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(74) Agent: **KAEDING, Konrad, S.;** E. I. DU PONT
DE NEMOURS AND COMPANY, LEGAL PATENT
RECORDS CENTER, 4417 Lancaster Pike, Wilmington,
Delaware 19805 (US).

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(71) Applicant (*for all designated States except US*): **E.I. DUPONT DE NEMOURS AND COMPANY** [US/US];
1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors; and

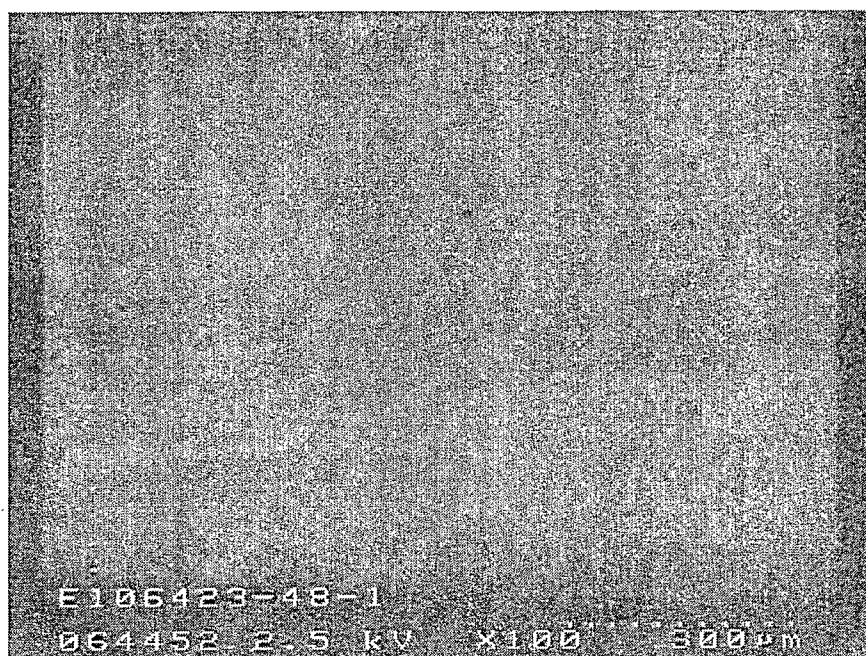
(75) Inventors/Applicants (*for US only*): **GAO, Feng** [US/US]; 48 Westwoods Boulevard, Hockessin, Delaware 19707 (US). **METH, Jeffrey, Scott** [US/US]; 106 Beacon Hill Road, Landenberg, Pennsylvania 19350 (US).

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(54) Title: METHOD FOR PREPARING CNT/PANI DISPERSIONS



(57) Abstract: This invention provides a method for preparing a carbon nanotube/polyaniline dispersion.

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

TITLE

METHOD FOR PREPARING CNT/PANI DISPERSIONS

FIELD OF THE INVENTION

This invention provides a method for preparing a carbon
5 nanotube/polyaniline dispersion.

BACKGROUND INFORMATION

Carbon nanotubes (CNTs) have a number of electronic and
dimensional attributes that are being exploited in the development of novel
compositions for use in electronic devices and other fields of use. For
10 example, CNTs have been incorporated into the conductive layer of
organic thin film transistors to enhance the performance of these devices.
In this and many other applications using CNTs, it is desirable to be able
to disperse the CNTs and maintain such dispersions to minimize
processing problems and to improve product performance.

15 WO 03/069032, WO 03/106600, WO 03/050332, and EP 1,336,672
disclose the use of dispersion aids to disperse CNTs.

EP 1,061,040 discloses a process for purifying carbon nanotubes,
in which washed carbon nanotubes are passed through a metal mesh filter
having a mesh size of 300 microns or less.

20 However, CNTs are often used in mixtures containing other
materials, such as polymers, and methods that are useful for forming CNT
dispersions may not provide adequate dispersions of CNTs in more
complex mixtures.

