A LIQUID THERMOSETTING INK

The present invention discloses liquid thermosetting inks useful for ink-jet applications, such as industrial solder masks; and to a method of producing the same. More specifically, a liquid thermosetting ink for ink-jet applications comprising one resin or more; at least one solid latent curing agent characterized by a maximal particle size of less than two microns; an inert filler having fine particles. The invention also discloses a method of producing a liquid thermosetting ink for ink-jet applications, in the manner that one-pack or two-pack ink characterized by a viscosity lower than 50 Cop at application temperature, surface tension lower than 80 dyn/cm at application temperature, and glass transition temperature of cured ink of greater than 120°C.
A LIQUID THERMOSETTING INK

FIELD OF INVENTION

The present invention generally relates to the field of liquid thermosetting inks useful for ink-jet applications, such as industrial solder masks and to a method for producing the same.

BACKGROUND OF THE INVENTION

Solder masks (SM) and photoinagable solder masks (PISM) are a permanent coating for a printed circuit board (PCB) that do not cover certain parts of the circuitry on the board such as the contact points (pads). Two component UV curing acrylates and epoxy-acrylate PSMs are traditionally employed by at least two subsequent steps (i) covering the PCB totally; and (ii) applying various photolithographic techniques to revealing underlined structures on the board while masking other, so that the solder may be applied to the exposed structures. This intricate process has many drawbacks such as requirement for many process steps before final curing, exposure of the board to aggressive developers, contamination throughout the PCB’s holes, and frequent damage to embedded components, obligation to utilize pollutant solutions that need expensive de-toxification and capital consuming equipment. Moreover, the long-term properties of the cured film are scarified for developability, which calls for water or solvent solubility.

Those drawbacks and other may be prevented by digital printing of the solder mask specifically to the targeted portions of the PCB. The most efficient method to do that is by ink-jet technology. Nevertheless, such machinery is by any means limited to liquid ink which is obligatorily characterized by a surface tension lower than 60 dyne/cm at application temperature; viscosity of less than 50 Cps at shear rate of 0.1 to 100,000 1/s at application temperature; incomparable stability which avoids sedimentation and segregation of pigments and fillers during storage and jetting; extended pot life of at least 1 week at ambient without increase of viscosity at jetting temperature by more than 2 Cps at shear rate of 0.1 to 100,000 1/s; very fast development of viscosity after deposition of drop, to keep highest resolution; contains minimal content of volatile matter, usually less than 25 % and most be free from acidic component because those may attack the printing head components.

A commercial SM is further characterized by suitable physical, chemical and mechanical properties to withstand presence of solder, fluxes, organic and inorganic cleaners without any
significant deterioration while maintaining its coverage over the portions of the board wherein solder or conductor or glass-epoxy substrate is to be masked, such as required at the IPC SM840-C specifications. The covered board should have at least the same flammability resistance as the original board, according to UL94 specification.

The chemical and physical resistance of commercially available solder masks is correlated to high Tg (glass transition temperature) values, which reflects the high density of the cross-linking and the rigidity of the molecular backbone due to high content of aromatic or heterocyclic structures. The solder mask should remain tough and flexible enough to withstand mechanical stresses without cracking or peeling and thus to outlast in ever changing environments. In order to meet this difficult trade-off, high molecular weight resins are required, usually having viscosity at ambient temperature, between 5,000 to 100,000 Cps. The chemical resistance of industrial solder masks is mostly achieved by epoxy resins and their curatives comprising respectively high content of aromatic, heterocyclic or cyclo-aliphatic ingredients. For lower end printed wiring boards, UV cured acrylic-based solder mask are applicable, but they are inferior in all respects relatively to the commercially available epoxy-based resins, usually due to inferior adhesion and heat resistance.

