds; definitions for both SWCNTs and MWCNTs must be clearly and unambiguously described in order to provide a clear legal basis to investigate patents. The American National Standards Institute (ANSI) is also aware of this identification issue,[14] noting numerous concerns related to the lack of universal terminology, including: i) commercial reasons; ii) patents and IP protection; iii) regulatory impacts (or the absence of regulatory standard) and iv) labeling concerns. Despite these concerns, ANSI is yet to release a universal terminology guide for carbon nanotubes.

Due to the absence of a standard, various descriptions of CNTs are reported in existing patents.

Claim 3 in IBM's U.S. Patent No. 5,424,054 recites the following SWCNT structure: *"A hollow carbon fiber having a wall consisting essentially of a single layer of carbon atoms."*

In claim 1 of Hyperion Catalysis U.S. Patent No. 4,663,230, a MWCNT is described as:

> *"An essentially cylindrical discrete carbon fibril characterized by a substantially constant 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."*

A CNT is not simply any hollow carbon structure. First, it must posses a diameter in the nanoscale range. Carbon structures seemingly meeting the following definition are not carbon nanotubes if this first

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[12] *See* Miller, *supra* note 11 at 436-37.

[13] USPTO, *Manual of Patent Examining Procedure,* § 2173.05(a) at pt. III, (Aug. 2001) ("Consistent with the well-established axiom in patent law that a patentee or applicant is free to be his or her own lexicographer, a patentee or applicant may use terms in a manner contrary to or inconsistent with one or more of their ordinary meanings if the written description clearly redefines the terms.") *available at* http://www.uspto.gov/web/offices/pac/mpep/documents/2100_2173_05_a.htm#sect2173.05a.

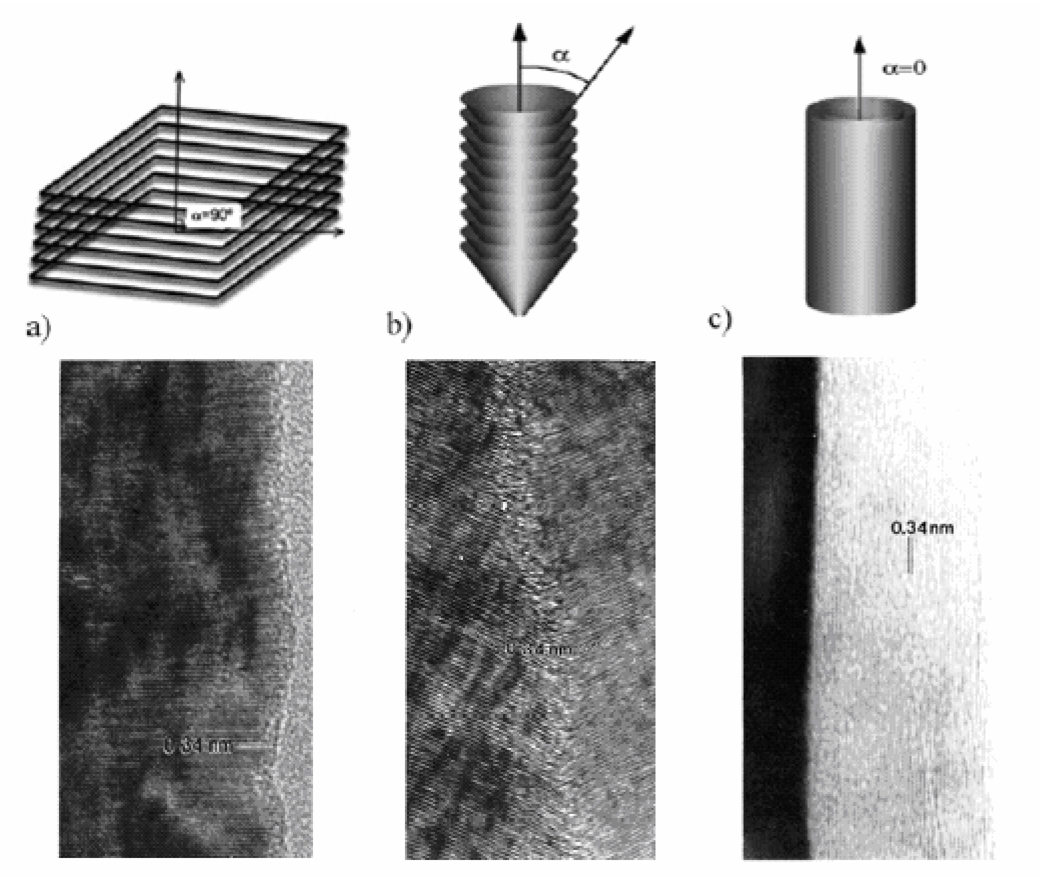
[14] AMERICAN NATIONAL STANDARDS INSTITUTE, NSP 022-2004 GROUP III: CARBON NANOSTRUCTURES, (2004) *available at* http://publicaa.ansi.org/sites/apdl/Documents/Standards%20Activities/ANSI-NSP/ANSI-NSP%20022-2004%20group%203.pdf.

dimension criterion is not satisfied. There are also limitations on minimum possible CNT diameters based on steric strain energy restrictions.[15]

Furthermore, to completely describe a CNT, one must completely depict the wall orientation and chiral structure. The three distinct structural types of carbon filaments that have been identified are stacked, herringbone and tubular[16] (Figure 1).

FIGURE 1: THREE DISTINCT STRUCTURAL FORMS OF FIBROUS CARBON: A) STACKED, B) HERRINGBONE, AND C) TUBULAR.

