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**ABA SEER CAA Nanotechnology Briefing Paper**

**American Bar Association  
Section of Environment, Energy, and Resources**

**June 2006**

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# ABA SEER CAA Nanotechnology Briefing Paper<sup>1</sup>

## EXECUTIVE SUMMARY

In reviewing the statute, regulations, guidance, science, engineering, and technology utilized in implementing the Clean Air Act (CAA), the American Bar Association (ABA) Section of Environment, Energy, and Resources (SEER) CAA Nanotechnology Subcommittee developed this paper outlining possible application of the CAA to engineered nanoparticles (specifically excluding non-engineered nanoparticles, such as naturally occurring nanoparticles or nanoparticles from combustion sources). Several critical issues arise in this application. The most important issues are summarized in the following paragraphs.

First, the U.S. Environmental Protection Agency (EPA) must distinguish between types of nanoparticles, identifying nanoparticles posing actionable risk, and determining appropriate regulatory approaches for each type of nanoparticle requiring regulatory control. Nanoparticles exist in many forms in our environment today from natural and manmade sources, such as smoke, pollen, and viruses. For the first time, however, technology has developed sufficiently to allow the intentional engineering of structures with dimensions in the range of one to 100 nanometers, however. The almost infinite variety of nanostructures renders generalizations difficult and problematic, while the process of developing regulation addressing nanoparticle emissions requires caution to ensure proper priority is utilized in determining which types of nanoparticles require more conservative regulatory approaches.

Second, EPA must develop appropriate methods of sampling, analysis, and control sufficiently effective for nanoparticles. In reviewing existing tools used by current regulatory approaches, it is clear that current sampling, analytical, and control methods are ineffective when applied to nanoparticles. These methods were developed by exploiting the chemical and physical characteristics of larger particles and chemical vapors, chemical and chemical characteristics that are not shared by nanoparticles. Yet recently developed technology can fill that void utilizing EPA's existing programs.

Third, EPA must recognize and adapt to a new form of "quantification" as number, rather than mass. Currently, all CAA standards are based upon mass limitations whether mass concentrations, such as micrograms per cubic meter, or mass limitations, such as tons per year. It does not appear as though nanoparticulate can be effectively regulated in terms of mass because each particle potentially subject to regulation has an insubstantial weight not practicably quantifiable using ordinary methods. Moreover, collecting nanoparticulate and then weighing once the mass is sufficiently substantial would render the measurement meaningless because the size distribution, and thus number of nanoparticles, would be lost due to agglomeration. Thus, it appears that nanoparticles must be measured in terms of number, rather than mass.

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<sup>1</sup> Mary Ellen Ternes, McAfee & Taft, authored this paper with the kind assistance of Kenneth Meade, Wilmerhale.

Fourth and finally, to avoid creating unnecessary delay in developing strategies to address nanoparticle emissions, which could result in overregulation stifling this new industry, EPA must recognize that the current CAA program already contains sufficient authority to adequately address each of the issues discussed above, as more thoroughly explored below. But most importantly, EPA needs to determine the most efficient method to assess the risk from engineered nanoparticles and establish an appropriate mechanism to prioritize which types of engineered nanoparticles require attention first.

## I. BASE ASSUMPTIONS

### A. Behavior of Nanoparticulate

When matter gets really small, it behaves differently, and it is this different behavior that those in the fields of nanoscale science and engineering now recognize as an incredible tool in achieving valuable benefits to our society.

The difference in behavior occurs because atomic properties become more significant as the atom or atoms are freed from the affects of surrounding material. An easy example is gravity -- gravity does not matter, almost.<sup>2</sup> Also, the surface area of an atomic-sized bit of particulate matter is much greater in proportion to the contents of that atomic-sized bit of matter than larger sized particulate matter, allowing the atomic-sized bit of matter to become more chemically reactive -- important for catalysts in, for example, fuel cells and batteries.<sup>3</sup> The behavior of the matter is also more influenced by “quantum effects,” which, simply put, is behavior of matter at the atomic level that is different than the behavior of that very same type of matter on a larger scale. For example, heat is absorbed continuously by normal scale matter, but only in discrete amounts for atomic sized matter,<sup>4</sup> while conductivity has been shown to occur in two dimensional nanoapplications, such as one layer of graphite (*i.e.*, pencil “lead”).<sup>5</sup> The difference in chemical and physical properties and behaviors of this material is one of the biggest challenges facing environmental regulation of this industry.

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<sup>2</sup> Physics Web, News for January 2002, Neutrons reveal quantum effects of gravity (Jan. 17, 2002) (“Physicists have observed quantized states of matter under the influence of gravity for the first time; ... cold neutrons moving in a gravitational field do not move smoothly [as predicted for gravitational fields by the equivalence theory] but jump from one height to another, as predicted by quantum theory; ... the effect of gravity is negligible at the atomic scale”), see <http://physicsweb.org/articles/news/6/1/9>.

<sup>3</sup> The Royal Society & The Royal Academy of Engineering (July 2004) at 5.

<sup>4</sup> Max Planck (1900) (energy can be released (or absorbed) by atoms only in “packets” of some minimum size; this minimum energy packet is called a quantum).

<sup>5</sup> Scientific American, “Graphite Found to Exhibit Surprising Quantum Effects” (Nov. 10, 2005) (“Albert Einstein, Paul Dirac and other founding physicists may have used pencils to work out the details of relativity and quantum mechanics. Now their modern successors are employing pencil lead in a new way to prove those theories -- and potentially point the way toward a whole new form of electronics.”).

Environmental policy and regulation developed to date relies on familiar chemical and physical properties:

- Solubility, the degree to which a substance can dissolve in another before reach saturation (*e.g.*, the difference between a positive analysis for BTEX versus free product in an UST cleanup);
- Reactivity, the degree to which a substance reacts with another (*e.g.*, the amount of a material necessary to neutralize an acid or base);
- Toxicity, calculated based upon assumed exposure routes and amounts for carcinogens and noncarcinogens; and
- Mass, a measure of the Earth's gravitational pull on a material (almost all environmental release restrictions are based on mass).