Epoxy-based solder masks are cost-effective matrices known of their excellent chemical and thermal properties; improved adhesion to metals, ceramics and plastics; ease of application; low toxicity; and comprised a wide spectrum of resins, diluents, modifiers and curing agents. The most popular epoxy resins for high performance applications are diglycidyl ethers of bisphenol A (hereinafter ‘DGEBA’), epoxy phenol novolacs (hereinafter ‘EPN’), epoxy cresol novolacs (hereinafter ‘ECN’), diglycidyl ethers of bisphenol F (hereinafter ‘DGEBF’), commercially available bisphenol A based novolac products or any mixture thereof.

Epoxy resins are cured by various compositions, such as amines, acids and anhydrides, mercaptans, sulfide and Lewis acids and inorganic salts. Most of the aforementioned curing agents react with the resin at ambient temperature, thus applicable only in two-pack systems, and have a significantly limited pot life.

Latent curatives are practically inactive hardeners until triggered by effective irradiation or heat means. One potential latent system is based on UV-initiated cationic initiators that supply the required Lewis acid to an epoxy system. Hence, US Pat. No. 6,319,652 to Akutsu et al. discloses an energy beam curable epoxy resin composition, essential including cationic polymerizing organic substance; sensitive initiator; organic substance, radically polymerizing
organic compound, and radical polymerization initiator. Similarly, US Pat. No. 6,210,862 to Day et al. teaches a very complicated non-brominated epoxy composition for use as solder mask consisting of two systems: (a) epoxy resin having a polyol resin which is a condensation product of epichlorohydrin and bisphenol A; epoxidized multifunctional bisphenol A formaldehyde Novolak resin and a solid epoxidized glycidyl ether of bisphenol A; and (b) a photoinitiator capable of initiating polymerization upon exposure to actinic radiation. Unfortunately, these epoxy-base solder masks are expensive, toxic, very sensitive to humidity and contaminations, and can utilize merely narrow spectrum of raw materials, thus limited for practical mass production applications. They have also limit of penetration of light and always requires extra heat post curing for cure completion and thermal relaxation. Another disadvantage of cationic curing photo initiated epoxy thermoset matrices is the high cost of photoinitiators and their toxicity.

Another family of latent curative is based on fine solid curative matrices that are only partially soluble in the epoxy resins at ambient temperature, however, after being melted in the polymer their solubility is increasing and the polymerization is initiate thereon. These curative compounds are usually selected from modified amines, such as the commercially available AJICURE product by Ajinomoto and ANCAMINE 2441 and 2442 by Air Products; imidazoles such as the CUREZOL commercially available by Shikoku (Japan) and Air Products; dicyandiamide (DICY) such as the AMICURE CG-1400 commercially available by Air Products; urea derivatives; inorganic compounds such as BF₃ and BCl₃ salts like the LeeCure commercially available catalyst by Leepoxy plastics Inc. In the presence of solvents or low molecular weight co-monomers, which is especially crucial for ink-jet applications, modified amines, unmodified imidazoles, BCl₃ and BF₃ and urea derivatives has some reactivity at ambient temperature, causing the viscosity to increase. Thus, those curative compositions are less applicative in mass industrial utilizations but may be used in small-volume applications, where pot life of less than one week is allowed.

DICY and some modified imidazoles have lowest solubility and once having size reduced to less than about 5 microns maximum, more preferred less than about 2 micron maximum, become very effective latent curing agent for ink jettable epoxy, even when the ink contains solvents and monomers, such as acrylic and methacrylic compositions. DICY/imidazole cures epoxy at curing temperatures of 130 to 170 °C to very high Tg values and much alike aromatic amines and anhydride curing agents, it is characterized by excellent chemical and physical properties suitable for solder masks. DICY is a commercially available pulverized powder. The
finest powders currently available are characterized by an average particle size of about 6 microns. Those powders are excluded from ink jet inks, because it contain fraction of up to about 20 micron particles, that clog ink jet filtering system and nozzles and disturb accurate drop formation and positioning. In order to be applied by ink-jet, DICY should be manipulated to maximal particle size of less than about 5 microns, and more preferred less than about 2 micron, wherein its particles are stable in a manner that their aggregation or agglomeration is avoided.

