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(54) **INK JET PRINTABLE COMPOSITIONS FOR  
PREPARING ELECTRONIC DEVICES AND  
PATTERNS**

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(76) Inventors: **Fernando de la Vega**, Zichron  
Yacov (IL); **Claudio Rottman**,  
Modieen (IL)

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Correspondence Address:  
**FISH & RICHARDSON P.C.**  
**PO BOX 1022**  
**MINNEAPOLIS, MN 55440-1022 (US)**

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(57) **ABSTRACT**

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In jet printable compositions that include nano particles in a  
liquid carrier.

# INK JET PRINTABLE COMPOSITIONS FOR PREPARING ELECTRONIC DEVICES AND PATTERNS

## TECHNICAL FIELD

[0001] This invention relates to ink jet printable compositions for printing electronic devices and patterns on a substrate.

## BACKGROUND

[0002] Ink jet printing is a widely used printing technique. Inks based on nano materials are suitable for ink jetting. The particle size and viscosity of the ink influence the suitability of the ink for ink jet printing.

## SUMMARY

[0003] We have discovered that compositions of different nano materials can be ink jetted to form electronic devices and patterns on a variety of substrates. The compositions can be dispersions or inks which can be composed of a nano metal for printing conductors, a mixture of a nano metal and a conductivity lowering material (i.e., a material that lowers the conductivity of the ink relative to its conductivity in the absence of the material) for printing resistors, a dielectric nano additive for printing capacitors, a semiconductor nano additive for printing transistors and other devices, and the like.

[0004] In one aspect, the conductive dispersions and inks include nano metal powders dispersed in a liquid carrier, as described in a previous application entitled "Ink Jet Printable Compositions" submitted on the 14<sup>th</sup> of Sep. 2004 (Ser. No. 60/609,750), hereby incorporated by reference in its entirety. The nano metal powders, which are produced by the Metallurgic Chemical Process (MCP) process described herein, have special properties, enabling the dispersion and de-agglomeration of the powder in a liquid carrier (organic solvent, water, or any combination thereof), with or without additives. Taking advantage of these attributes we have been able, with the MCP-produced nano metal powders, to design compositions with very low viscosities, as required for ink jet printing at high metal concentrations, by selecting appropriate combinations of the nano metal powder, liquid carrier, and, optionally, additives. The ability to combine high metal concentrations with very low viscosities makes the compositions particularly useful for ink jet printing.

[0005] The present compositions include these nano metal powders in combination with a conductivity lowering additive. The compositions also have properties that render them ink jettable (e.g., the ability to be printed through ink jet print heads that possess small nozzles, usually in the micron range). These properties include the following: low viscosities between 1 and 200 cP (at room temperature or at jetting temperature), surface tension between 20-37 dyne/cm for solvent based dispersions and 30-60 dyne/cm for water based dispersions, loadings of metal nano particles between 1% and 70% (weight by weight), and low particle size distribution of the metal nano particles having a particle size distribution (PSD) D90 below 150 nm, preferably below 80 nm. The compositions have stabilities sufficient to enable jetting with minimum settling, and without clogging the print head or changing the properties of the compositions. The compositions can be printed by different technologies including continuous ink jet technologies, drop on demand ink jet technologies

(such as piezo and thermal) and also additional techniques like air brush, flexo, electrostatic deposition, wax hot melt, etc.

[0006] In a second aspect, ink jet printable compositions are described that include a nano powder other than an electrically conductive metal nano powder that is dispersed in a liquid carrier. The compositions have viscosities no greater than about 200 cP at ink jet printing temperatures. Examples of suitable non-electrically conductive metal nano powders include dielectric nano powders, semiconducting nano powders, and the like. Devices that can be prepared by ink jet printing these compositions onto a substrate include capacitors, transistors, and the like.

[0007] The details of one or more embodiments of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description, and from the claims.