Environmental policy and regulation of nanoparticles, however, may introduce an entirely new set of critical parameters, including aerodynamic size, surface area, shape, composition (organic, metallic, or both), conductivity, and reactivity.

Moreover, in attempting to evaluate the risk posed by these nanostructures, if we look merely at the base element, such as carbon in a carbon sheet, nanotube, or buckyball, these forms seem relatively benign. When the properties of carbon in such forms reveal increased conductivity depending on the “chirality” or relative twisting of the structure as in DNA’s double helix, however, we are reminded that engineered nanostructures are engineered precisely for these unique properties that arise from the structure itself, rather than the mere element or molecule alone, causing the properties of the structure to be the characteristic properly subject to regulation, rather than the properties of the element or molecule, as is currently regulated.

Evaluating the risk posed by different types of engineered nanoparticles becomes even more challenging when the structures utilize elements or chemicals currently regulated due to their systemic toxicity or carcinogenicity, and even more so due to the potential synergistic effects of structures combining these high risk elements or chemicals.

#### 1. Targeted Nanoparticle As Engineered Product

Nanoparticles have always existed in the natural world and are a commonly recognized product of naturally occurring combustion (*i.e.*, forest fires and volcanic eruptions). It is not a stretch to understand that internal combustion engines, power plants, fire places, charcoal grills and scented candles all generate nanoparticles as well. These particles are merely byproducts of combustion and, though man-made, are not “engineered,” however.

“Engineered” nanoparticles are those products manufactured through construction at the molecular level. Recent developments in methods and equipment can now be used to

manipulate single atoms. Single atoms have been manipulated into sheets, tubes, and spheres called “buckyballs,”<sup>6</sup> all made of simple carbon. Other types of nanoengineering include:

- Attaching benzene molecules to carbon sheets to conduct electricity;
- Using the M13 virus to attract and bind cobalt oxide ions on its outside layer to create positive electrodes;<sup>7</sup> and
- Killing cancer cells with a nanoparticle of polymer loaded with toxic docetaxel, studded with aptamers (tiny proteins) and polyethylene glycol molecules.<sup>8</sup>

The types of equipment used to manipulate atoms include the “scanning tunneling microscope” in 1982, and the atomic force microscope in 1986.<sup>9</sup> This equipment actually allows us to pick up an atom, slide or drag an atom, and build nanostructures.

Generally, nanoscale manufacturing occurs in either a “top-down” or “bottom-up” method, and in either a wet or dry environment. Top-down manufacturing involves breaking down a surface through cutting, edging, or grinding or imposing a pattern through lithography to create computer chips, or optical mirrors. Bottom-up manufacturing involves building materials through chemical synthesis, including both self-assembly (*i.e.*, growing crystals) and positional assembly, to create a variety of products, including cosmetics, fuel additives, displays, or experimental atomic or molecular devices.<sup>10</sup>

These manufacturing methods generally begin by subjecting a medium of solid, liquid, or gas to a reaction, which results in a transformation with a particular efficiency, creating a product of a particular purity which must be separated from unreacted byproducts.<sup>11</sup> Essentially, these production stages are very similar to those currently used in manufacturing, in either continuous or batch processes. Thus, points of potential waste generation and possible routes of exposure to waste byproducts would likely be similar and thus somewhat predictable.

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<sup>6</sup> See <http://www.nanotech-now.com/nanotube-buckyball-sites.htm>.

<sup>7</sup> Researchers trying to make tiny machines have turned to the power of nature, engineering a virus to attract metals and then using it to build minute wires for microscopic batteries. Reuters (Apr. 6, 2006).

<sup>8</sup> Nanoparticles Annihilate Prostate Cancer, Scientific American (Apr. 11, 2006).

<sup>9</sup> The Royal Society & The Royal Academy of Engineering (July 2004) at 6.

<sup>10</sup> *Id.* at 25 (Table 4.1).

<sup>11</sup> See generally *id.* at 26 (Table 4.2).

Examples of manufacturing sectors currently utilizing nanotechnology include:<sup>12</sup>

- Structural applications -- ceramics, catalysts, composites, coatings, thin films, powders, metals;
- Skincare products -- metal oxides (titanium dioxide, zinc oxide, iron oxide);
- ICT -- single wall nanotubes, nano electronics, optic-electro materials (titanium dioxide, zinc oxide, iron oxide), organic light-emitting diodes;
- Biotechnology -- nanoencapsulates, targeted drug delivery, bio-compatible quantum dots, composites, biosensors;
- Instruments, sensors, characterization -- MEMs, NEMs, SPM, dip-pen lithography; and
- Environmental -- nanofiltration, membranes.

A manufacturing process that utilizes nanotechnology, in one form or another, may produce manufactured nanoparticulates that escape the manufacturing process, as well as byproducts that do not conform to the desired product specifications (and may be discarded as waste or allowed to escape as air pollutant emissions). Current air pollution monitoring methods, ambient air modeling methods, sampling and analytical methods, and control methods, do not perform adequately when applied to nanoparticles because they were created to identify, measure by mass, capture, and control elements or molecules of no particular physical shape or structure (other than size greater than 1000 to 1500 nanometers that behave in predictable ways both chemically and physically)

## II. STATUTORY MODEL: THE CLEAN AIR ACT

The CAA established a process by which EPA can attempt to regulate releases of pollutants into the ambient air. This process includes identifying the types of pollutants, characterizing the risk of exposure to these pollutants once released to the atmosphere, controlling the release of these pollutants to the degree necessary to protect human health and the environment (based upon the potential risk once released), and monitoring the ability of regulated entities to capture these pollutants to prevent or mitigate their release.