The angle (α) to the principal axis is shown in the drawings, adapted from Melechko et al.[17] *TEM images from Rodriguez et al.*[18]



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[15] *See, e.g.*, Hongying Peng et al., *Smallest Diameter Carbon Nanotubes*, 77 APPLIED PHYSICS LETTERS 2831, 2832 (2000).

[16] Kenneth B. Teo et al., *Catalytic Synthesis of Carbon Nanotubes and Nanofibers*, 1 ENCYCLOPEDIA OF NANOSCI. & NANOTECH. 665, 665 (2004).

[17] Anatoli V. Melechko et al., *Vertically Aligned Carbon Nanofibers and Related Structures: Controlled Synthesis and Directed Assembly*, 97 J. APPLIED PHYSICS 041301, 041301-3 (2005).

[18] Nelly M. Rodriguez et al., *Catalytic Engineering of Carbon Nanostructures*, 11 LANGMUIR 3862, 3863-65 (1995).

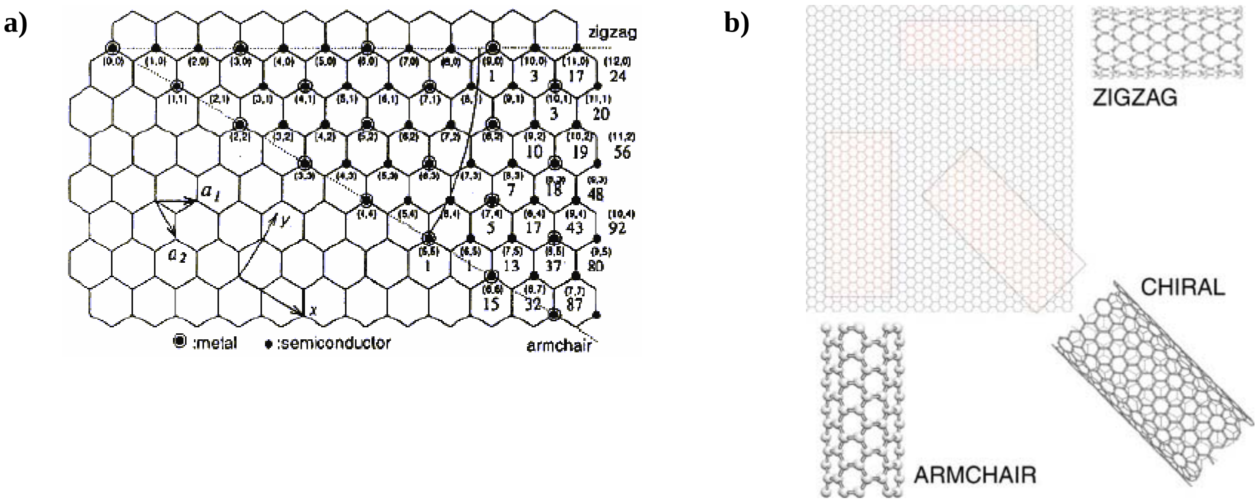
The only configuration of the three structural types that can be termed a "carbon nanotube" is the tubular configuration. The tubular configuration consists of walls that are parallel to the principal axis; if multiple walls exist, they will have a spacing of approximately 0.34 nm. Walls must consist only of single tubular graphene sheets (i.e. one carbon atom thick), and cannot consist of layers of graphite or amorphous carbon sheets of multiple atom thickness arranged in a similar manner to that of graphene sheets. We cannot emphasize these points strongly enough, as the unique physical, chemical, and electrical properties reported for nanotubes apply only to this specific geometry.[19] Any filamentous carbon structure lacking this precise orientation should be described as a "carbon nanofiber" to more accurately distinguish its morphology and properties. It is also worth noting that the majority of TEM images presented in patent documents are inadequate, in both magnification and quality, to accurately determine wall structure.

A further concern is the arrangement of carbon atoms within the CNT. Three broad arrangements exist, described by the chiral angle; i) armchair, ii) zig-zag, and iii) chiral (Figure 2). Each chirality variation results in CNTs with often disparate electrical properties; for example, a "zig-zag" CNT can be either metallic or semi-conducting, where an "armchair" CNT is strictly metallic. Thus CNTs with different chirality could be treated as a different material.

FIGURE 2: VARIATIONS OF CNT STRUCTURAL TYPE

a) demonstrates how the chiral vector and chiral angle combine to give specific CNT structures. A chiral angle of 0° results in 'zig-zag' CNTs, either metallic or semi conductive; a chiral angle of 30° results in 'armchair' CNTs, which are strictly metallic; a chiral angle of 0° - 30° results in chiral CNTs, either metallic or semi conductive. Figure from Dresselhaus et al.[20]

b) demonstrates how a single graphene sheet can be 'rolled' to form the different CNTs. Figure from University of Pennsylvania Engineering.[21]



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[19] *See* Teo, *supra* note 16, at 665-66.

[20] MILDRED S. DRESSELHAUS ET AL., SCIENCE OF FULLERENES AND CARBON NANOTUBES 4 (1996).

[21] Univ. of Penn. Materials Sci. & Eng'g, Research: What is a Carbon Nanotube? http://www.seas.upenn.edu/mse/research/nanotubes.html (last visited Feb. 23, 2008).

The issue of a rigorous CNT definition is further complicated by the fact that some of these theoretical descriptive parameters are often difficult to physically detect and measure; methods to selectively produce nanotubes with a specific chirality, and testing methodologies to infer what type are produced have not been extensively reported in the literature. As a result, the door may be left open for a wave of patents that more accurately describe CNT products. We must also stress that common CNT production techniques generally result in a variety of products under a given set of experimental conditions. It may therefore be difficult, and perhaps impossible, to avoid infringing a valid composition of matter patent that is directed to a particular CNT structure or type, if randomly produced CNTs fall within the scope of the patent claims.