## DETAILED DESCRIPTION

[0008] Dispersions and inks containing electrically conductive nano metal particles generally have conductivities that are too high for preparing devices such as resistors, capacitors, transistors, and the like. It is undesirable to lower the conductivity by reducing the amount of deposited electrically conductive material. This is because when the total amount of conductive material is too low, it is difficult to accurately control the amount deposited. In addition, it is also possible that not enough metal will be deposited to obtain percolation, and as a result the resistance will be infinite, rather than within a defined range.

[0009] One way of addressing this problem is to combine highly conductive nano metal particles with an electrical conductivity lowering additive. The additive has an electrical conductivity that is lower than the electrical conductivity of the nano metal particle, thereby reducing the overall electrical conductivity of the composition. At the same time, the properties that enable the composition to be ink jet printable are retained. Examples of suitable electrical conductivity lowering additives, which or may not be in the form of nano powders, include electrically conductive carbon black, electrically conductive organic polymers, and the like. The amount of the additive is selected to achieve the desired electrical conductivity for the intended application of the ink because the ratio between the highly conductive nano metal and the electrical conductivity lowering additive will determine the ultimate resistance obtained. Regardless of the application, however, the amount of electrically conductive nano metal particles is sufficient to achieve percolation.

[0010] A second way of addressing this problem involves dispersing a nano powder other than an electrically conductive metal nano powder in a liquid carrier. The compositions have viscosities no greater than about 200 cP at ink jet printing temperatures. Examples of suitable non-electrically conductive metal nano powders include dielectric nano powders, semiconducting nano powders, and the like. Specific examples include metal oxides such as antimony oxide and indium tin oxide.

[0011] Examples of suitable nano metal particles include silver, silver-copper alloys, silver-palladium alloys, and other metals and metal alloys produced by the process described in U.S. Pat. No. 5,476,535 ("Method of producing high purity ultra-fine metal powder") and PCT application WO 2004/000491 A2 ("A Method for the Production of Highly Pure Metallic Nano-Powders and Nano-Powders Produced

Thereof”), both of which are hereby incorporated by reference in their entirety. Highly conductive dispersions and inks incorporating these nano metal particles have been described in a provisional patent application entitled “Ink Jet Printable Compositions” submitted on the 14<sup>th</sup> of Sep. 2004 (Ser. No. 60/609,750) and hereby incorporated by reference entirely.

**[0012]** The dispersions can be prepared as described in the patents hereby cited or can be prepared by mixing dispersions of the separate nano additives. The compositions can be printed by different technologies including continuous ink jet technologies, drop on demand inkjet technologies (such as piezo, thermal and continuous) and also additional techniques like air brush, flexo, electrostatic deposition, wax hot melt, etc.

**[0013]** The resulting printed patterns produced hereby can be treated post printing in any suitable way to adjust their conductivity. The treatments may be any of the following methods or combinations thereof: methods described in PCT applications WO 2004/005413 A1 (“Low Sintering Temperatures Conductive Inks—a Nano Technology Method for Producing Same”) and WO03/106573 (“A Method for the Production of Conductive and Transparent Nano-Coatings and Nano-Inks and Nano-Powder Coatings and Inks Produced Thereby”), application of radiation, microwave, light, flash light, laser sintering, applying pressure, rubbing, friction sintering, thermal heat (applied in any form, e.g. forced air oven, hot plate, etc), continuous radiation, scanned beam, pulsed beam, etc. The treatment may also be a “chemical sintering method” (CSM) described in a provisional patent application No. 60/609,751 entitled “Low Temperature Sintering Process for Preparing Conductive Printed Patterns on Substrates, and Articles Based Thereon” filed Sep. 14, 2004, and in WO 03/106573.

**[0014]** The dispersions and inks may be printed onto a wide range of surfaces, including flexible, rigid, elastic, and ceramic surfaces. Specific examples include paper, polymer films, textiles, plastics, glass, fabrics, printed circuit boards, epoxy resins, and the like.

**[0015]** The invention will now be described further by way of the following examples. All amounts are weight percent and are calculated based upon the weight of the final dispersion unless otherwise noted.