The risk posed by exposure to nanoparticles in general is currently not well defined. Much work has been done to characterize the risk posed by certain types of

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<sup>12</sup> *Id.* at 27; *see also* EPA, External Review Draft: Nanotechnology White Paper (Dec. 2, 2005), available at [http://www.epa.gov/osa/pdfs/EPA\\_nanotechnology\\_white\\_paper\\_external\\_review\\_draft\\_12-02-2005.pdf](http://www.epa.gov/osa/pdfs/EPA_nanotechnology_white_paper_external_review_draft_12-02-2005.pdf); Nanomaterials a risk to health at Work? First International Symposium on Occupational Health Implications of Nanomaterials; Nanoparticles and the Environment, Pratim Biswas, Chang-Yu Wu.

nanoparticles, particularly nanoparticles produced by conventional combustion technologies used, for example, in mobile sources and power plants. While nanoparticles may consist of constituents that are currently regulated pursuant to the CAA, they behave very differently from those currently regulated due to their small size, negligible mass, and higher reactivity resulting from larger surface areas. As a result, application of conventional methods to identify, monitor and measure, and control nanoparticles is, for the most part, inappropriate.

The CAA does provide the statutory framework and authority to both regulate these emissions of engineered nanoparticles, as well as to support the development of the appropriate tools to identify, monitor, and measure emissions of engineered nanoparticles and establish proper emission limitations and compliance tools, however. The following discussion addresses the provisions of the CAA relevant to EPA's regulation of engineered nanoparticle emissions.

A. Subchapter I, Part A -- Air Quality and Emission Limitations, §§ 101, 103, 108, 109, 110, 111, 112, 123

1. Sec. 101. Findings and Purpose

In enacting the CAA, Congress found, in relevant part, that the growth in the amount and complexity of air pollution brought about by industrial development had resulted in mounting dangers to the public health and welfare, including hazards to air. Congress additionally found that federal leadership would be essential for the development of cooperative federal, state, regional, and local programs to prevent and control air pollution.

Congress thus declared the purpose of the CAA was to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population, as well as to initiate and accelerate a national research and development program to achieve the prevention and control of air pollution.

This statutory authority applies with equal force to regulation of nanoparticle emissions where such emissions present a threat to the public health and welfare.

2. Sec. 103. Research, Investigation, Training, and Other Activities

With Section 103, Congress provided the Administrator with authority to establish a national research and development program for the prevention and control of air pollution, giving the Administrator broad authority to coordinate with other federal departments and agencies, and to develop a program of research, testing, and development of methods for sampling, measurement, monitoring, analysis, and modeling of air pollutants, including consideration of individual as well as complex mixtures of air pollutants and their chemical transformations in the atmosphere.

Nanoparticulate emissions would certainly seem to fall well within "complex mixtures" and "their chemical transformations in the atmosphere." Certainly, EPA's current

regulatory and policy development structure created in reliance on Section 103 is well-suited to address air emissions resulting from the emerging nanotech industry.

a. Air Pollutant Emissions Measurement

The Emission Measurement Center (EMC) of the EPA Office of Air Quality Planning and Standards (OAQPS) develops procedural methods used to characterize and measure air pollutant emissions. The EMC is divided into two groups -- Source Measurement Analysis Group and Source Measurement Technology Group. The EMC is part of the Emissions Monitoring and Analysis Division in OAQPS. Bringing together research scientists in EPA's Office for Research and Development (ORD) and those in OAQPS that are responsible for developing national performance and emissions standards, the EMC has developed methods for measuring air pollutants generated by the entire spectrum of industrial stationary sources. The EMC also serves as a conduit between regulators and the regulated community in providing technical expertise and guidance necessary to implement the rules, especially in specifying emission testing methods for pollution control evaluations, compliance determinations, and performance testing. The EMC is the EPA's focal point for planning and conducting field test programs to provide quality data in support of regulatory development, producing validated emission test methods, and providing expert technical assistance for EPA, state, and local enforcement officials and industrial representatives involved in emission testing.

The EMC publishes methods for emissions testing and monitoring in five categories differentiated by (1) the legal status of the methods with regard to their application under federally enforceable regulations and (2) the validation information available on the method and EPA's corresponding confidence in application of the method for its intended use. The EMC has published methods in the *Federal Register* that have been codified in 40 C.F.R. Parts 51 (SIP), 60 (NSPS), 61 (NESHAP) and 63 (MACT). In addition, the EMC also develops source category approved alternative methods (EPA approved alternatives to promulgated methods), conditional methods (methods reviewed and potentially applicable to specific source categories), preliminary methods (not well-defined but potentially useful in specific scenarios as gap-filling methods), and "idea box" methods (intended to promote information exchange only).<sup>13</sup> Methods developed by the EMC to date cover a wide variety of industry sectors and air pollutants.

It is clear from the breadth of the methods that EMC has developed to date that the EMC has statutory authority and the technical expertise to investigate and develop methods, using and building upon current state-of-the-art laboratory procedures, that would be adequate for at least quantifying nanoparticulate emissions.

Any effort to do so faces significant challenges. For example, there are detailed discussions in the docket materials supporting EPA's PM<sub>2.5</sub> rule regarding the struggles that are faced in attempting to capture and quantify nanoparticulate emissions. Though EPA recognizes many categories of ultra-fine particles less than 1 micron in diameter ("ultrafine particles" less than 0.1 micron in diameter that grow by coagulation or condensation and accumulate; "Aitkin-

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<sup>13</sup> See <http://www.epa.gov/ttn/emc/tmethods.html>.