SUMMARY OF THE INVENTION

25 This invention provides a method for preparing a carbon
nanotube/polyaniline dispersion, comprising:

- a. sonicating a first mixture comprising: carbon nanotubes; a first solvent
selected from a group consisting of chlorinated and non-chlorinated
aromatic solvents, chlorinated and non-chlorinated aliphatic solvents,
30 C4–C10 alcohols and C4–C10 ethers; and a dispersion aid selected
from a group consisting of polyamine amides, polymers with tertiary
amine affinic groups, polymers with ethylene oxide and hydroxy affinic
groups, unsaturated polycarboxylic acid polymers, alkyl ammonium
salts of polycarboxylic acids, and carboxylic acid salts of polyamine
35 amides, to form a dispersion of carbon nanotubes; and
- b. sonicating a second mixture comprising: the dispersion of carbon
nanotubes, polyaniline, xylenes and a second solvent selected from a

group consisting of 2-butoxyethanol, 1-butanol, 1-hexanol and diethylether.

This invention also provides a composition comprising:

- a. carbon nanotubes;
- 5 b. a dispersion aid selected from a group consisting of polyamine amides, polymers with tertiary amine affinic groups, polymers with ethylene oxide and hydroxy affinic groups, unsaturated polycarboxylic acid polymers, alkyl ammonium salts of polycarboxylic acids, and carboxylic acid salts of polyamine amides; and
- 10 c. polyaniline.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is an SEM image of a coating of CNTs in DNNSA-doped PANI prepared using Disperbyk®163 as a dispersion aid.

15 Figure 2 is an SEM image of a coating of CNTs in DNNSA-doped PANI prepared without a dispersion aid.

DETAILED DESCRIPTION OF THE INVENTION

Definition of terms. As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a
20 process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A
25 or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, use of the "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to
30 give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of
35 ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications,

patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

- 5 Dispersion Process. This invention provides a method for preparing a carbon nanotube/polyaniline dispersion comprising:
- a. sonicating a first mixture comprising: carbon nanotubes; a first solvent selected from a group consisting of chlorinated and non-chlorinated aromatic solvents, chlorinated and non-chlorinated aliphatic solvents,
- 10 C4–C10 alcohols and C4–C10 ethers; and a dispersion aid selected from a group consisting of polyamine amides, polymers with tertiary amine affinic groups, polymers with ethylene oxide and hydroxy affinic groups, unsaturated polycarboxylic acid polymers, alkyl ammonium salts of polycarboxylic acids, and carboxylic acid salts of polyamine amides, to
- 15 form a dispersion of carbon nanotubes; and
- b. sonicating a second mixture comprising: the dispersion of carbon nanotubes, polyaniline, xylenes and a second solvent selected from a group consisting of 2-butoxyethanol, 1-butanol, 1-hexanol and diethylether.

- 20 Optionally, the second mixture can further comprise dinonylnaphthalene sulfonic acid, DNNSA. PANI-DNNSA solutions can be prepared by an emulsion process.

The dispersion process of this invention can be conducted using single-walled CNTs, multi-walled CNTs, or mixtures thereof.

- 25 Suitable organic solvents for the initial dispersion of carbon nanotubes include non-polar as well as somewhat polar organic solvents, such as non-chlorinated aromatic solvents, non-chlorinated alkanes, chlorinated aromatics, chlorinated alkanes, alcohols (C4–C10) and ethers. Examples of suitable solvents include toluene, benzene, xylenes,
- 30 chlorobenzene, dichlorobenzene, dichloroethane, hexane, cyclohexane, 2-butoxyethanol, 1-butanol, 1-hexanol and diethylether. Xylenes, or a mixture of xylene isomers, are preferred. In the second sonication step, the preferred dispersion solvent also comprises xylenes and at least one of 2-butoxyethanol, 1-butanol, 1-hexanol and diethylether.