SUMMARY OF THE INVENTION

The one objective of the present invention to enable printing of high performance thermosetting epoxy compound by ink-jet onto PCBs, without scarifying the performance of cured film as described by IPC SM840-C specifications.

It is hence according to one embodiment of the present invention to provide a novel liquid thermosetting ink for ink-jet applications, comprising one epoxy resin or more; at least one solid latent curing agent characterized by a maximal particle size of less than about 5 microns; pigment, and optionally an inert filler having fine particles, most preferably particles having maximal particle size of about 0.7 microns, and acrylate monomers, wherein said single-pack or two-pack ink is characterized inter alia by a viscosity lower than about 50 Cps at shear rate of 0.1 to 100,000 1/s at application temperature, surface tension lower than about 50 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than about 80 °C.

It is further according to yet another fundamental embodiment of the present invention to provide a cost effective liquid thermosetting epoxy-based ink as defined above, wherein at least a portion of the resin ingredients is an epoxy-based resin. This ink is characterized inter alia by a viscosity, which is lower than about 20 Cps at shear rate of 0.1 to 100,000 1/s at application temperature; surface tension ranging from about 24 to about 40 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than about 80 °C. More specifically, said ink is adapted for solder mask applications; for marking inks in electronic manufacturing, for bonding devices or components in the electronic manufacturing; for passive component such as capacitors and/or resistors in electronic manufacturing, and/or for conductive lines pads and/or bumps in electronic manufacturing. It is further according to another fundamental embodiment of the present invention to provide the aforementioned ink, wherein
the curing agent is selected from compositions containing modified amines, urea derivatives, imidazoles, dicyandiamide or any mixture thereof, and/or wherein the major portion of the epoxy comprising polymers selected from group containing aromatic, heterocyclic, cycloaliphatic ring and at least two oxirane (e.g., epoxy) groups, for example Epoxy compound selected from bisphenol S epoxy resins, Diglycidyl terephthalate resin, heterocyclic epoxy resins, bixylenol epoxy resins, biphenol epoxy resins, tetragnocidyl xyleneoylethene resins, bisphenol A epoxy resins, hydrogenated bisphenol A epoxy resins, bisphenol F epoxy resins, brominated bisphenol A epoxy resins, Novolak epoxy resins, Novolak epoxy resins of bisphenol A, chelate epoxy resins, glyoxal epoxy resins, amino group-containing epoxy resins, rubber-modified epoxy resins, dicyclpentadiene phenolic epoxy resins, silicone-modified epoxy resins, heterocyclic ring containing polyepoxide such as tris (2, 3-epoxy propyl) isocyanurate and epsilon-caprolactone-modified epoxy resins, or a mixture thereof. It is according to another fundamental embodiment of the present invention wherein the ink is additionally comprised of reactive diluents like monoepoxides; and especially those that are selected from aromatic, heterocyclic, and/or cycloaliphatic compositions. The ink may also comprising impact modifiers and/or flexibilizers having rubbery moieties or blocks in their chain, and especially those that are selected in a non-limiting manner from amine, epoxy, carboxyl or anhydride terminated rubbers. The rubber is selected in a non-limiting manner form butadiene copolymers, polyurethanes, polysulfide, silicone elastomers, acrylic and methacrylic acid ester copolymers. The ink may also comprising adhesion promoters; and especially those being selected in a non-limiting manner from isocinate, titanate, aluminate organosilanes and siloxanes, organotitanium and organozirconium compounds any mixture thereof.

