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(54) **SOLVENT-BASED INKS COMPRISING COATED MAGNETIC NANOPARTICLES**

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C09D 11/00 (2006.01)

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(58) **Field of Classification Search** 106/31.6, 106/31.65, 31.9, 31.92
See application file for complete search history.

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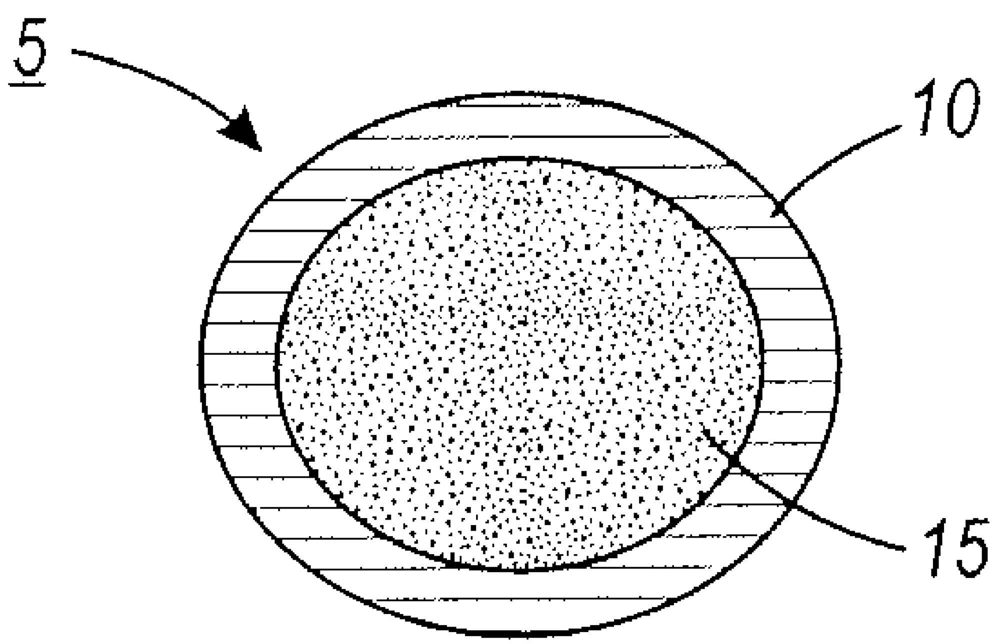
(57) **ABSTRACT**

Solvent-based ink compositions which can be used for ink jet printing in a variety of applications. In particular, the present embodiments are directed to magnetic inks having desirable ink properties. The ink of the present embodiments comprise magnetic nanoparticles that are coated with various materials to prevent the exposure of the nanoparticles to oxygen, and provides robust prints.