Mode Particles between 0.01 and 0.1 micron, and Nucleation-Mode Particles less than 0.01 microns), EPA's own draft Staff Paper addressing PM<sub>2.5</sub> monitoring<sup>14</sup> provides that the PM<sub>2.5</sub> rule requires ambient monitoring using technology that is capable of capturing merely 50% of particles with aerodynamic diameter of 2.5 microns, 50% collection efficiency being deemed the effective cut off point.<sup>15</sup> However, the Staff Paper goes on to recognize various types of non-mass reliant ultra fine monitoring devices that count number, rather than capture and weigh mass,<sup>16</sup> including the nano-scanning mobility particle sizer (NSMPS), which counts particles between 0.003 to 0.15 µm range (as opposed to a standard scanning mobility particle sizer (SMPS), which counts particles in the 0.01 to 1 µm range). All of these techniques are discussed as "widely used in aerosol research."<sup>17</sup>

EPA's Staff Paper also recognizes, however, that while it may be possible to count ultrafine particulates, they change so quickly that the time distribution over the counting process may render the final count meaningless.<sup>18</sup> These changes affect the distribution of size, volume, and surface area of the nanoparticles. For example, while the Staff Paper discussed "typical distribution" of ambient particles,<sup>19</sup> all of these distributions may vary across locations, conditions, and time due to differences in sources, atmospheric conditions, topography, and the age of the particulate.

b. Air Pollutant Emissions Modeling

EPA also has a wide variety of resources that are used to model air pollution. EPA currently operates the Support Center For Regulatory Air Models (SCRAM) site, which provides information about mathematical models used to predict the dispersion of air pollution, such as computer codes, meteorological input data, documentation and guidance on usage. EPA's Regional Modeling Center provides information and data associated with regional applications, including a description of modeling projects, tabular and graphical summaries of the emissions scenarios, simulated model results, and access to emissions and meteorological inputs and predictions. EPA's The Modeling Clearinghouse is used for review of modeling techniques in specific applications. In its modeling, EPA utilizes Models-3, a flexible software

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<sup>14</sup> Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information, Table 2-1, OAQPS Staff Paper -- First Draft (EPA-452/D-03-00) (Aug. 2003).

<sup>15</sup> See also 40 C.F.R. Part 50, Appendix L; 40 C.F.R. Part 53, Subpart F, Table F-3 (showing "fine" particulate as 0.85 microns).

<sup>16</sup> See Staff Paper at Section 2.4.2.

<sup>17</sup> See Continuous and Semi-Continuous Methods for PM Mass and Composition, Paul Solomon and Constantinos Sioutas, EM (Apr. 2006) at 17.

<sup>18</sup> Staff Paper at 2-4 and 2-5.

<sup>19</sup> The largest number of ambient particles in a typical distribution are very small, below 0.1 µm in diameter; however, most of the particle volume, and therefore most of the mass, is found in particles with diameters larger than 0.1 µm. Most of the surface area is between 0.1 and 1.0 µm, the distribution of which peaks around 0.2 µm. *Id.*

design system to simplify the development and use of environmental assessment and decision support tools for a wide range of applications from regulatory and policy analysis to understanding the interactions of atmospheric chemistry and physics. The initial version of Models-3 contains a Community Multiscale Air Quality (CMAQ) system with capabilities for urban to regional scale air quality simulation of tropospheric ozone, acid deposition, visibility, and fine particulate. EPA's Air Quality Modeling Group provides support in atmospheric and mathematical technique.

EPA also has models specifically designed for air toxics, including the Industrial Source Complex (ISC3) model, or, for more simple screening, the TSCREEN model. Stationary sources can also utilize EPA's "Guidance on the Application of Refined Dispersion Models for Hazardous/Toxic Air Releases," which provides guidance on the use of dense gas models.

The major barrier preventing use of EPA's current modeling resources to characterize the fate and transport of nanoparticle pollutant emissions in the atmosphere is that the current set of models utilize parameters (*i.e.*, follow rules) that describe the behavior of the target pollutants that are either measurable particulate in steady state or are chemicals, in each case regulated by mass. Because nanoparticles are neither steady state, nor properly regulated as mass, these models simply cannot be used for purposes of modeling nanoparticles. Thus, until measurement and modeling methods are developed for nanoparticles that take into account the unique nature of these pollutants, nanoparticulate emissions cannot be reliably measured, and their fate and transport in the atmosphere cannot be predicted. Because there are so many different types of nanoparticles that can vary so widely, work to develop proper measurement and modeling parameters must be carefully managed to ensure efficient use of resources and development of appropriate priorities.

### 3. Sec. 108. Air Quality Criteria and Control Techniques

Section 108(a) requires EPA to publish a list including each criteria air pollutant for the purpose of establishing national primary and secondary ambient air quality standards within 30 days after December 31, 1970, to be revised "from time to time, thereafter." Thus, theoretically, EPA could revise the NAAQS to include nanoparticles. A simpler path forward may be to simply revise the tools used to monitor the current PM<sub>2.5</sub> NAAQS so that nanoparticles are included in the PM<sub>2.5</sub> compliance requirements.

Section 108(b) requires EPA to publish air pollution control techniques simultaneously with the publication of the criteria pollutants list or a revision to that list. If EPA decided to designate nanoparticles as a criteria pollutant (which seems unworkable given the time consuming process of criteria pollutant process), then EPA would be required to also publish air pollution control techniques. EPA enforces air pollution control efficiencies and even specific technologies in implementing many sections of the CAA as discussed below, however.

a. Conventional Air Pollution Control Technology

The CAA requires the use of specific pollution control technologies and work practices at stationary sources through several different sections of the CAA: Standards of Performance for New Stationary Sources (NSPS pursuant to Section 111), Prevention of Significant Deterioration/New Source Review (PSD/NSR pursuant to Sections 108 and 109, and 160 through 193), and National Emission Standards for Hazardous Air Pollutants (NESHAPs pursuant to Section 112). Each of these statutory programs requires certain control technologies and work practices, and/or equivalent control efficiencies.