It is according to another embodiment of the present invention wherein the ink is comprised of unsaturated monomers, oligomers and photoinitiators that are activated by means of an effective actinic irradiation. Those monomers and/or oligomers are selected in a non-limiting manner from styrene, acrylic or methacrylic acid and esters thereof; acrylated or methacrylated epoxies; acrylated or methacrylated urethanes. More specifically, the unsaturated monomers are selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, N-vinylpyrrolidone, methoxytetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, polyethylene glycol diacrylate, N,N-dimethyl acrylamide, N-methylol acrylamide, N,N-dimethylaminopropyl acrylamide, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminopropyl acrylate, melamine acrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polypropylene glycol diacrylate,
phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, cyclohexyl acrylate, glycerin diglycidyl ether diacrylate, glycerin triglycidyl ether triacrylate, isoborneol acrylate, cyclopentadiene mono- or di-acrylate; polyfunctional acrylates of polyhydric alcohols such as hexane diol, trimethylol propane, pentaerythritol, ditrimethylol propane, dipentaerythritol, and tris-hydroxyethyl isocyanurate and of ethylene oxide or propylene oxide adducts thereof; methacrylates corresponding to the acrylates enumerated above; and mono-, di-, tri-, and higher polyesters of polybasic acids with hydroxyalkyl (meth)acrylates, acylated DGEBA epoxy, acylated Novolac TM epoxy, Acrylated polyurethane, acrylated polyester, acrylated polybutadiene, acrylated polyacrylate or any mixture thereof. Those compositions may further comprised of photoinitators and secondary thermal initiators adapted to initiate and cure unsaturated ingredients, most preferred organic peroxides. A method of controlling feature dimensions of ink jet printed ink by exposing said ink to effective UV or visible light, in synchronization to jetting, so drop is cured adjacent to its contact with substrate. This ink, defined in any of the above, may additionally comprising amino resins characterized by an impart adhesion and/or high cross-link density, imparted flame retardancy (e.g., halogen free FR) selected from melamine-based resins, urea resins, benzoguanamine resins or any mixture thereof.

Those amino resins are adapted to react with free hydroxyl groups of the backbone of epoxy resins (DGEBA for example), hydroxyl acrylates and methacrylates (HEMA for example), and/or polyfunctional acrylates of polyhydric alcohols (partially acrylated pentaerythritol for example).

It is according to another embodiment of the present invention to provide non-halogenated flame retardant ink that meets the UL 94 V0 requirements.

Moreover, the hereto-defined ink may be additionally comprised of mineral fillers, having maximal particle size of 2 micron in final concentration ranges between 1 to 30 % by weight. More specifically, those mineral fillers are may further characterized by a maximal particle size of about 300 to 700 nm.

It is according to another embodiment of the present invention to provide an ink as defined in any of the above additionally comprising additives selected from surface active agents and/or colloid stabilizers; rheology modifiers; pigments and dyes; matting agents; adhesion promoters; solvents; co-solvents; diluents and mixture thereof. More specifically, the aforementioned solvents; co-solvents or diluents may be at least partially volatile or unsaturated.
It is another object of the present invention to provide an industrially applicable method for producing liquid thermosetting ink for ink-jet applications. This novel method is *inter alia* comprised of the following steps: (a) dissolving at least one solid latent curing agent in a solvent to form a clear solution; (b) admixing under high shear an inert filler having maximal prime particle size of 2 microns with the solution obtained above to form a homogenized dispersion where the curing agent/filler ration is from 0.01/100 to 3/1; (c) precipitating said curing agent as a layer or in the form of small crystals onto said filler surface and/or inside the internal porosity of said filler; (d) evaporating said solvent; (e) drying or concentrating the same; and then (f) milling with monomers, polymers, pigments, epoxy resins, solvents, photoinitiators, adhesion promoters, rheology modifiers, dispersing agents, wetting agents, filler, heat stabilizers, corrosion inhibitors, by media mill, rotor stator homogenizer or attritor to an ink having particles lower than about 2 microns, as indicated by filterability through filter of about 2 micron pore size. This genuine method is provided for either one-pack or two-pack ink characterized by a viscosity lower than about 50 Cps at shear rate of 0.1-100,000 1/s at application temperature, surface tension lower than about 50 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than about 180 °C is obtained.