19 Claims, 1 Drawing Sheet



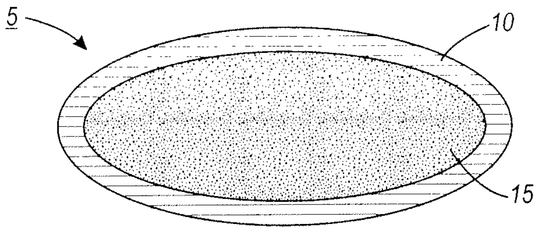


FIG. 1

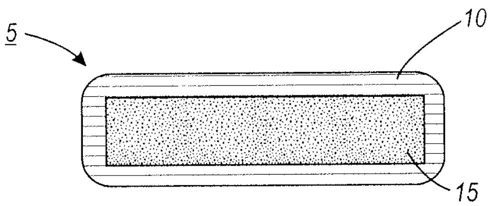


FIG. 2

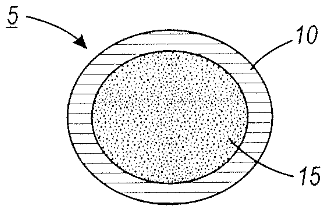


FIG. 3

SOLVENT-BASED INKS COMPRISING COATED MAGNETIC NANOPARTICLES

CROSS REFERENCE TO RELATED APPLICATIONS

Reference is made to commonly owned and co-pending, U.S. patent application Ser. No. 13/050,268 entitled "Curable Inks Comprising Inorganic Oxide-Coated Magnetic Nanoparticles" to Iftime et al.; U.S. patent application Ser. No. 13/050,152 entitled "Solvent-Based Inks Comprising Coated Magnetic Nanoparticles" to Iftime et al.; U.S. patent application Ser. No. 13/050,403 entitled "Magnetic Curable Inks" to Iftime et al.; U.S. patent application Ser. No. 13/049,936 entitled "Phase Change Magnetic Ink Comprising Carbon Coated Magnetic Nanoparticles And Process For Preparing Same," to Iftime et al.; U.S. patent application Ser. No. 13/049,937 entitled "Solvent Based Magnetic Ink Comprising Carbon Coated Magnetic Nanoparticles And Process For Preparing Same" to Iftime et al.; U.S. patent application Ser. No. 13/049,942 entitled "Phase Change Magnetic Ink Comprising Coated Magnetic Nanoparticles And Process For Preparing Same" to Iftime et al. U.S. patent application Ser. No. 13/049,945 entitled "Phase Change Magnetic Ink Comprising Inorganic Oxide Coated Magnetic Nanoparticles And Process For Preparing Same" to Iftime et al.; U.S. patent application Ser. No. 13/050,341 entitled "Curable Inks Comprising Surfactant-Coated Magnetic Nanoparticles" to Iftime et al.; U.S. patent application Ser. No. 13/050,383 entitled "Curable inks Comprising Polymer-Coated Magnetic Nanoparticles" to Iftime et al.; U.S. patent application Ser. No. 13/049,950entitled "Phase Change Magnetic Ink Comprising Surfactant Coated Magnetic Nanoparticles and Process For Preparing the Same" to Iftime et al.; and U.S. patent application Ser. No. 13/049,954 entitled "Phase Change Magnetic Ink Comprising Polymer Coated Magnetic Nanoparticles and Process for Preparing the Same" to Iftime at al., all filed electronically on the same day as the present application, the entire disclosures of which are incorporated herein by reference in its entirety.

BACKGROUND

Non-digital inks and printing elements suitable for Magnetic Ink Character Recognition (MICR) printing are generally known. The two most commonly known technologies are ribbon-based thermal printing systems and offset technology. For example, U.S. Pat. No. 4,463,034 discloses heat sensitive magnetic transfer element for printing MICR, comprising a heat resistant foundation and a heat sensitive imaging layer. The imaging layer is made of ferromagnetic substance dispersed in a wax and is transferred on a receiving paper in the form of magnetic image by a thermal printer which uses a ribbon. U.S. Pat. No. 5,866,637 discloses formulations and ribbons which employ wax, binder resin and organic molecule based magnets which are to be employed for use with a thermal printer which employs a ribbon. MICR ink suitable for offset printing using a numbering box are typically thick, highly concentrated pastes consisting for example in about over 60% magnetic metal oxides dispersed in a base containing soy-based varnishes. Such inks are, for example, commercially available at Heath Custom Press (Auburn, Wash.). Digital water-based ink-jet inks composition for MICR applications using a metal oxide based ferromagnetic particles of a particle size of less than 500 microns are disclosed in U.S. Pat. No. 6,767,396. Water-based inks are commercially available from Diversified Nano Corporation (San Diego, Calif.).

The present embodiments relate to solvent-based ink compositions. These ink compositions can be used for ink jet printing in a variety of applications. In addition to providing desirable ink qualities, the present embodiments are directed to magnetic inks for use in specific applications. The ink of the present embodiments comprise magnetic nanoparticles that are coated with various materials to prevent the exposure of the nanoparticles to oxygen. The present embodiments are also directed to a solvent-based magnetic ink that provides robust prints.

The present embodiments are directed to solvent-based magnetic inks which comprise an organic solvent, an optional dispersant, an optional synergist, an optional antioxidant, an optional viscosity controlling agent, an optional colorant, and coated magnetic nanoparticles comprising a magnetic core and a coated shell disposed thereover. These magnetic inks are required for specific applications such as Magnetic Ink Character Recognition (MICR) for automated check processing and security printing for document authentication. One of the challenges in formulating such a solvent-based ink, however, is that many of these metal nanoparticles are pyrophoric and extremely sensitive to air and water. For example, iron nanoparticles can burst into flame instantly upon exposure to air. As such, uncoated magnetic metal nanoparticles are a serious fire hazard. As such, large scale production of the solvent-based inks comprising such particles is difficult because air and water need to be completely removed when handling the particles. In addition, the ink preparation process is particularly challenging with magnetic pigments because inorganic magnetic particles are incompatible with organic base components. Lastly, a problem associated with the use of the magnetic solid inks is the solid ink vehicle is designed for normal office use and not the highly abrasive environment of multiple passes through a magnetic reader. As a result, a magnetic solid ink print may wear off quickly during machine-reading process, either for MICR or for document authentication procedures.