From our review of current CNT related patents, we are of the opinion that the quality of future patent descriptions and the evidence of the produced CNTs within the patent document must be improved in line with current scientific knowledge.

III. COMPOSITION OF MATTER PATENTS

The second issue to address is the patentability of the carbon nanotube itself. Two of the most widely cited and discussed composition of matter patents are IBM's U.S. Patent No. 5,424,054 and NEC's U.S. Patent No. 5,747,161, related to single-walled carbon nanotubes and multi-walled carbon nanotubes, respectively. However, one must also consider earlier patents, such as Howard G. Tennent's U.S. Patent No. 4,663,230, to fully assess the issue of structural patentability. These fundamental CNT patents have widespread implications for the emerging carbon nanotube industry. In the following discussion we are careful to clearly differentiate single and multi-walled carbon nanotubes, as the evidence for and against patent composition of matter claims is often distinctly different.

1. Multi-Walled Carbon Nanotubes

MWCNTs are stable, tubular forms of crystalline carbon. According to popular belief, the multi-wall carbon nanotube was discovered in 1991 by Sumio Iijima,[22] although this view has recently been challenged.[23]

Determining when the MWCNT was initially discovered, and by whom, is difficult. It is not novel that carbon can form nanoscale tubular structures; this fact can be traced back at least to the 1950s,[24] corresponding to technological developments in transmission electron microscopy. What are probably MWCNTs were also apparently rediscovered in the 1970s.[25] Although complete and unambiguous descriptions of MWCNTs are not given in these early works, the various findings can be combined to obtain a wall definition approaching that of Iijima's.

While there is periodic evidence of MWCNTs described in the literature, we believe Iijima was the first to assemble and elucidate a complete depiction of MWCNTs, particularly with respect to the chiral

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[22] Sumio Iijima, *Helical Microtubules of Graphitic Carbon*, 354 NATURE 56, 56-58 (1991).

[23] Marc Monthioux & Vladimir L. Kuznetsov, *Who Should be Given the Credit for the Discovery of Carbon Nanotubes?* 44 CARBON 1621,1621-23 (2006).

[24] *See, e.g.,* M. Hillert & N. Lange, *The Structure of Graphite Filaments*, 111 Zeitschrift fur Kristallographie, 24, 24-34 (1958); L.J.E. Hofer et al., *Structure of the Carbon Deposited from Carbon Monoxide on Iron, Cobalt and Nickel*, 59 J. PHYSICAL CHEM. 1153, 1153-55 (1955); L.V. Radushkevich & V. M. Lukyanovich, *O Strukture Ugleroda, Obrazujucegosja Pri Termiceskom Razlozenii Okisi Ugleroda na Zeleznom Kontakte*, 26 ZURNAL PHIZICHESKOI XEMEI 88, 88-95 (1952) *available at* http://carbon.phys.msu.ru/publications/ 1952-radushkevich-lukyanovich.pdf (Journal of Physical Chemistry, article in Russian).

[25] *See* Agnes Oberlin et al., *Filamentous Growth of Carbon Through Benzene Decomposition*, 32 J. CRYSTAL GROWTH 355, 355-59 (1976).

angle, in a cohesive manner for publication. This conclusion gives credence to the patent defense argument of Miller and Harris suggesting that holders would "*likely argue they had isolated and characterized the carbon nanotube structure, and thus are entitled to patent it*."[26] In fact, Iijima and NEC's U.S. Patent No. 5,747,161 is one of the few uncovered with any mention of chiral angle.

However, there exist several patents and patent applications for possible MWCNT structures production prior to 1991 (Table 1). Although descriptions in these patents are seemingly incomplete compared to the more thorough definition offered, crucially they are generally no less descriptive than the descriptions offered in current patents.

TABLE 1: POSSIBLE MWCNT PATENTS AND APPLICATIONS FILED/ISSUED PRIOR TO 1991.

Patent Number	Issued to	Date Issued
U.S. 4,663,230	Tennent, Hyperion Catalysis International	5/5/1987
W.O. 89/07163	Snyder et al., Hyperion Catalysis International	10/8/1989
W.O. 90/07023	Mandeville et al., Hyperion Catalysis International	28/6/1990
U.S. 5,165,909	Tennent et al., Hyperion Catalysis International	24/11/1992*
U.S. 5,171,560	Tennent, Hyperion Catalysis International	15/12/1992*

*Note that these patents were initially filed in 1990, prior to Iijima's work.

The importance of the preceding discussion is that the prior disclosure of what are potentially MWCNTs, both in the literature dating back to the 1950's (i.e. "*known or used by others*" and "*described in a printed publication*") and patents dating back to at least 1987 (i.e. "*patented*"), has the potential to render current MWCNT structural patents invalid according to § 102 of the U.S. Patent Act.

There is also a possibility that CNTs are a naturally occurring form of carbon and therefore, potentially, cannot be patented according to the *Diamond v. Chakrabarty* clarification of § 101.[27] In any discussion into CNT natural occurrence, the clear distinction must be made between spontaneous formation of CNTs given the correct conditions by man (i.e., 'self-assembly') and true natural occurrence (i.e., has not been influenced or derived from any artificial, man-made process). Theoretically, the tubular structure of MWCNTs, and indeed all CNTs, arises from the fact that this structure minimizes 'dangling' bonds and can therefore often represent the lowest energy configuration available for the carbon atoms.[28] Because the lowest energy configuration is the natural preference of matter, the CNT should spontaneously form if it represents a low energy configuration under a given set of conditions (i.e., is thermodynamically favorable under those conditions) and if such spontaneous formation has sufficient time to occur under those conditions (i.e., is not kinetically limited under those conditions). Thus from a theoretical perspective, CNTs might be naturally occurring if the specific conditions (e.g., temperature,

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[26] *See* Miller *supra* note 12.