It is according to one embodiment of the present invention wherein the curing agent is admixed up to a measure that curing agent to filler weight ratio is ranges 0.01:100 to 3:1 respectively. The mixture is exposed to high shear mixing such as high speed dissolver or rotor stator, so filler agglomerates are broken and maximal surface area is available for deposition of the latent curing agent. It is also in the scope of the present invention wherein an additional step is provided, comprising evaporating the solvent by means known in the art, selected in a non limiting manner from introducing of at least one another solvent to the said admixture; changing the temperature; lowering pressure by applying vacuum, pH shifting; altering or any combination thereof. Additionally or alternatively, this method may be also comprised of the step of stabilizing the obtained slurry by means of admixing a sufficient measure of dispersing agents and/or rheology modifiers. It is acknowledged in this respect that according to yet another embodiment of the present invention, the obtained latent curing agent is admixed up to a measure that curing agent to ink weight ratio is ranges form 1 to 25 % from the epoxy resins w/w. respectively; and/or wherein the one-pack or two-pack ink is adapted for solder masks, marking ink, passive electronic components, underfill and globe-top encapsulant or adhesives applications.
It is according to yet another embodiment of the present invention wherein the above-mentioned method is *inter alia* comprised of the following steps: (a) dissolving at least one solid latent curing agent or its precursors in a solvent to form a clear solution; (b) admixing an inert filler having maximal prime particle size of about 2 microns with the solution obtained above to form a homogenized dispersion; (c) precipitating said curing agent as a layer or in the form of small crystals onto said filler surface and/or inside the internal porosity of said filler; (d) evaporating said solvent, (e) drying or concentrating the same; and then (f) admixing a predetermined measure of epoxy-based resin; (g) milling with monomers, polymers, pigments, solvents, photoinitiators, adhesion promoters, rheology modifiers, dispersing agents, wetting agents, filler, heat stabilizers, corrosion inhibitors, by media mill, rotor stator homogenizer or attritor to an ink having particles lower than about 2 microns, as indicated by filterability through filter of 2 micron pore size. This method is provided for either one-pack or two-pack ink characterized by a viscosity which lower about 20 Cps at shear rate 0.1-100,000 l/s at application temperature; surface tension ranging from about 24 to 40 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than about 80 °C is obtained. It is acknowledged in this respect that according to yet another embodiment of the present invention, the obtained latent curing agent is admixed up to a measure that curing agent to ink weight ratio is ranges form 1 to 25 % from the epoxy resins w/w respectively; and/or wherein the one-pack or two-pack ink is adapted for solder masks, electronic components, or adhesives applications.

**DETAILED DESCRIPTION OF THE INVENTION**

The following description is provided, alongside all chapters of the present invention, so as to enable any person skilled in the art to make use of said invention and sets forth the best modes contemplated by the inventor of carrying out this invention. Various modifications, however, will remain apparent to those skilled in the art, since the generic principles of the present invention have been defined specifically to provide liquid thermosetting ink for ink-jet applications in the various electronic technologies and to a method for producing said ink.

It is in the scope of the present invention wherein the aforementioned term "electronic technologies " is referring to any electronic and/or microelectronic and/or optical components or devices manufacturing processes suitable to be applied by ink jet technology. More specifically, the electronic technologies according to the present invention are selected from solder masks,
marking ink, dielectrics, resistors, optical waveguides, conductive modules, capacitance layers, adhesives, protective coatings, encapsulants or any combination thereof.

It is further in the scope of the present inventor wherein the term “one-pack ink” is referring to any ink comprising a curing agent distributed at the same liquid medium with the resin.

It is further in the scope of the present inventor wherein the term “latent curing agent” is refereeing to any insoluble low molecular weight chemicals that are dispersed in monomers, oligomers and polymers or their mixtures. Those components are practically inactive at ambient temperature and become active at elevated temperatures. When activated, the dispersed insoluble particles of latent curing agent dissolve and react or initiate polymerization with polymers to form a cross-linked, and thus hardened polymeric network. It is acknowledged in this respect that the term ‘controlled flow ink’ is also referring to any agent for either one-pack or two-pack ink providing an instantaneous viscosity increase of one order of magnitude or more as soon as the drop is positioned on substrate to fixate, cure and/or immobilize the ink jet applied drop, using actinic irradiation, such as IR, visible light or UV or by thixotropic change from low viscosity (high shear during jetting) to high viscosity (low to zero shear after landing of drop on surface).