Thus, there is a need for a magnetic ink which can be printed with piezoelectric print-heads and which can be made both safely and provides robust prints compatible with solvent-based compositions.

Thus, while the disclosed solid ink formulation provides some advantages over the prior formulations, there is still a need to achieve a formulation that not only provides the desirable properties of a solvent-based ink but is also more easily produced and derived from components that do not require special handling conditions.

SUMMARY

According to embodiments illustrated herein, there are provided solvent-based ink compositions which produce robust prints and which can be used for ink jet printing in a variety of applications. The ink of the present embodiments comprise magnetic nanoparticles that are coated with various materials, such as for example, polymers, surfactants and inorganic oxides, to prevent the exposure of the nanoparticles to oxygen. The present embodiments are also directed to a solvent-based magnetic ink that provides robust prints.

In particular, the present embodiments provide a magnetic ink comprising: an organic solvent carrier; an optional dispersant; an optional synergist; an optional antioxidant; an optional viscosity controlling agent; an optional colorant; an optional binder; and coated magnetic nanoparticles, wherein the coated magnetic nanoparticles are comprised of a magnetic metal core and a protective coating disposed on the magnetic metal core, the coated magnetic nanoparticles being dispersed in the solvent carrier and further wherein the protective coating is selected from the group consisting of polymeric materials, inorganic oxides, surfactants and mixtures thereof.

In further embodiments, there is provided a magnetic ink comprising: a solvent carrier; an optional dispersant; an optional synergist; an optional antioxidant; an optional viscosity controlling agent; an optional colorant; an optional binder; and coated magnetic nanoparticles comprising a magnetic metal core and a protective coating disposed on the magnetic metal core, the coated magnetic nanoparticles being dispersed in the solvent carrier and wherein the protective coating comprises a protective material selected from the group consisting of polymeric materials, inorganic oxides, surfactants and mixtures thereof and further wherein the protective coating has a thickness of from about 0.2 nm to about 100 nm.

In yet other embodiments, there is provided a magnetic ink comprising: a solvent carrier; an optional dispersant; an optional synergist; an optional antioxidant; an optional viscosity controlling agent; an optional colorant; an optional binder; and coated magnetic nanoparticles comprising a magnetic metal core and a protective coating disposed on the magnetic metal core, the coated magnetic nanoparticles being dispersed in the solvent carrier and the protective coating is selected from the group consisting of polymeric materials, inorganic oxides, surfactants and mixtures thereof, and further wherein the ink is used for Magnetic Ink Character Recognition (MICR) applications.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the present embodiments, reference may be had to the accompanying figures.

FIG. **1** illustrates a cross-section of a coated magnetic nanoparticle according to the present embodiments;

FIG. **2** illustrates a cross-section of a coated magnetic nanoparticle according to an alternative embodiment to FIG. **1**; and

FIG. **3** illustrates a cross-section of a coated magnetic nanoparticle according to an alternative embodiment to FIG. **1** or FIG. **2**.

DETAILED DESCRIPTION

In the following description, it is understood that other embodiments may be utilized and structural and operational changes may be made without departure from the scope of the present embodiments disclosed herein.

Solvent ink technology broadens printing capability and customer base across many markets, and the diversity of printing applications will be facilitated by effective integration of printhead technology, print process and ink materials. As discussed above, while current ink options are successful for printing on various substrates, there is a need a less complicated method to produce magnetic solvent inks comprising magnetic metal nanoparticles which avoids the safety risks associated with the nanoparticles. In addition, solvent-based magnetic inks provide for enhanced robustness of the prints.

The present embodiments are directed generally to solvent-based magnetic solid inks. In particular, the present embodiments provide inks that are made with coated magnetic metal nanoparticles dispersed in a solvent ink base. One of the inherent properties of uncoated magnetic metal nanoparticles which precludes their use in the fabrication of commercial inks is their pyrophoric nature; uncoated (bare) magnetic nanoparticles of a certain size, typically in the order of a few tens of nanometers or less, ignite spontaneously when exposed to oxygen in the ambient environment. For example, bare iron, cobalt and alloys nanoparticles are a serious fire hazard. Thus, the present embodiments provide a safe method for preparation of stable inks suitable for applications that require the use of magnetic inks. The present embodiments provide coated magnetic metal nanoparticles which are protected from exposure to water and air. These nanoparticles have a coating of various materials, such as for example, carbon, polymers, inorganic oxides, surfactants, or mixtures thereof, which acts as a barrier to water or air.