Processes that combust hazardous and solid waste, and the pollutants that are emitted by these processes, are regulated by a wide variety of conventional air pollution control methods proscribed by these programs. These industries combust extremely varied waste streams, creating nanoparticles of every type. Air pollution control methods currently used by waste combustion sources are designed to control a wide variety of pollutants, including acid gases such as chlorides or other halogen acid gases, criteria pollutants such as nitrogen oxides and sulfur dioxides, volatile organic compounds which are photoreactive and can form ozone, and particulate emissions. Any attempt to control nanoparticulate emissions, however, must be focused on ultrafine particulates that are much less than 2.5 microns (2500 nanometers) in diameter (also commonly referred to as aerosols, fumes, or very fine dust). A wide variety of air pollution control equipment is currently utilized to control types of emissions from stationary sources that may contain nanoparticulates such as fumes, mists, dusts, sprays, smokes, fly ash, coal dust, metal fumes and dust, carbon black, pulverized coal, and alkali fumes. Those methods include cyclones, scrubbers, filters, and electrostatic precipitators. Higher efficiency scrubbers and filters include ultrasonic venturi scrubbers, liquid scrubbers and packed beds, and high efficiency particulate air filters.<sup>20</sup>

All of these gas scrubbing techniques utilize one of four types of mechanisms for collecting particulate matter: interception, gravitational force, impingement, or contraction and expansion. Interception causes an effective increase in size of the fine particle, allowing it to be affected by gravity and thus easier to remove through settling, or slowing of the gas stream sufficiently to allow particles to fall out. Impingement occurs when an obstacle is placed in the gas stream itself such that particles that are too heavy to flow around the obstacle strike the obstacle itself. Contraction involves condensation of the moisture in the stream in an area of

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In ultrasonic venture scrubbers, the stack gas is accelerated through an impact zone, causing the particulate to stick together or “agglomerate,” after which the gas is circulated through a settling chamber to allow gravity to pull down the larger sized particulates. Scrubbers and packed beds remove particulate by causing the gas stream to percolate through, and contact, absorbing liquid, frequently utilizing packing to increase surface area for maximum contact between gas and liquid; HEPA filters remove particulate by filtering small particles from the gas stream while electrical precipitators collect oppositely charged particles. Handbook of Incineration Systems, Calvin Brunner, P.E., D.E.E., Chapter 22, Figure 22.1.

high turbulence, resulting in improved contact between solid and liquid particles which, through agglomeration, become heavy enough to separate from the gas stream.<sup>21</sup>

The removal efficiency achieved by each of these methods is dictated in large part by particle size (without considering operational parameters that are unrealistic in application, such as attempting extraordinarily high pressure drops to achieve greater impacts), either initial particle size or the size of the agglomerated particle created by the control device. Beginning with particles less than 100 nanometers, however, the chemical and physical characteristics of these particles do not behave as larger particles do, rendering these conventional control device techniques ineffective.

As an example, solid waste incinerator emissions treated with multistage controls, including a venturi and spray scrubber, achieved particulate removal efficiencies approaching 100% for all particulate matter over 5 microns in diameter, with 54.6% of the particulate emissions less than 760 nanometers in size. Thus, after applying all the stages of current air pollution control technology, approximately one half of the remaining particulates that will be emitted by this combustion source will be less than 760 nanometers.

Recent literature describing a study of venturi scrubbers utilizing a fine-water mist spray to achieve nucleation and agglomeration did achieve reportable removal efficiencies of particles between one and 100 nanometers.<sup>22</sup> With the aid of the fine-water mist spray to first cause the ultra-fine particulate to stick together into larger particles, the scrubber achieved 40% removal efficiency for 50 nm particulate, and 80% removal for 100 nm particulate.<sup>23</sup>

b.      Enhancements Benefitting Nanoparticulate Removal

Currently, devices relying primarily on impact and agglomeration have not yet been developed for nanoparticulate removal in industry, though devices such as cyclones enhanced through operation at low pressures or addition of electrical fields may show some promise.<sup>24</sup>

Filtration systems, such as conventional HEPA filters and ultra-low particulate air-rated filters, have reportedly achieved relatively high removal efficiencies of fine particulate, such as 99.97% removal at 7300 nm and 99.9999% removal at 100 nm, but only if using very high-pressure drops. Use of a filtration system with very high pressure drops is not a widespread

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<sup>21</sup>      *Id.* at 22.14.

<sup>22</sup>      *An Efficient Venturi Scrubber System to Remove Submicron Particles in Exhaust Gas*, Cheun-Jinn Tsai, Chia-Hung Lin, Yu-Min Wang et. al, Journal of the Air & Waste Management Association, Vol. 55, p. 319 (Mar. 2005).

<sup>23</sup>      *Id.* at 323.

<sup>24</sup>      *Nanoparticles and the Environment*, Pratim Biswas and Chang-Yu Wu, Journal of Air & Waste Management Association, Volume 55, p. 708, 720 (June 2005).

practice, as it requires maximum performance, very high power usage and may damage the filtration equipment. The performance of these filters may be enhanced without using such great pressure drops by using electrostatically augmented air filters and dielectric screens.<sup>25</sup> These applications, however, are expensive and typically used only where absolutely necessary, such as ultra-clean rooms for micro-electronics component assembly or hospital surgeries. It is not yet clear whether this type of filtration will be feasible, adequate, or practical for industrial applications.