It is further in the scope of the present inventor wherein the term “latent curing agent” is referring to the agents themselves and/or to their various latent precursors, adapted to react at elevated temperature.

The term ‘fine particles’ is referring according to the present invention to any solid particles, matrices, agents or powders characterized by a maximal particle size of less than about 5 microns when dispersed in the ink. Preferably, yet not exclusively, the term ‘fine’ is referring hereinafter to particles, having maximal particle size lower 1 micrometer, and especially to those particles having an average particle size of about 300 nanometers; e.g., particles ranging from about 50 to 700 nanometers. The term ‘about’ refers hereinafter to ± 25% of the defined value. More specifically, the term refers to ± 5% of the defined value.

The present invention relates to a process of making either one-pack or two-pack inks characterized by low viscosity so it can be applied by ink jet, high glass transition temperature (Tg) values suitable for ink jet applications in electronic manufacturing processes.

One general approach for this method is a process comprising inter alia the steps of (a) dissolving at least one latent curing agent in a solvent to form a clear solution; (b) admixing an inert filler having maximal particle size of 2 microns (after milling) with the solution obtained above to form a homogenized dispersion; (c) precipitating said curing agent as a layer or in the
form of small crystals onto said filler surface and/or inside the internal porosity of said filler; (d) evaporating said solvent; (e) drying or concentrating the same; and, (f) admixing a predetermined measure of ink and milling to composition in the manner that one-pack or two-pack ink characterized by a viscosity lower than about 50 Cps at application temperature at shear rate 0.1-100,000 1/s, surface tension lower than about 50 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than about 80 °C is obtained.

This process has some advantages over other size reduction processes essentially including the steps of either milling or pulverizing of solid curing agents: (a) no heat buildup during size reduction is required, and deterioration or re-melting of the curative is avoided; (b) the present invention relates to wet process, so no hazardous dust nor explosion risks are provided; (c) nano-size products are available, wherein the single limit is the size of the carrier filler used in this novel process; (d) the obtained product is a ready-to-use dispersion in the manner that energy and time consuming milling is not required; (e) sophisticated product final packages are enabled: multilayer conformation; structures which enable a sequence of several curing steps, controlled release potential mechanisms and/or significant extended pot life and shelf life; (f) the obtained nano-size product is provided the cured matrix to be characterized by respectively higher Tg values, lower flammability, lower solvent and humidity permeability, improved mechanical and physical properties; and (g) a simple and cost-effective means approaching a wide processing possibilities suitable for most solid curatives. Another advantage, especially applicable in solder mask and other filled thermoset polymers, is the nano-composite effect, i.e., the carrier filler reinforces the matrix and lower its shrinkage and coefficient of thermal expansion. The filler that carry the latent curing agent is of a submicron size such that its nano-size enables highest reinforcement efficiency at lowest percentage.

This low viscosity thermosetting latent curing agent is especially useful for ink jet applications: It is a fine enough whereas particles that are bigger than about 2 to 5 microns are usually forbidden problematic in print heads adapted for high resolution and low drop volume, which create high Tg matrix when cures epoxy resin. The said epoxy is selected in a non-limiting manner from a resin comprising two or more oxirane groups per molecule at level of about 10 to 80% (by weight) of the formula. Hence, typical epoxy resins with good trade off between viscosity and performance may be selected from the following commercially available products: epoxy compound selected from bisphenol S epoxy resins, diglycidyl terephthalate resin, heterocyclic epoxy resins, bixylenol epoxy resins, biphenol epoxy resins, tetracyclidyl xylenoyl
ethane resins, bisphenol A epoxy resins, hydrogenated bisphenol A epoxy resins, bisphenol F epoxy resins, brominated bisphenol A epoxy resins, Novolak epoxy resins, Novolak epoxy resins of bisphenol A, chelate epoxy resins, glyoxal epoxy resins, amino group-containing epoxy resins, rubber-modified epoxy resins, dicyclopentadiene phenolic epoxy resins, silicone-modified epoxy resins, heterocyclic ring containing polyepoxide such as tris (2, 3-Epoxy propyl) isocyanurate and epsilon-caprolactone-modified epoxy resins, or a mixture thereof. It is acknowledged in this respect that at least a portion of the resin may be selected from any high Tg resins, such as polyimide, silicone resin, cyanate ester, or bismaleimides.