Magnetic inks are required for two main applications: (1) Magnetic Ink Character Recognition (MICR) for automated check processing and (2) security printing for document authentication. The resulting solvent-based ink can be used for these applications. Moreover, as mentioned above, solid ink compositions are not normally designed for multiple passes across a magnetic reader. Thus, magnetic solid ink print may wear off during the machine-reading process, either for MICR or for document authentication procedures. The present embodiments provide a magnetic ink that is solvent-based. More specifically, the ink of the present embodiments is made by dispersing coated magnetic metal nanoparticles in a solvent-based composition containing a solvent, an optional viscosity controlling agent, an optional dispersant, an optional synergist and optional binder. These solvent-based inks comprising the coated magnetic nanoparticles are jetted as a liquid dispersion onto the print substrate. Because the ink is in a liquid state when applied to the substrate, such as paper, the magnetic ink penetrates into the substrate when printed. In contrast to conventional solid inks which sit on top of the substrate, the solvent carrier allows the ink of the present embodiments to penetrate the substrate coating and fibers to ensure deposition of the ink components. As a result, the inks proved robust magnetic prints that can pass the machine-reading process steps of MICR or document authentication procedures, and be overprinted with other ink types. The added robustness also removes the need for adding a clear protective overcoat layer over the print, which increases the amount of ink used and adds to the pile height of the printed documents.

The resulting solvent ink can also be applied using with piezoelectric inkjet print heads. Currently only water based MICR inkjet ink are commercially available. Water based inks require special care of the printhead to prevent evaporation of the ink or deposition of salts within the channel rendering the jetting ineffective. Furthermore high quality printing with aqueous inks generally requires specially treated image substrates. In addition, there is generally a concern with respect to possible incompatibility when operating both organic materials based inks like solid, solvent or curable solid inks and water-based inks within the same printer. Issues like water evaporation due to the proximity to the organic heated ink tanks, rust, high humidity sensitivity of the organic inks are key problems which may prevent implementation of the water-based MICR solution. Thus, the present embodiments further avoid these issues.

The present embodiments provide a solvent-based ink made from coated metal magnetic nanoparticles dispersed in a solvent-based ink base. The process of ink fabrication comprise the following key steps: (1) preparation of a solvent solution containing appropriate dispersant and optionally a synergist; (2) addition and breaking of solid aggregates of the coated nanoparticles (this step can be achieved by various processes including ball milling, attrition or high speed homogenizer mixing); (3) optional addition of viscosity controlling agents; and (4) filtration of the ink.

The inks are suitable for use in various applications, including MICR applications. In addition, the printed inks may be used for decoration and for security printing purposes, even if the resulting inks do not sufficiently exhibit coercivity and remanence suitable for use in MICR applications. The ink of the present disclosure exhibits stability, dispersion properties and magnetic properties that are superior to that of an ink including magnetite.

The coated magnetic nanoparticles **5** are made of a core magnetic nanoparticle **15** coated on the surface with a coating material **10** as shown in FIGS. **1-3**. The coated magnetic nanoparticles can be produced to have different shapes such as oval (FIG. **1**), cubed (FIG. **2**), and spherical (FIG. **3**). The shapes are not limited to those depicted in these three figures. Suitable coating materials may include a variety of materials, including for example, polymers, inorganic oxides, surfactants and mixtures thereof. Polymeric materials may be selected from the group consisting of amorphous, crystalline, polymers and oligomers with a low molecular weight (for example, a Mw of from about 500 to about 5000, polymers with a high molecular weight (for example, a Mw of from about 5000 to about 1,000,000), homopolymers, copolymers made of one or more types of monomers, and the like, and mixtures thereof. Inorganic oxides may be selected from the group consisting of silica, titanium oxide, iron oxide, zinc oxide, aluminum oxide, and the like, and mixtures thereof. Surfactants may be selected from the group consisting of anionic, cationic, non-ionic, zwitterionic surfactants, and the like, and mixtures thereof. The magnetic ink is made by dispersing the coated nanoparticles in a solvent ink base. The coating present on the surface of the nanoparticles provides air and moisture stability such that the nanoparticles are safe to handle. The amount of the different materials used in the coatings depends on the densities of the materials used. In general embodiments, the polymer may be present in the coating in an amount of from about 0.1 to about 50 percent by weight of the total weight of the coating, the surfactant may be present in the coating in an amount of from about 0.1 to about 30 percent by weight of the total weight of the coating, and the inorganic oxide may be present in an amount of from about 0.5 to about 70 percent by weight of the total weight of the coating.