## EXAMPLES

### Example 1

#### Comparative

**[0016]** 1.88% Disperbyk® 163 (available from BYK-Chemie, Wesel Germany) and 0.28% BYK® 333 (also available from BYK-Chemie) were added to a solvent mixture of 36.11% BEA (Ethylene glycol butyl ether acetate) and 36.11% PMA (Propylene glycol mono methyl ether acetate), and stirred with a magnetic stirrer until all the additives completely dissolved. Next, 0.62% Butvar®B-76 (available from Solutia) was added slowly. To enhance its dissolution, the addition was performed in an ultrasonic bath. Next, 25.0% by weight of silver nano powder (prepared as described in U.S. Pat. No. 5,476,535 and PCT application WO 2004/000491 A2) was added in portions while mixing with a magnetic stirrer. Next, an ultrasonic device, Bandelin Sonopuls Ultrasonic, was applied to the dispersion according to the following profile: 3 consecutive times at 50% for 2 min, followed by 60% for 2 min, then at 70% for 2 min and finally at 80% for 2 min (taking care to prevent the temperature from rising

above 50-60° C.). Particle size distribution measurements were performed by using Coulter LS laser diffraction equipment and demonstrated a D90 of 0.053  $\mu$ m. The viscosity was measured with a Brookfield RVDV-II+Viscometer and found to be 3.9 cP (at 25° C.). The dispersion was used to coat a Kapton® film (35  $\mu$ m wet thickness using a wire wound rod) and sintered at 150° C. for 60 minutes. The resistance of the resulting coating, measured using a four probe method, was 14.5 $\Omega$ /□.

### Example 2

**[0017]** The conductive dispersion prepared as in Example 1 was mixed with 10.00% of conductive carbon ink R-4148 BGA Black (available from Degussa). Ultrasonic energy was applied to the mixture until complete de-agglomeration, as measured by the particle size distribution, occurred. Particle size distribution measurements were performed using Coulter LS laser diffraction equipment and demonstrated a D90 of 0.053  $\mu$ m. The viscosity was measured with a Brookfield RVDV-II+Viscometer and found to be 5.7 cP (at 25° C.). The dispersion was used to coat a Kapton® film (35  $\mu$ m wet thickness using a wire wound rod) and sintered at 150° C. for 60 minutes. The resistance of the resulting coating was measured using a four probe method and found to be 414 $\Omega$ /□. The resistance of the conductive carbon ink (25% carbon) when measured under the same conditions was over 2000 $\Omega$ /□.

### Example 3

**[0018]** The conductive dispersion prepared as in Example 1 was mixed with 30.00% of conductive carbon ink R-4148 BGA Black (available from Degussa). Ultrasonic energy was applied to the mixture until complete de-agglomeration, as measured by the particle size distribution, occurred. Particle size distribution measurements were performed using Coulter LS laser diffraction equipment and demonstrated a D90 of 0.053  $\mu$ m. The viscosity was measured with a Brookfield RVDV-II+Viscometer and found to be 10.7 cP (at 25° C.). The dispersion was used to coat a Kapton® film (35  $\mu$ m wet thickness using a wire wound rod) and sintered at 150° C. for 60 minutes. The resistance of the resulting coating was measured using a four probe method and found to be 660 $\Omega$ /□.

**[0019]** A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

1. A composition comprising 1-70% by weight of a nano metal powder and 1-70% by weight of an electrical conductivity lowering additive, dispersed in a liquid carrier, wherein the composition has a viscosity no greater than about 200 cP at ink jet printing temperatures and is ink jet printable.

2. A composition according to claim 1 where the electrical conductivity lowering additive comprises carbon black.

3. A composition according to claim 1 where the electrical conductivity lowering additive comprises indium tin oxide.

4. A composition according to claim 1 where the electrical conductivity lowering additive comprises antimony tin oxide.

5. A composition according to claim 1 where the electrical conductivity lowering additive comprises a metal oxide.

6. A composition according to claim 1 where the electrical conductivity lowering additive comprises an electrically conductive organic polymer.