It is in the scope of the present invention wherein said ink composition also comprising reactive diluent, especially monoeoxides, comprising aromatic, heterocyclic, and/or cycloaliphatic at level of about 2 to 20% by weight of the formula.

It is further in the scope of the present invention wherein said latent curing agents based ink also comprising impact modifiers and flexibilizers having rubbery moieties or blocks in their chain, selected in a non-limiting manner from amine/epoxy/hydroxy terminated rubber, e.g., polybutadiene, polyisoprene, hydrogenetaed polybutadiene or polyisoprene, ethylene-propylene copolymers, polydimethyl siloxane elastomer, polysulfides, polyurethanes, soft polyacrylate esters etc. at level of about 0.2 to 10% by weight of the formula.

It is further in the scope of the present invention wherein said latent curing agents comprising adhesion promoters, selected in a non-limiting manner from organometallic compounds having organo functionality, e.g., siloxane, zirconate, titanate, aluminate at a concentration range between about 0.01 to 2% by weight of the formula.

It is further in the scope of the present invention wherein said latent curing agent based ink comprising unsaturated monomers and oligomers that enables "freezing" of printed drops by exposure to actinic irradiation. When the drop deposited on the substrate, it starts to propagate due to wetting and to broaden. Controlled curing by UV or visible irradiation that is continuous or timed with drop, enables improved resolution and excellent homogeneity of printed features. The unsaturated monomers are preferably selected in a non-limiting manner from styrene, acrylic or methacrylic acid and esters thereof; acrylated or methacrylated epoxies; acrylated or methacrylated urethanes; and more specific the unsaturated monomers are selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, N-vinylpyrrolidone, methoxtetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, polyethylene glycol diacrylate, N,N-dimethyl acrylamide, N-methylol acrylamide, N,N-dimethylaminopropyl acrylamide, N,N-
dimethylaminoethyl acrylate, N,N-dimethylaminopropyl acrylate, melamine acrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polypropylene glycol diacrylate, phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, cyclohexyl acrylate, glycerin diglycidyl ether diacrylate, glycerin triglycidyl ether triacrylate, isoborneol acrylate, cyclopentadiene mono- or diacrylate; polyfunctional acrylates of polyhydric alcohols such as hexane diol, trimethylol propane, pentaerythritol, ditrimethylol propane, dipentaerythritol, and tris-hydroxyethyl isocyanurate and of ethylene oxide or propylene oxide adducts thereof; methacrylates corresponding to the acrylates enumerated above; and mono-, di-, tri-, and higher polyesters of polybasic acids with hydroxyalkyl (meth)acrylates, acrylated DGEBA epoxy, acrylated Novolac epoxy, acrylated polyurethane, acrylated polyester, acrylated polybutadiene, acrylated polyacrylate or any mixture thereof. Said monomers are preferably at a concentration range between about 1 to 50% by weight of the formula.

Another advantage of using unsaturated monomers is the low viscosity that enables compensation of the high viscosity of the epoxy resins while keeping solid content of at least 40 % by weight.

It is further in the scope of the present invention wherein said latent curing agent based ink comprising photoinitiators and optionally secondary thermal initiators such as organic peroxide, adapted to initiate and cure unsaturated ingredients. It is further in the scope of the present invention wherein said latent curing agent based ink comprising amino resin such as one selected from melamine resin, urea resin, benzoguanamine resin, characterized by an impart adhesion, cross-link density, compatible with both the epoxy resins and the vinyl-containing backbone, ability to improve flame retardancy of the cured film, and especially wherein its concentration is between 0.5 to 20% by weight of the formula.