Solvent Carrier Material

The ink composition includes a carrier material, or a mixture of two or more carrier materials. In the present embodiments, there is provided a liquid inkjet ink composition in which the carrier is one or more organic solvents.

In the present embodiments, the coated magnetic metal nanoparticles are dispersed into the solvent ink base. The solvent may be selected from the group consisting of isoparaffins like ISOPAR® manufactured by the Exxon Corporation, hexane, toluene, methanol, ethanol, n-propanol, n-butanol, benzyl alcohol, methyl cellosolve, ethyl cellosolve, acetone, methyl ethyl ketone, cyclohexanone, chlorobenzene, methyl acetate, n-butyl acetate, dioxane, tetrahydrofuran, methylene chloride and chloroform, and mixtures and combinations thereof. Additional commercially available hydrocarbon liquids that may be used include, for example, the NORPAR series available from Exxon Corporation, the SOLTROL series available from the Phillips Petroleum Company, and the SHELLSOL series available from the Shell Oil Company. In embodiments, the solvent is present in the overall ink composition in an amount of from about 0.1 to about 99 percent, or of from about 10 to about 90 percent, or of from about 30 to about 90 percent by weight of the total weight of the ink, although the specific amount can be outside of these ranges.

In embodiments, the ink exhibits a viscosity, typically on the order of less than 15 centipoise (cP) or about 2 to 12 cP at jetting temperature (jetting temperature ranging from about 25° C. to about 140° C.

Coating Materials for Magnetic Metal Nanoparticles

Various materials may be used for the nanoparticle coating materials, for example, polymers, inorganic oxides, surfactants and mixtures thereof. The coating is disposed on the surface of the magnetic metal nanoparticles and may have a layer thickness of from about 0.2 nm to about 100 nm, or from about 0.5 nm to about 50 nm, or from about 1 nm to about 20 nm.

Polymers

Various polymers are suitable for producing protective coating layers for the magnetic metal cores in nanoparticles. Suitable examples include Poly(methyl methacrylate) (PMMA), polystyrene, polyesters, and the like. Additional suitable polymer materials include, without limitation, thermoplastic resins, homopolymers of styrene or substituted styrenes such as polystyrene, polychloroethylene, and polyvinyltoluene; styrene copolymers such as styrene-p-chlorostyrene copolymer, styrene-propylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalene copolymer, styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-butyl acrylate copolymer, styrene-octyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-methyl α-chloromethacrylate copolymer, styrene-acrylonitrile copolymer, styrene-vinyl methyl ether copolymer, styrene-vinyl ethyl ether copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, styrene-acrylonitrile-indene copolymer, styrene-maleic acid copolymer, and styrene-maleic acid ester copolymer; polymethyl methacrylate; polybutyl methacrylate; polyvinyl chloride; polyvinyl acetate; polyethylene; polypropylene; polyester; polyvinyl butyral; polyacrylic resin; rosin; modified rosin; terpene resin; phenolic resin; aliphatic or aliphatic hydrocarbon resin; aromatic petroleum resin; chlorinated paraffin; paraffin wax, and the like. In embodiments, the protective coating comprises a polymer terminated with a functional group which is selected from a group of amide, amine, carboxylic acid, phosphine oxide, carboxyklic ester, alcohol, thiol. Polymers can be homopolymers or copolymers, linear or branched, random and block copolymers. In further embodiments, oxygen barrier polymeric materials are particularly suitable coating materials. Examples of oxygen barrier polymeric materials include polyvinylidene chloride (PVDC), Ethylene Vinyl Alcohol (EVOH), High Density Polyethylene (HDPE), NYLON 6 and the like. Suitable oxygen barrier materials are also available from Dow Chemicals (SARAN series resins (e.g., SARAN 168 and SARAN 519)).

Copolymers are also suitable polymeric coating materials. For example, a copolymer made of PVDC and methyl acrylate monomers may be used for coating. This copolymer is also available from Dow Chemicals (e.g., SARAN XU 32019). Other examples include 10L Blend, SARAN XU 32019.39 Blend and SARAN XU 32019.40 Blend. Additionally, some of the oxygen barrier polymers, particularly copolymers of PVDC with other co-monomers, are soluble in various solvents at various temperatures as shown in Table 1.

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