[27] Diamond v. Chakrabarty, 447 U.S. 303, 309 (1980) ("The laws of nature, physical phenomena, and abstract ideas have been held not patentable.").

[28] *See* MILDRED S. DRESSELHAUS ET AL., TOPICS IN APPLIED PHYSICS: CARBON NANOTUBES. SYNTHESIS, STRUCTURE, PROPERTIES, AND APPLICATIONS 11-28 (Vol. 80, 2001).

pressure) under which their formation is both thermodynamically and kinetically favorable are actually present in nature without the assistance of man.

While this theory indicates that MWCNTs could occur in nature without the assistance of man given the right conditions, a review of the literature has uncovered that there is very little evidence to support any argument that MWCNTs actually do occur in nature. Velasco-Santos et al.[29] claim to have found MWCNTs in oil well samples; however, by their own admission, the tubes "*are not composed only by carbon, inasmuch as the stripped structure seems to be formed by other elements*", and thus fail the correct definition of MWCNTs. The most compelling evidence of naturally occurring MWCNTs we have uncovered is from Esquivel and Murr[30] who analyzed 10,000 year old Greenland ice core samples. Their Figure 2 shows ~15-20 nm hollow carbon structures that may potentially be MWCNTS however this alone cannot be regarded as definitive proof of natural occurrence because the wall structure is not observable. Furthermore, the MWCNTs generally appear to be more defective in structure than those presently being synthesized (particularly by high temperature techniques), perhaps suggesting that nature can only produce defective CNTs due to the lack of homogeneous conditions. Ignoring these concerns, if it was assumed that the image (or one similar) offered conclusive proof of a naturally occurring relatively straight MWCNT of ~20 layers, it offers no evidence of the natural occurrence or otherwise of MWCNTs with a different number of layers (right down to SWCNTs), quality, purity and morphology (see Part 3). For this reason it will be interesting to observe how the courts might approach the issue of natural occurrence given that the prior art mentioned above admittedly does not show the wall structure, quality, purity or morphology of the disclosed CNTs.

What most legal commentators typically give as evidence for naturally occurring CNTs is actually proof of fullerenes (particularly C_{60}). While this may initially appear erroneous and without legal importance to the CNT patent debate, two issues must be noted. First, the CNT can be thought of in terms of an elongated fullerene[31] (Figure 3), where the fullerene molecule essentially comprises the CNT end caps; thus to someone in the CNT field it may be a natural progression that the presence of C_{60} might also indicate the presence of CNTs given that they form under similar conditions.

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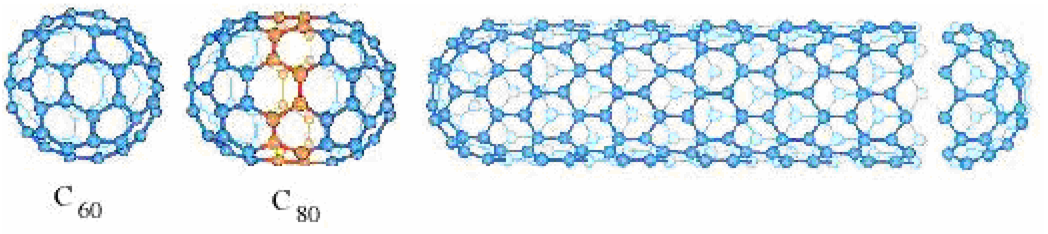
[29] Carlos Velasco-Santos et al., *Naturally Produced Carbon Nanotubes*, 373 Chem. PHYSICS LETTERS 272, 273 (2003).

[30] Erika V. Esquivel & Lawrence E. Murr, *A TEM Analysis of Nanoparticulates in a Polar Ice Core*, 52 MATERIALS CHARACTERIZATION 15, 15-25 (2004).

[31] This is not to imply that CNTs require fullerenes to form, they are simply both low energy configurations for a number of carbon atoms.

FIGURE 3: THE FULLERENE STRUCTURE AND PROGRESSION TO CNTS BY THE INSERTION OF ADDITIONAL CARBON ATOMS.[32]



Second, Suchanek et al.[33] have actually demonstrated the ability of C_{60} fullerenes to transform into MWCNTs, presumably to form a lower energy configuration, given the correct conditions. If these two issues are sufficient for a court to link the natural occurrence of fullerenes with the natural occurrence of CNTs, then there is abundant literature to offer proof, e.g., fullerenes have been found in coal,[34] flame deposits,[35] even meteorite crash[36] and lightening strike sites.[37]

Other possible evidence showing spontaneous MWCNT formation and indicating potential naturally occurring MWCNTs are experiments using naturally occurring materials but in an artificial setting to produce the CNTs[38] or their unintentional creation as by-products of other man-made processes, e.g., in spent fluidized bed catalytic cracking catalysts.[39]

While the above-cited references may provide some evidence that certain forms of MWCNTs are naturally occurring, and thus not patentable, the final ruling must (eventually) be made by a court of law. From a scientific perspective, MWCNTs should occur spontaneously because they represent a low energy configuration of $\sim C_{60+2j,\ j\rightarrow\infty,\ j>5}$ carbon atoms. However we are not entirely convinced that the references mentioned above show that these thermodynamic considerations (i.e., spontaneous formation) necessarily translate to true natural occurrence. This should not be misconstrued as suggesting that MWCNTs are not naturally occurring, simply that, at present, there is no conclusive evidence that could be used by a court on the issue; convincing evidence may yet be presented.[40] Again we reiterate; the immaturity of the

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[32] Viktor Zólyomi & Jenő Küurti, Science of Fullerenes and Carbon Nanotubes, http://virag.elte.hu/kurti/science.html (last visited Feb. 23, 2008).