Another potential method of nanoparticulate control may involve utilizing a temperature gradient to direct nanoparticulate direction. In areas with higher temperatures, the nitrogen and oxygen molecules in the air are more excited and, thus, move around more. This movement effectively pushes the nanoparticle to an area of less molecular excitation (*i.e.*, a cooler area). This type of collection is called “thermophoretic collection” or “thermogenic separation.” The potential benefit of this type of particulate collection for nanoparticles is that the effect is independent of size, as long as the size is nanoscale. Another benefit of thermophoretic collection is that many nanoscale synthesis systems utilize high temperatures to enhance chemical reactions necessary to achieve the molecular state from which the desired nanoparticle can be assembled through nucleation (preferred joining together, as in agglomeration or crystallization). The nucleation process occurs in a quench zone with high temperature gradients from hot to cool. Thus, thermophoretic collection systems may be a natural method for nanoparticulate collection, although the issue of removal remains.<sup>26</sup>

Another promising method for nanoparticulate removal, especially for systems with low-pressure drops (relatively constant pressure systems with low gas stream velocity), is the use of electrical fields. Particles that are electrically charged and subjected to an electric field become attracted to collector walls. Studies have indicated, however, that some particles fail to achieve a charge using standard electrical methods, resulting in less efficient capture (*i.e.*, from 90% for 60 nm particulate to less than 10% for 10 nm particulate). Enhancement of the process with additional directed ionization sources (“soft X-ray irradiation and unipolar coronas”), however, greatly enhances the capture efficiencies, raising them to greater than 99.99% for 5 to 100 nm particles.<sup>27</sup>

Thus, it is clear that air pollution control technologies exist upon which EPA can rely in implementing specific air emission standards pursuant to the various sections of the CAA.

#### 4. Sec. 109. National Ambient Air Quality Standards

If EPA determined to regulate emissions of engineered nanoparticles as a new criteria pollutant pursuant to CAA Section 109, a fundamentally different approach would be in order. The criteria pollutants adopted to date by EPA pursuant to Section 109 (and their precursors) are regulated in terms of mass per volume of air. Nanoparticles may very well be

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<sup>25</sup> *Id.*

<sup>26</sup> *Id.* at 721.

<sup>27</sup> *Id.*

PM<sub>2.5</sub>, behave like VOC ozone precursors, or they may contain lead. It is unlikely that regulation of engineered nanoparticles based on mass limitations would be sufficient or adequate in terms of eliminating or minimizing the health impacts of ambient concentrations of these nanoparticles, however. Section 109 does not require that the regulation of identified criteria pollutants be based upon mass limitations or concentrations determined by mass. Therefore, Section 109 does not prevent EPA from adopting criteria pollutant primary or secondary standards based upon “number” of particles, rather than mass. The question may be, given the relatively smaller number of nanotechnology-based manufacturers that may release engineered nanoparticulates over the next few decades, compared to existing manufacturing sectors, could engineered nanoparticle emissions cause engineered nanoparticle concentrations (numerically based) in the ambient air sufficient to justify regulation as a criteria pollutant. As discussed above, EPA is not even regulating non-engineered nanoparticle emissions from mobile sources or power plants (carbonaceous particulate and condensable vapors) because they are not captured by the PM<sub>2.5</sub> monitor. Would EPA single out engineered nanoparticles as a PM<sub>2.5</sub> or VOC precursor? Or would EPA simply create a general nanoparticle PM<sub>2.5</sub> [1-100 nm] category and regulate all nanoparticulate ambient concentrations?

EPA could choose to regulate engineered nanoparticles as precursors to PM<sub>2.5</sub> or VOC (and thus ozone), as a form of an existing criteria pollutant, or EPA could choose to regulate engineered nanoparticles as Hazardous Air Pollutants (HAP) and develop new Maximum Achievable Control Technology (MACT) Standards for these new industries. The latter seems more workable, but either appears possible.

5. Sec. 111. Standards of Performance for New Stationary Sources

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Section 111 provides the Administrator with authority to specifically limit criteria pollutant emissions from new stationary sources and to require specific types of pollution control technologies and/or work practices. If EPA decided to regulate nanoparticles as criteria pollutants, presumably as something akin to PM<sub>0.01-0.10</sub> (to capture nanoparticulate much smaller than PM<sub>2.5</sub>), EPA could exercise its discretion to adopt new standards regulating nanoparticulate emissions pursuant to Section 111. This would be a burdensome task, as New Source Performance Standards and Emissions Guidelines (NSPS/EG) promulgated pursuant to Section 111 are developed on a source-category specific basis. As a result, in order to meet statutory requirements, EPA would be required to amend current NSPS/EG, or adopt new NSPS/EG, for each source category emitting the covered criteria pollutant -- in this case PM<sub>0.01-0.10</sub>.

6. Sec. 112. National Emission Standards for Hazardous Air Pollutants

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Section 112 provides the Administrator with authority to regulate a pollutant as a HAP if it is on the list established by Congress at Section 112(b)(1). Nanoparticles are not specifically listed in Section 112(b)(1). Constituents contained in nanoparticles may be listed; however, the statutory list does not generically identify nanoparticles, based on physical form or size, on the list.

Paragraph (b)(2) does provide the Administrator with the authority to revise the list:

(b)(2) Revision of the list.- The Administrator shall periodically review the list established by this subsection and publish the results thereof and, where appropriate, revise such list by rule, **adding pollutants which present, or may present, through inhalation or other routes of exposure, a threat of adverse human health effects** (including, but not limited to, substances which are known to be, or may reasonably be anticipated to be, carcinogenic, mutagenic, teratogenic, neurotoxic, which cause reproductive dysfunction, or which are acutely or chronically toxic) or adverse environmental effects whether through ambient concentrations, bioaccumulation, deposition, or otherwise, but not including releases subject to regulation under subsection (r) as a result of emissions to the air. **No air pollutant which is listed under section 108(a) may be added to the list under this section, except that the prohibition of this sentence shall not apply to any pollutant which independently meets the listing criteria of this paragraph and is a precursor to a pollutant which is listed under section 108(a) or to any pollutant which is in a class of pollutants listed under such section.** No substance, practice, process or activity regulated under title VI of this Act shall be subject to regulation under this section solely due to its adverse effects on the environment.