- 35 Suitable dispersion aids are selected from a group consisting of polyamine amides, polymers with tertiary amine affinic groups, polymers with hydroxy affinic groups, unsaturated polycarboxylic acid polymers,

alkyl ammonium salts of polycarboxylic acids, and carboxylic acid salts of polyamine amides. Preferred dispersion aids include:

- Disperbyk®107 – poly(carboxylic acid ester) with tertiary amines and hydroxy affinic groups;
- 5 Disperbyk®108 – poly(carboxylic acid ester) with tertiary amines and hydroxy affinic groups;
- Disperbyk®130 – a solution of polyamine amides of unsaturated carboxylic acids;
- Disperbyk®163 – a polyurethane with tertiary amine affinic groups;
- 10 Byk®345 – a polyether modified poly-dimethyl siloxane with ethylene oxide and hydroxy affinic groups;
- Byk®P104 – a solution of low molecular weight unsaturated polycarboxylic acid polymers;
- Byk®9076 – an alkylammonium salt of a high molecular weight
- 15 copolymer;
- Byk®9077 – high molecular weight polymer with secondary and tertiary amine affinic groups;
- Anti-Terra®202 – a solution of an alkylammonium salt of a polycarboxylic acid, electro-neutral;
- 20 Anti-Terra®204 – a solution of a carboxylic acid salt of polyamine amides, electro-neutral;
- Anti-Terra®U- a solution of a salt of unsaturated polyamine amides and lower molecular weight polymers, electro-neutral.
- Disperbyk®163, Disperbyk®-107, Disperbyk®-108, BYK®-345,
- 25 BYK®-9077, and BYK®-9076 are preferred. Disperbyk®163 is especially preferred.

The amount of CNTs used is generally 0.001–2 wt%, more preferably 0.01–0.7 wt% of the mixture comprising CNT, dispersion aid and solvent. The amount of dispersion aid used is generally at least about

30 10% (based on weight) of the amount of CNT used, preferably at least 100% (based on weight) of the amount of CNT used. More preferably, an excess of dispersion aid (i.e., >100%, based on weight) is used.

The ratio of PANI or PANI-DNNSA to CNTs in the dispersion mixture is generally from about 5:1 to about 200:1 (by weight).

35 The sonication process steps can be carried out using a sonic probe or sonic bath/probe combination. Preferably, the mixtures are placed in a thermostatically controlled bath. Suitable bath temperatures are from 0°C to about 80°C, preferably from about 20°C to about 50°C.

Sufficient dispersion is usually achieved in each step in 10-20 minutes. The sonication steps can be interrupted periodically to scrape or rinse down the walls of the reaction vessel to return to the mixture any CNTs or other solids that have been splashed or sprayed onto the vessel walls.

5 In the process of this invention, it is preferable that the mixture of carbon nanotubes, first solvent and dispersion aid be sonicated for 10-20 minutes. After the addition of the PANI (or PANI-DNNSA), xylene and the second solvent, the resulting mixture is typically sonicated for an additional 1-20 minutes.

10 An optional filtration step can also be carried out after either the first or second sonication step to remove undispersed CNT agglomerates and/or other particulate materials. Typically, such a filtration is carried out using a filter comprising a woven metal or polymer mesh. Generally, filters with high mesh counts (i.e., small pore sizes) are preferred. Mesh counts
15 or greater than 400 x 400 are especially preferred. The metal or polymer mesh can be any material that is non-reactive with the components of the dispersion, including but not limited to stainless steel, polyester, nylon, and PEEK (polyetheretherketone). Suitable filters are available from Sefar America Inc., Kansas City, MO.

20 The effectiveness of the dispersion can be tested by coating the dispersion onto a suitable substrate, removing the solvent, and imaging the coated substrate by optical or other imaging techniques. SEM is particularly useful in this regard.

EXAMPLES

25 The carbon nanotubes (MGP/HiPco R0236) used in these examples were obtained from Carbon Nanotechnologies, Inc. (Houston, TX) and used as received. The dispersion aid, Disperbyk®-163, was obtained from BYK Chemie USA (Wallingford, CT) and used as received. The solution of PANI-DNNSA was prepared by an emulsion process, as
30 described in Macromolecules, 1998, 31, 1735-44. The glass slides were cleaned before use with isopropanol. The CNT/PANI-DNNSA solutions were blade-coated onto the glass slides with a 50 micron gap to give a final (dried) coating thickness of about 1-4 micron.

The sonication was conducted using a DUKANE Model 40TP200
35 sonicator, Transducer Model 41C28 with a ¼ inch diameter tip and a backend diameter of ¾ inch (Dukane Corporation, St. Charles, IL).