[33] *See* Wojciech L. Suchanek et al., *Behavious of C60 under Hydrothermal Conditions: Transformation to Amorphous Carbon and Formation of Carbon Nanotubes*, 160 J. SOLID STATE CHEM. 184, 184-88 (2001).

[34] *See* DEVELOPMENTS IN FULLERENE SCIENCE: NATURAL FULLERENES AND RELATED STRUCTURES OF ELEMENTAL CARBON (Frans J.M. Rietmeijer ed., 2006).

[35] *See* Lawrence E. Murr & Karla F. Soto, *A TEM Study of Soot, Carbon Nanotubes, and Related Fullerene Nanopolyhedra in Common Fuel-Gas Combustion Sources*, 55 MATERIALS CHARACTERIZATION 50, 50-65 (2005).

[36] *See* Dieter Heymann et al., *Terrestrial and Extraterrestrial Fullerenes*, 11 FULLERENES, NANOTUBES, & CARBON NANOSTRUCTURES 333, 333-70 (2003).

[37] *See* Terry K. Daly et al., *Fullerenes from a Fulgurite*, 259 SCI. 1599, 1599-1601 (1993).

[38] *See, e.g.*, Yury Gogotsi & Joseph A. Libera, *Hydrothermal Synthesis of Multiwall Carbon Nanotubes*, 15 J. MATERIALS RES., 2591, 2591-94 (2000); Henning Richter et al.. *Formation of Nanotubes in Low Pressure Hydrocarbon Flames*, 34 Carbon 427, 427-29 (1996).

[39] *See* Chee Howe See & Andrew T. Harris, *Spent FCC Catalysts: An Untapped Resource of Carbon Nanotubes?* 53 AM. INST. OF CHEM. ENG'GS J. 2198, 2198-2200 (2007).

[40] We must emphasise how time consuming the process of testing samples for CNTs really is, particularly those from nature where CNTs may be scarce. Thoroughly investigating via TEM, for example, using a single 3mm grid (~28mm^2) at an appropriate magnification (image size 1μm x 1μm) would require ~7 million images. To

nanotechnology field in general means it is uncertain what level of prior art review will be required and what evidence will be necessary to overcome the statutory presumption that existing patent claims are valid.[41]

2. Single Walled Carbon Nanotubes

SWCNTs, like MWCNTs, are a stable form of crystalline carbon. Here again, we have been unable to find any evidence to confirm that SWCNTs are naturally occurring, although the same points as MWCNTs must be noted. From a theoretical perspective, SWCNTs form spontaneously given the correct conditions for both energy minimization and chemical kinetics. And, while synthesizing SWCNTs is more difficult than MWCNTs, generally requiring metal catalyst and more precise conditions, the absence of any natural occurrence evidence should not be regarded as proof that SWCNTs do not occur naturally. The discovery of SWCNTs in 1993 is accredited to two independent research groups, lead by Iijima[42] and Bethune,[43] using almost identical equipment and conditions for the original synthesis of MWCNTs; the only major point of difference was the addition of catalyst metal to the experiment. While these teams were the first to provide definitive TEM images of SWCNTs, they were not the first to theorize the existence of SWCNTs[44] or to confirm that their structure was theoretically stable.

Whether SWCNTs, as with MWCNTs, ought to be patentable remains in debate. Due primarily to magnification limitations of older electron microscopy equipment, we have been unable to uncover published evidence of SWCNTs *images* conclusive enough to provide grounds for invalidation of SWCNT composition of matter claims under § 101 or § 102.

However a possible argument against the patentability of SWCNT structure exists based on § 103 of the U.S. Patent Act. Section 103 might potentially be used to argue that the theoretical link between the fullerene and SWCNT structures (Figure 3) could be seen as a natural extension to the prior art, and that the SWCNT is therefore obvious to those in the field. For example, Mintmire et al.[45] submitted a paper with an exact model and properties of a SWCNT derived purely from the fullerene structure and speculation of "*fullerene tubules*" approximately one month prior to Ijima's 1991 "discovery" of MWCNTs.

Alternatively, SWCNTs may be considered obvious based on pre-1993 theoretical work undertaken following the 1985 discovery of fullerenes,[46] and Iijima's 1991 "discovery" of MWCNTs.[47] These theoretical studies clearly demonstrated that the SWCNT structure was stable, and even theorized most of the known SWCNT properties prior to 1993. It is also worth noting that Miller and Harris[48] show U.S.

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conclusively settle the natural occurrence debate using this method, the process must be repeated for many different samples potentially containing CNTs. While other testing methods may potentially be used, the search for naturally occurring CNTs clearly dependent on time, money and a good deal of luck.

[41] 35 U.S.C. § 282 (2008) ("A patent shall be presumed valid.").

[42] Sumio Iijima & Toshinari Ichihashi, *Single-Shell Carbon Nanotubes of 1-nm Diameter*, 363 NATURE 603, 603-05 (1993).