EPA, therefore, has the statutory authority to add nanoparticles to the list of HAPs, assuming that it has a scientific basis to do so, pursuant to the criteria set forth in Section 112(b)(2). If EPA were to do so, it could adopt MACT Standards, on a source category basis, for source categories emitting nanoparticles above threshold levels. As is the case with criteria pollutants, the statutory scheme contemplates regulating sources based on mass -- in this case, sources that have the potential to emit greater than ten (10) tons per year (tpy) of individual HAPs, or 25 tpy HAPs in the aggregate. EPA does have the authority, however, to also regulate HAP sources with potential emissions below those thresholds (so-called area sources).

Subsection (b)(4) further provides EPA with the authority to establish, by rule, test measures and other analytic procedures for monitoring and measuring emissions, ambient concentrations, deposition, and bioaccumulation of manufactured pollutants, including nanoparticles, should EPA determine that nanoparticles should be a listed HAP in Section 112.

Section 112(r) provides a mechanism for further regulation, in the context of preventing and mitigating accidental releases, for pollutants designated by EPA as “extremely hazardous substances.” Nanoparticles are not currently so designated, but could be.

## 7. Sec. 123. Stack Heights

Section 123 prohibits the use of stack height as a means of circumventing emission limitations, thereby ensuring that sources cannot engineer a stack to exceed stack height “good engineering practices” in order to rely on dispersion rather than emissions limitations to reduce the impact of emitted pollutants on human health and the environment. This is not to say that some dispersion is not included when assessing emission impacts and potential control strategies; rather, the prohibition is to ensure that artificially high stacks are not used as a control strategy. For some transient forms of nanoparticulate emissions, dispersion may be an appropriate method of control strategy, particularly for those forms that quickly change or degrade when exposed to sunlight and other atmospheric conditions.

### B. Subchapter I, Part C -- Prevention of Significant Deterioration of Air Quality, §§ 160 through 193

The CAA’s Prevention of Significant Deterioration provisions provide EPA with authority to limit emissions of criteria pollutants into the ambient air to maintain compliance with the NAAQS. Given that nanoparticles could theoretically be regulated under one or more different categories (*i.e.*, under NAAQS, either as in VOCs (ozone precursors) or ultrafine particles not counted as PM<sub>2.5</sub>, and/or HAPs), addressing Part C (which applies to areas that currently meet established NAAQS for criteria pollutants) is premature at this point. It is clear, however, that how EPA decides to classify nanoparticles (*i.e.*, as an ozone precursor, as PM<sub>2.5</sub>, or as a HAP) will determine whether, and how, nanoparticles will be treated for purposes of Part C.

Currently, PM<sub>2.5</sub> monitors demonstrate low capture efficiency below 1 micron, and none below 0.5 micron, and even then there is no particle size distribution. Further, the smaller nanoparticles and precursors of larger particulate are not captured by the current monitoring method for PM<sub>2.5</sub>, which has a 50% cut point at 2.5 microns (see footnote 14) and falls outside the scope of the current PM<sub>2.5</sub> standard.

If future developments in monitoring technology allow, EPA could propose revisions to the current PM<sub>2.5</sub> standard, and specifically the monitoring provisions of that standard, to include monitors that capture submicron particulate. However, inclusion of submicron particulate in the PM<sub>2.5</sub> standard, which is simply a mass limitation per volume of air, alone will not adequately protect public health if, for example, it is demonstrated that forms of the submicron particulate are extremely harmful at exposures more properly characterized as numbers of particles, rather than mass of particles.

### C. Subchapter II, Part A -- Motor Vehicle Emission and Fuel Standards, §§ 202 and 211

A significant percentage of nanoparticles in the ambient air in developed countries today is generated by mobile sources. The types of nanoparticles normally emitted from mobile sources, without considering nanoparticle fuel additives, are generally carbonaceous combustion byproduct and nitrogen oxides. These nanoparticles are not regulated by the current

PM<sub>2.5</sub> NAAQS, as indicated above. As is the case with these types of nanoparticles that are emitted from stationary sources, they could be regulated through an additional PM standard, should EPA choose to do so. Additionally, if developments in technology allow, EPA could incorporate nanoparticle emission standards into existing auto emission standards pursuant to Section 202.

Additional issues arise as a result of the development and widespread use of fuel additives to enhance motor vehicle performance. There are many different types of fuel additives developed through “nanotechnology” on the market today. Some of these may be harmless, such as the H2OIL Corporation’s “F2-21” fuel additive, which appears to be merely water with a small amount of surfactant creating an emulsion, resulting in water droplets with diameters less than 100 nanometers.<sup>28</sup> Other types of “nano-fuel additives” may pose more risk, such as cerium oxide, however. According to Azonano.com, Oxonica’s nano fuel additive “Envirox” is essentially cerium oxide in particles of ten nanometer in diameter, which creates a larger surface area for catalysis.<sup>29</sup> Cerium oxide is a lung irritant, however, and at nanometer particle size it may be even a greater irritant, as greater surface area may cause greater reactivity.<sup>30</sup> Thus, EPA should ensure that it exercises its authority under the CAA to carefully evaluate the health impacts of existing and new nanoparticulate fuel additives, similar to the manner in which EPA used the CAA to ultimately phase out the use of tetraethyllead as an additive.

Section 211 provides EPA with authority to require manufacturers to provide information regarding all fuels and fuel additives and to regulate such fuels or fuel additives based on concerns arising from such information.<sup>31</sup> Sections 211(a), (b), and (c) allow EPA to require fuel additive manufacturers to provide information regarding health effects of both fuels and fuel additives, while (c) also allows EPA to regulate fuels and fuel additives generally if EPA believes any emission product of the fuel or fuel additives will cause or contribute to air pollution, or if the fuel or fuel additive will damage the vehicle’s emissions control equipment or impair its performance.