EXAMPLE 1

Dispersion of Single-Wall Carbon Nanotubes

Into a 2 oz wide-mouth bottle were added carbon nanotubes (MGP/HiPco R0236, 0.0601 g), xylenes (17.84 g) and Disperbyk®163 (0.0670 g). The bottle containing the mixture was put in a room temperature water bath and dispersed with probe sonication for 10 minutes, during which time the mixture was stirred gently with a spatula at 5-minute intervals. PANI-DNNSA (7.1050 g, 27.30% solids in a mixture of 2-butoxyethanol and xylenes, 1:4 weight ratio) was added to the dispersed carbon nanotubes and then the bottle was put in a water bath at 45°C for 5 minutes to allow temperature equilibration. The mixture was dispersed with probe sonication for 5 minutes, during which time the mix was stirred gently with a spatula at 1-minute intervals.

A 1 g portion of the resultant mixture containing dispersed CNTs and PANI-DNNSA was blade-coated with a 50 micron gap on a glass slide and dried at room temperature for 10 min. An SEM image of the coated substrate is shown in Figure 1.

COMPARATIVE EXAMPLE A

A mixture of CNTs and PANI-DNNSA was prepared as above, except that no dispersion aid was used. A coated substrate was prepared as in Example 1. An SEM image of the coated substrate is shown in Figure 2.

The size and number of defects in the coated substrate is clearly greater in the sample prepared without a dispersion aid.

25

CLAIMS

What is claimed is:

1. A method for preparing a carbon nanotube/polyaniline dispersion, comprising:
 - 5 a. sonicating a first mixture comprising: carbon nanotubes; a first solvent selected from a group consisting of chlorinated and non-chlorinated aromatic solvents, chlorinated and non-chlorinated aliphatic solvents, C4–C10 alcohols and C4–C10 ethers; and a dispersion aid selected from a group consisting of polyamine amides, polymers with tertiary amine affinic groups, polymers with ethylene oxide and hydroxy affinic groups, unsaturated polycarboxylic acid polymers, alkyl ammonium salts of polycarboxylic acids, and carboxylic acid salts of polyamine amides, to form a dispersion of carbon nanotubes; and
 - 10 b. sonicating a second mixture comprising: the dispersion of carbon nanotubes, polyaniline, xylenes and a second solvent selected from a group consisting of 2-butoxyethanol, 1-butanol, 1-hexanol and diethylether.
2. The method of Claim 1, wherein the carbon nanotubes are single-walled carbon nanotubes.
3. The method of Claim 1, wherein the first solvent is an aromatic solvent.
- 25 4. The method of Claim 1, wherein the dispersion aid is selected from a group consisting of Disperbyk®107, Disperbyk®108, Disperbyk®130, Disperbyk®163, Byk®345, Byk®P104, Byk®9076, Byk®9077, Anti-Terra®202, Anti-Terra®204, and Anti-Terra®U.
- 30 5. The method of Claim 1, wherein the second mixture further comprises DNNSA.
6. The method of Claim 1, wherein the sonication is carried out using a sonic probe or a sonic bath/probe combination
- 35 7. The method of Claim 1, wherein the temperature of the mixture is controlled by use of a thermostatically controlled bath.

8. The method of Claim 1, further comprising filtering the second mixture before sonication.

9. The method of Claim 1, further comprising filtering the second mixture
5 after sonication.

10. A composition comprising:

- a. carbon nanotubes;
- b. a dispersion aid selected from a group consisting of polyamine
10 amides, polymers with tertiary amine affinic groups, polymers with hydroxy affinic groups, unsaturated polycarboxylic acid polymers, alkyl ammonium salts of polycarboxylic acids, and carboxylic acid salts of polyamine amides; and
- c. polyaniline.

15

11. The composition of Claim 10, further comprising DNNSA.

12. The composition of Claim 10, wherein the carbon nanotubes are
single-walled carbon nanotubes.

20

13. The composition of Claim 10, wherein the dispersion aid is selected from a group consisting of Disperbyk®107, Disperbyk®108, Disperbyk®130, Disperbyk®163, Byk®345, Byk®P104, Byk®9076, Byk®9077, Anti-Terra®202, Anti-Terra®204, and Anti-Terra®U.