[43] Donald S. Bethune et al., *Cobalt-Catalysed Growth of Carbon Nanotubes with Single-Atomic-Layer Walls*, 363 NATURE 605, 605-07 (1993).

[44] *See* Oberlin *supra* note 25.

[45] John Mintmire et al., *Are Fullerene Tubules Metallic?* 68 PHYSICAL REV. LETTERS 631, 631-34 (1992).

[46] Harold W. Kroto et al., *C60: Buckminsterfullerene*, 318 NATURE 162, 162-63 (1985).

[47] *See, e.g.*, Mildred S. Dresselhaus et al., *Carbon Fibers Based on C60 and their Symmetry*, 45 PHYSICAL REV. B 6234, 6234-42 (1992); Noriaki Hamada et al., *New One-Dimensional Conductors: Graphitic Microtubules*, 68 PHYSICAL REV. LETTERS 1579, 1579-81 (1992); Amand A. Lucas et al., *On the Energetics of Tubular Fullerenes*, 54 J. PHYSICS & CHEM. SOLIDS 587, 587-93 (1993); Kazuyoshi Tanaka et al., *Electronic Properties of Bucky-Tube Model*, 191 CHEM. PHYSICS LETTERS 469, 469-72 (1992).

[48] *See* Miller *supra* note 12 at 444.

Patent No. 5,424,054 for SWCNTs actually referenced some earlier work in their application. IBM differentiated its process and product by claiming it was able to produce SWCNTs of less than 5 nm.[49] However, in 1992 Dresselhaus et al.[50] calculated that SWCNTs could occur with diameters down to 9.61 Å (0.961 nm) based on a C_{60} molecule; the smallest possible diameter for a SWCNT has now been revised to 0.4 nm.[51]

While the literature presented is purely theoretical in its derivation of SWCNTs, it is not entirely devoid of SWCNT synthesis enablement. First, the literature demonstrates that the SWCNT structure can readily occur and is theoretically stable based on energy calculations. Second, the papers all introduce their work in light of the then recently synthesized fullerenes and MWCNTs via arc-discharge. It would appear that most are implying a similar approach could also be used in the creation of SWCNTs, which it ultimately was, particularly in Dresselhaus et al.[52] Third, as previously stated, the only significant variation to the fullerene and MWCNT production process via arc discharge was the addition of trace amounts of catalyst metal (iron and cobalt for Iijima and Bethune respectively). In fact, the apparatus and conditions are so similar that Bethune et al. explicitly state that "*[F]ullerenes form abundantly at the same time.*" The use of catalyst metal for generating carbon fibers was also a well know approach, with Dresselhaus et al. stating "*conventional fibers require use of a small transition metal particle (~100 Å diameter) as a catalyst*" citing the work of Endo, who seemingly rediscovered what are potentially MWCNTs in 1976.[53] Finally the early theoretical work by Dresselhaus et al. also discussed ways of detecting the SWCNTs based on Raman spectroscopy results; a method used extensively today in CNT research for characterizing product.

Whether these papers show sufficient enablement, or whether we are interpreting the papers with the benefit of hindsight is an important issue to determine if the SWCNT "*would have been obvious at the time…to a person having ordinary skill in the art to which said subject matter pertains.*"[54] If the papers presented are deemed to not have adequately enabled a person skilled in the art to actually make the theorized SWCNT structure at the time the theoretical work was published, this failure to enable the patented SWCNTs would cut against an argument that the theoretical work renders the patented SWCNTs obvious under § 103. Indeed, as Baluch et al. have explained, U.S. courts have stated that a patented invention is not obvious under § 103 if the prior art fails to enable the patented invention.[55] Here again, it is uncertain whether the prior art known to us is sufficient to overcome the statutory presumption that existing patent claims are valid.

3. Collective Composition of Matter Issues

Numerous composition of matter issues apply collectively to both SWCNTs and MWCNTs, e.g. morphology, length, defects, wall structure and/or impurities. These characteristics are important as they greatly influence CNT properties, and hence, end-use applications. The following discussion, generally excerpts from MacKenzie et al., is by no means a complete summary of composition of matter issues; instead we felt it most beneficial to focus on CNT-related issues that may be have been overlooked

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[49] U.S. Patent No. 5,424,054 (filed May 21, 1993) (claims carbon nanotube product of < 3.5nm but preferably less than approximately 1.5nm).

[50] *See* Dresselhaus *supra* note 47..

[51] *See* Peng *supra* note 15.

[52] *See* Dresselhaus *supra* note 47.

[53] *See* Oberlin *supra* note 25.

[54] 35 U.S.C. § 103(a) (2008).

[55] Andrew S. Baluch et al., *In re Kumar: The First Nanotech Patent Case in the Federal Circuit*, 2 NANOTECH L. & BUS. 342, 345 (2005) ("[I]n order to render an invention unpatentable for obviousness, the prior art must enable a person of ordinary skill to make and use the invention.") (quoting *In re Kumar*, 418 F.3d, 1361, 1368 (Fed. Cir. 2005) (citing *Beckman Instruments, Inc. v. LKB Produkter AB*, 892 F.2d 1547, 1551 (Fed. Cir. 1989)).

previously in legal analysis. Determining the validity and scope of CNT composition of matter claims will ultimately be difficult with a multitude of factors potentially impacting on CNT structure, and properties, and ambiguities surrounding nanotechnology patents in general.