Section 211(f) prohibits regulated fuel and fuel additive manufacturers from distributing new fuels or fuel additives unless the fuel or fuel additive is “substantially similar” to any fuel or fuel additive used in vehicle certification. EPA may waive the prohibition if the manufacturer can prove that the new fuel or fuel additive and its emission products will not cause a violation of the vehicle’s emission standards.

Thus, with Sections 202 and 211, EPA currently has sufficient authority to regulate emissions of engineered nanoparticles from motor vehicles, particularly resulting from the introduction of fuel additives.

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<sup>28</sup> See, e.g., <http://www.foresight.org/nanodot/?p=1930>.

<sup>29</sup> See, e.g., <http://www.azonano.com/details.asp?ArticleID=31>.

<sup>30</sup> See, e.g., [http://physchem.ox.ac.uk/MSDS/CE/cerium\\_IV\\_oxide.html](http://physchem.ox.ac.uk/MSDS/CE/cerium_IV_oxide.html).

<sup>31</sup> The Clean Air Act Handbook, Martineau and Novello, “Regulation of Fuel and Fuel Additives,” at 300.

A word regarding *Massachusetts, et al., v. Environmental Protection Agency*<sup>32</sup> may be appropriate here. EPA's denial of the rulemaking petition seeking regulation of greenhouse gas emissions from motor vehicles pursuant to Section 202 does not prevent EPA from regulating emissions from facilities manufacturing engineered nanoparticles. First, Section 202(a)(1) gives EPA "considerable discretion" in deciding whether to make a threshold judgment to regulate.<sup>33</sup> Second, the situations are wholly different. With greenhouse gas emissions, EPA would have strained under the CAA to address the tenuous and uncertain global effects of solely anthropogenic greenhouse gas emissions into the stratosphere. With emissions of engineered nanoparticles, EPA would address emissions of substances that are more clearly "pollutants" released into the ambient air, resulting in direct and largely local impact. Moreover, there is no argument that engineered nanoparticles are solely anthropogenic. Thus, EPA can utilize its broad discretion to address emissions of engineered nanoparticles from motor vehicles, should it choose to do so.

D. Subchapter III – General Provisions, §§ 302, 303, 304

The general provisions of the CAA provide EPA with broad authority to protect public health and welfare from air pollutant emissions. The definitions provided by Section 302 provide the Administrator with broad authority to regulate any "air pollution agent or combination of such agents," including their precursors. The definition of welfare is also very broad and expands coverage to include impacts arising from the transformation, conversion, or combination with other air pollutants, which is characteristic of how nanoparticles behave in the atmosphere.

Section 303 provides EPA with authority to take emergency regulatory action when presented with evidence that a pollution source or combination of sources (including mobile sources) is presenting an imminent and substantial endangerment to the public health or welfare, or to the environment. EPA has broad authority to initiate a civil action, or issue orders for the protection of the public health or welfare, or the environment. Should EPA receive any evidence that nanoparticulate emissions from a particular source or sources pose such an endangerment, EPA has emergency powers sufficient to cause such a source or sources to cease and desist.

Section 304 allows citizens to file suit against EPA where EPA fails to perform any nondiscretionary duty or act under the CAA. At some point, should EPA fail to properly regulate nanoparticulate emissions, a good attorney will undoubtedly seek to find a nondiscretionary duty that EPA failed to perform with respect to regulating nanoparticulate emissions, and force EPA to act appropriately.

Section 320 provides EPA with authority to reconvene every three years to review its air quality modeling practices. If EPA finds itself needing additional statutory authority to

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<sup>32</sup> 415 F.3d 50 (D.C. Cir. 2005).

<sup>33</sup> *Id.* at 58.

support developing parameters to describe behavior of nanoparticulate in standard air models, EPA could look to this provision.

E. Subchapter IV -- Acid Deposition Control

Nanoparticles often contain sulfur and nitrogen; however, the small overall mass contribution to the acid deposition issue that would seem to result from emission of nanoparticles may render Title IV less of a priority in this briefing paper. Additionally, the literature provides that some sulfur is actually helpful in serving as a nucleation base for agglomerating nanoparticles. At this point, Title IV seems less applicable than the CAA provisions discussed above.

F. Subchapter V -- Permits

Should nanoparticles become regulated pursuant to other sections of the CAA, then the provisions of Title V would apply accordingly. Implementation of Title V will be particularly affected by the timeline necessary to develop and adopt appropriate technology for the identification, capture, and monitoring of nanoparticles.

G. Subchapter VI -- Stratospheric Ozone Protection, §§ 601, 602

The science of nanoparticles is not yet sufficiently developed to know whether ambient levels of certain manufactured nanoparticles could cause a detrimental effect on stratospheric ozone.

Section 601 lists Class I and Class II substances in a chemical-specific manner similar to the listings of HAPs in Section 112. Thus, the discussion above regarding Section 112 applies here as well.

Pursuant to Section 602(c), EPA may add any substance to the list of Class I or Class II substances that the Administrator finds is known or may reasonably be anticipated to cause or contribute to harmful effects on the stratospheric ozone layer. If nanoparticle substances were to be added to the lists of Class I or Class II substances, then the remaining provisions of Section 602 would apply.

## CONCLUSION

Based on the foregoing, the ABA SEER CAA Nanotechnology Subcommittee believes that EPA must: (1) distinguish between types of nanoparticles, identifying nanoparticles posing actionable risk, and determining appropriate regulatory approaches for each type of nanoparticle requiring regulatory control; (2) develop appropriate methods of sampling, analysis, and control sufficiently effective for nanoparticles; (3) recognize and adapt to a new form of “quantification” as number, rather than mass; and (4) to avoid creating unnecessary delay in developing strategies to address nanoparticle emissions, which could result in overregulation stifling this new industry, recognize that the current CAA program already contains sufficient authority to adequately address each of the issues discussed in this paper.