7. A composition according to claim 1 wherein the composition has a viscosity of 1-200 cP at ink jet printing temperatures.

8. A composition according to claim 1 wherein the composition has a viscosity of 1-100 cP at ink jet printing temperatures.

9. A composition according to claim 1 wherein the composition has a viscosity of 2-20 cP at ink jet printing temperatures.

10. A composition according to claim 1 comprising 10-60% by weight of the nano metal powder.

11. A composition according to claim 1 comprising 20-60% by weight of the nano metal powder.

12. A composition according to claim 1 comprising about 60% by weight nano metal powder and having a viscosity of about 18 cP at ink jet printing temperatures.

13. A composition according to claim 1 wherein the composition has a viscosity no greater than about 200 cP at room temperature.

14. A composition according to claim 1 wherein the composition has a viscosity of 1-200 cP at room temperature.

15. A composition according to claim 1 wherein the composition has a viscosity of 1-100 cP at room temperature.

16. A composition according to claim 1 wherein the composition has a viscosity of 2-20 cP at room temperature.

17. A composition according to claim 1 comprising about 60% by weight nano metal powder and having a viscosity of about 18 cP at room temperature.

18. A composition according to claim 1 wherein the liquid carrier comprises water and the composition has a surface tension of about 30-60 dynes/cm.

19. A composition according to claim 1 wherein the liquid carrier comprises an organic solvent and the composition has a surface tension of about 20-37 dynes/cm.

20. A composition according to claim 1 wherein the nano metal powder has an average particle size no greater than about 150 nm.

21. A composition according to claim 1 wherein the nano metal powder has an average particle size no greater than about 100 nm.

22. A composition according to claim 1 wherein the nano metal powder has an average particle size no greater than about 80 nm.

23. A composition according to claim 1 wherein the nano metal powder is prepared according to the MCP process.

24. A composition according to claim 1 or 14 wherein the nano metal powder comprises silver.

25. A composition according to claim 1 or 14 wherein the nano metal powder comprises a silver-copper alloy.

26. A composition according to claim 1 or 14 wherein the nano metal powder comprises non-uniform spherical particles and includes up to about 0.4% by weight aluminum.

27. A composition according to claim 1 wherein the composition is stable against particle settling.

28. A composition according to claim 1 wherein the liquid carrier comprises (a) at least one organic solvent and (b) at least one agent selected from the group consisting of surfactants, wetting agents, rheology modifying agents, adhesion promoters, humectants, binders, and combinations thereof.

29. A composition according to claim 1 wherein the liquid carrier comprises (a) water, a water-miscible organic solvent, or combination thereof and (b) at least one agent selected from the group consisting of surfactants, wetting agents, rheology modifying agents, adhesion promoters, humectants, binders, and combinations thereof.

30. A composition according to claim 1 wherein the liquid carrier comprises (a) at least one organic solvent, (b) a curable monomer, and (c) at least one agent selected from the group consisting of surfactants, wetting agents, rheology modifying agents, adhesion promoters, humectants, binders, and combinations thereof.

31. A method comprising printing the composition of claim 1 onto a substrate using an ink jet printer.

32. A method according to claim 31 wherein the ink jet printer is a continuous ink jet printer.

33. A method according to claim 31 wherein the ink jet printer is a drop on demand inkjet printer.

34. A method according to claim 31 wherein the substrate is selected from the group consisting of paper, polymer films, textiles, plastics, glass, printed circuit boards, epoxy resins, and combinations thereof.

35. A method according to claim 31 comprising sintering the composition after applying it to the substrate.

36. A composition comprising 1-70% by weight of a nano powder other than an electrically conductive nano metal powder, dispersed in a liquid carrier, wherein the composition has a viscosity no greater than about 200 cP at ink jet printing temperatures and is inkjet printable.

37. A composition according to claim 8 where the nano powder comprises a dielectric material.

38. A composition according to claim 8 where the nano powder comprises a semiconducting material.

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