3.1 Morphology

CNTs come in many different morphologies including straight, "bent" through to defective/broken CNTs, Y-shape and coiled/spiral/helical; and each of these morphologies will posses slightly different properties and end-use applications. Are CNTs with different morphologies all encompassed under the same composition of matter claims simply because they have the same number of walls? Given there are patents on other morphologies, e.g., CN Patent No. 1,648,038, JP Patent No. 2005097015, and W.O. Patent No. 2004052973, how do these impact the reading of other patents that do not give specific morphologies? Furthermore, what exactly are patents seeking protection for if they fail to provide a specific morphology? Are we to assume that the absence of a detailed morphological description (and very few provide this) therefore means that patents encompass all forms of CNTs or only straight CNTs? This raises further problems such as the legal definitions of the various morphologies; whether patents lacking this information are valid under § 112 because they lack a full "*written description of the invention*;" and the situation where subsequent patents are filed claiming apparently identical CNT structures but providing a complete and unambiguous description.

3.2 Chiral Structure

As discussed previously, chiral nature influences various properties of the CNT. Despite this, there are few patents that mention chirality, for example U.S. Patent No. 5,747,161 claim a "*tubular structure comprising a helical structure of carbon hexagons*," although there is no mention of angle or vector. U.S. Patent No. 6,683,783 also make note of product chirality; SWCNTs are mentioned in claim 5 and (10,10) SWCNTs in later claims. The probable reason for the lack of chiral information is the difficulty associated with detecting the angle and actually producing CNTs with specific chiralities. This raises obvious issues for patent interpretation: what do patents actually encompass?

For example IBM's U.S. Patent No. 5,424,054 patent claims "*hollow carbon fiber having a wall consisting essentially of a single layer of carbon atoms*." Does this imply that this patent applies to CNTs with any chiral angle? Or does it apply to only SWCNTs with no chiral angle? Is the patent lacking sufficient description to be valid under § 112? Can another patent be filed claiming an identical SWCNT but providing a specific chiral structure? Does a metallic CNT infringe on this patent? What about semi-conducting? Chirality is even more complex for MWCNTs. For energy minimization reasons carbon atoms from CNT walls generally do not stack directly on top of each other.[56] The effect of these staggered wall chiralities gives rise to MWCNTs with slightly different properties—an issue that must be addressed to determine the scope of many patent claims.

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[56] Severin Amelinckx et al., *Electron Diffraction and Microscopy of Nanotubes.* 62 REPORTS ON PROGRESS IN PHYSICS 1471, 1471-1524 (1996).

3.3 Length

Miller and Harris discuss the legal possibility of patenting varying CNT lengths:

> Under U.S. law, patentees can claim a particular species of previously know genus compositions. Therefore, if an inventor is the first to synthesize a species of nanotubes with a certain, unique property X, the patentee may be able to obtain a claim covering a selection of those unique nanotubes notwithstanding the genus of prior art nanotubes. For example, it is believed that carbon nanotubes with greater lengths might be superior to shorter nanotubes for a variety of applications. Different inventors racing to synthesize longer (and longer) nanotubes are likely to seek claims such as "nanotubes having at least a length of X." The result could be several issued patents with claims on nanotubes of different sizes. Similarly, inventors seeking to optimize the electrical properties of nanotubes might file patent applications claiming compositions of matter having different levels of resistance.[57]

The longest individual carbon nanotube we are aware of is a (supposedly) SWCNT of approximately 4 cm grown by Zheng et al. in 2004.[58] As Miller and Harris explain, these long CNTs introduce further complications in composition of matter claims. It is extremely unlikely that such long CNTs could form naturally, thus § 101 appears satisfied. However, as there are no theoretical limitations on the length of CNT structures,[59] the presumption that longer and longer lengths will inevitably be synthesized seems clear, although the actual means of making such structures might not yet be enabled.

3.4 Degree of Wall Graphitization and Wall Defects

The extent of wall graphitization influences the mechanical and electrical properties of the CNT. The degree of wall graphitization, or "quality" of the CNT, is typically measured via visual inspection with high resolution TEM or Raman spectroscopy, where it is represented as a G/D ratio. Simplistically, the G/D ratio is the ratio of structured graphitic carbon to disordered (amorphous) carbon; the higher this ratio, the "better" the quality of the CNT. We have not uncovered any mention of G/D ratios in patents reviewed, although numerous patents provide worded descriptions. For example, U.S. Patent No. 6,979,433 specifies "*well-graphitized*" walls, U.S. Patent No. 6,683,783 states "*substantially defect-free*" while U.S. Patent No. 6,361,861 does not mention wall graphitization. Is a well-graphitized CNT from U.S. Patent No. 6,979,433 a different composition of matter than a CNT from U.S. Patent No. 6,361,861 with "poor" wall quality given that the properties are likely to be different? Furthermore, what legal ruling will a court give on what constitutes "*well graphitized*" walls and "*substantially defect free*," given that the interpretations of these terms will vary depending on their end use application. For example, CNTs used in electronics will require a much lower defect rate than CNTs used as additives in composite materials.

3.5 Contaminants, Amorphous Carbon, and Uniformity

CNTs are often contaminated with metal catalyst particles and amorphous carbon on both external and internal walls. Will a CNT contaminated with metal catalyst and/or amorphous carbon be considered

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[57] *See* Miller *supra* note 12 at 437-38.

[58] Lianxi Zheng et al., *Ultralong Single-Wall Carbon Nanotubes*, 3 NATURE MATERIALS 673, 673-76 (2003).

[59] *See* Shengdong Li et al., *Electrical Properties of 0.4 cm Long Single-Walled Carbon Nanotubes*, 4 NANO LETTERS 2003, 2003-07 (2004).

the same composition of matter as JP Patent No. 8,027,279 "*preferably the entire fibril is substantially free of thermal carbon overcoat*?"