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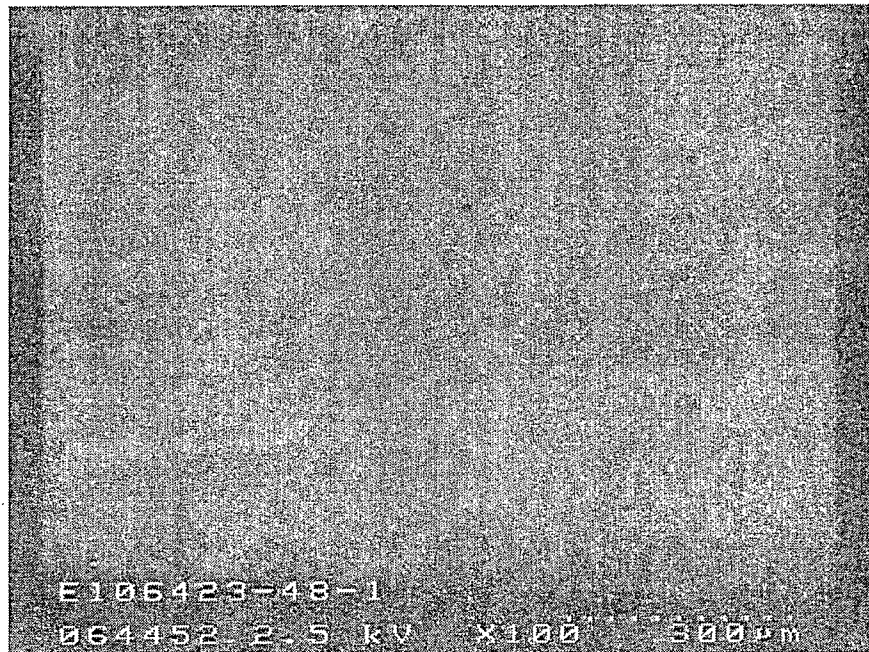


FIG. 1

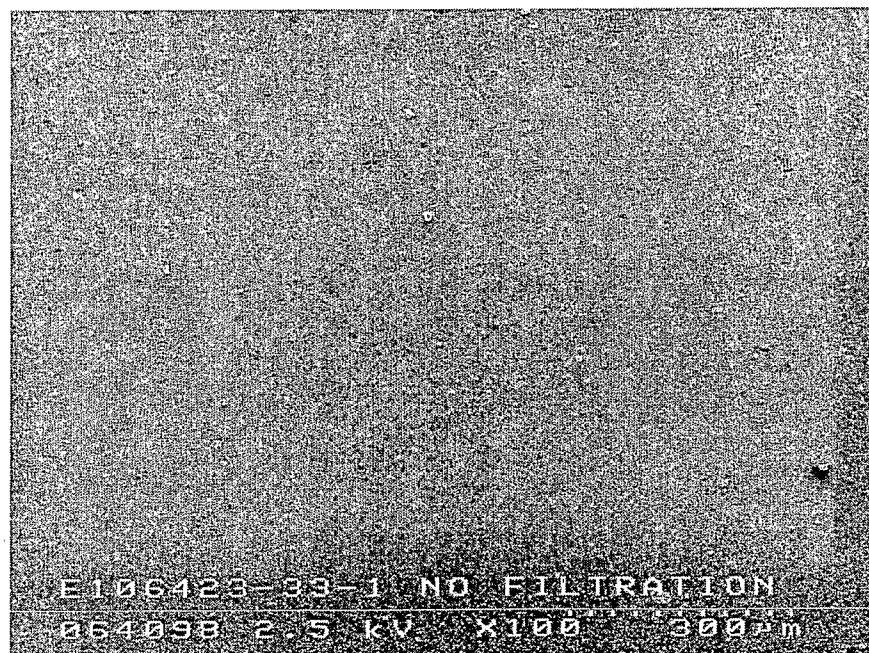


FIG. 2