Furthermore, MWCNTs with uniform wall spacing are considered more desirable than those with variations due to their superior properties. From our TEM analysis of CNT products, it is possible to find CNTs changing from a tubular structure to a herringbone or stacked wall configuration along its length due to defects or minute changes in growth conditions. Courts should appreciate and distinguish the difference between "perfect" and "imperfect" CNTs when reviewing patents.

3.6 Nanotube Ends/Caps

Does the end/cap of the CNT impact on the composition of matter claim? There are a number of CNT ends/caps described in the literature; regular half fullerene caps, as claimed in U.S. Patent No. 6,683,783 "[*the end] is a hemispherical fullerene cap having at least six pentagons and the remainder hexagons*,"[60] but also tapered edges that come to a point, or even open-ended tubes.[61] Furthermore variations can be present on one or both of the ends, giving rise to different CNT properties.

3.7 Nanotube functionalisation

The deliberate addition of certain chemical groups to the CNT structure can result in CNTs with modified properties and applications (e.g. WO Patent No. 2007/067079). It is yet to be discussed whether a functionalized CNT will be considered a separate composition of matter, or whether they will infringe on single and multi-wall composition of matter patents. Furthermore would this ruling change if the functionalized CNTs were produced directly in the reaction zone (1-step) or via post-synthesis CNT treatment (2-step)?

IV. METHOD CLAIMS

Numerous authors have commented on the validity of patents based on § 112, specifically the best mode and enablement requirements. We have previously published an investigation of these issues from a science perspective,[62] however we wish to briefly comment on some relevant issues again here.

This section focuses on the chemical vapor deposition (CVD) method of CNT synthesis because this method is widely regarded as the most promising for large-scale CNT synthesis, in particular using a fluidized-bed apparatus (FBCVD). Reasons for this include favorable heat and mass transfer characteristics, continuous production capabilities, and low operating and capital cost requirements.

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[60] U.S. Patent No. 6,683,783, claim 4 (filed Sept. 11, 1998).

[61] *See, e.g.*, Murr *supra* note 35 at 50.

[62] *See* MacKenzie *supra* note 10.

Patent applicants are required to disclose "sufficient" information to satisfy the requirements of § 112. There are an extraordinary number of variables influencing CNT products synthesized via FBCVD (and indeed any CVD technology). Some of these include: temperature, reaction duration, hydrocarbon source, the presence of an inert gas, other promoter gases or additives, catalyst metal(s) and particle size, catalyst loading, catalyst preparation method, pressure, gas flow-rate, gas ratios, and purification method.[63] In fact, there are so many variables in the published literature that there is no universal consensus as to the effect, if any, of the variables on CNT growth or their interactions with one another. For example, some claim that higher temperatures give small diameter CNTs[64] while others find that increasing synthesis temperature causes an increase in CNT diameter.[65]

The particular variant of CVD technology and the apparatus used can also materially impact the final product. For example, the specific geometries, characteristic gas flow, and heat and mass transfer attributes of a particular apparatus create an additional layer of variable complexity that is inexorably linked to the synthesized product and may not be decoupled.

V. CONCLUSIONS

Recent patent activity in the CNT field raises several issues that need to be addressed in order to narrow the gap between science and underlying patent protection. Not only is the actual patentability of CNTs in question, but there also exists a need for accurate and agreed-upon definitions for the various CNT structural types. These definition issues have obvious implications when patent disputes arise. We have demonstrated that many factors influence CNT properties including: morphology, chiral structure, number of walls, length, degree of wall graphitization, defects, amorphous carbon overcoat, ends/caps, and fictionalization. These structural differences need to be addressed and incorporated into universally recognized descriptions for the various CNT types.

From our review of the scientific literature, we can conclude that both multi-wall and single-wall CNTs are theoretically stable and self assemble under certain conditions in order to attain a lower energy configuration. While this suggests that CNTs could theoretically occur in nature if thermodynamically and kinetically favorable conditions were present someplace in the world without the assistance of man, very little evidence is available to prove this theory. Indeed, TEM images of MWCNTs are inconclusive due to their relatively poor quality, and no evidence has been found to support the natural occurrence of SWCNTs. It is, however, an erroneous conclusion to use the lack of evidence to conclusively state that CNTs do not occur naturally.

With regard to novelty, there is potential evidence that MWCNTs were synthesized and patented prior to 1991, but we believe Iijima's work was the first to completely describe a MWCNT. SWCNTs were almost certainly first produced in 1993, however debate is required on the issue of "obviousness" given the pre-1993 theoretical derivations of SWCNTs and their properties, and whether the presented literature was sufficient to reasonably enable someone to actually synthesize SWCNTs. We believe this will be a difficult undertaking. The requirements of § 112 may also require patents to provide a detailed

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[63] CNT purification techniques are important because they are capable of altering the final properties of CNT product. Purification removes impurities such as metal catalyst and substrate, and can also alter wall structure by the removal of amorphous carbon.

[64] *See* Dong-Hau Kuo & Mei-Yun Su, *The Effects of Hydrogen and Temperature on the Growth and Microstructure of Carbon Nanotubes Obtained by the Fe(CO)5 Gas-Phase-Catalytic Chemical Vapor Deposition*, 201 SURFACE & COATINGS TECH. 9172, 9172-78 (2007).

[65] Yun Tack Lee et al., *Temperature-Dependent Growth of Vertically Aligned Carbon Nanotubes in the Range 800-1100 C*, J. PHYSICAL CHEM. B 7614, 7614-18 (2002).

description of synthesis apparatus in conjunction with the product because they are inexorably linked and there is insufficient prior art available to act as a guide.