It is further in the scope of the present invention wherein said latent curing agent based ink comprising mineral fillers, having maximal prime particle size of about 5 micron, and preferably about 200 to 700 nm. Said mineral fillers are thermally and chemically inert and preferably imparts enhanced mechanical properties, chemical resistance etc. Those fillers are preferably in concentration ranges between about 1 to 30% by weight of the formula. Most suitable fillers are barium sulfate, talc, silica, kaolin, mica and glass.

It is further in the scope of the present invention wherein said latent curing agent based ink comprising surface active additives to control surface tension and to stabilize colloid particles,
rheology modifiers, pigments and dyes, stabilizers, matting agents, solvents and co-solvents, selected in a non-limiting manner from glycol ethers, esters, ether-esters, ketones, alcohols, aromatic diluents, such as toluene, and high surface tension solvents such as gamma butyrolactone or propylene carbonate.

As set forth above, the present invention also relates to a plurality of innovative and most efficient methods for producing (a) a novel latent curing agent having particle size smaller than any prior invention; (b) a set of at least three novel methods for preparing ink for ink-jet printers comprising the aforementioned latent curing agent.

Hence, the general approach for the production of the latent curing agent according to the present invention is a simple process comprised inter alia of the following five steps: (a) dissolving at least one solid latent curing agent or its precursors in a solvent to form a clear solution; (b) admixing under high shear an inert filler having potentially maximal particle size of 2 microns with the solution obtained above to form a homogenized dispersion where the curing agent/filler ratio is from 0.01/100 to 3/1; (c) precipitating said curing agent as a layer or in the form of small crystals onto said filler surface and/or inside the internal porosity of said filler; (d) evaporating said solvent; (e) drying or concentrating the same; and then (f) milling with at least one compound selected from the group of monomers, polymers, pigments, epoxy resins, solvents, photoinitiators, adhesion promoters, rheology modifiers, dispersing agents, wetting agents, filler, heat stabilizers, corrosion inhibitors, by media mill, rotor stator homogenizer or attritor to an ink having particles lower than about 2 microns, as indicated by filterability through filter of 2 micron pore size. The novel ink composition in the manner that either one-pack or two-pack ink characterized by a viscosity lower than 50 Cps at application temperature at shear rate 0.1-100,000 1/s, surface tension lower than 50 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than 80 °C is obtained.

e It is well acknowledged in this respect that a third approach may equally be taken, wherein the precursors of the curing agent are being admixed with the filler at the reaction medium. Reference for that is made by US Pat No. 6,235,865 to Shimizu et al., which discloses phosphonium borate compounds useful as a curing catalyst in epoxy and other resin compositions, and US Pat No 6,492,437 to Musa et al., which teaches for solvent-based processes for producing latent curing catalysts without causing an extreme exotherm.

Lastly, a method of producing liquid thermosetting ink for ink-jet applications, wherein the filler particles are coated in at least a significant portion of their surface with solid latent curing agents.
is provided. Said method comprising *inter alia* the steps of (a) spraying at least one latent curing agent or its precursors, as organic or aqueous solution or aerosol or vapor towards particles of inert filler, having potentially maximal particle size of about 2 microns; and finally; (b) milling said powder or slurry so maximal particle size is about 5 micron, or preferably about 2 micron, (c) admixing a predetermined measure of ink composition, in the manner that either one-pack or two-pack ink characterized by a viscosity lower than about 50 Cps at application temperature at shear rate 0.1-100,000 1/s, surface tension lower than about 50 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than 80 °C is obtained.

EXAMPLE

To enable continuous filtration of the ink as required in industrial ink jet machines and enable introducing into the print head, a process of deposition of DICY and imidazole catalyst onto particles smaller than 2 μm was developed.

53.34 gr of DICY, e.g., commercially available Dyhard UR100 SF by Degussa were dissolved in 1,013.39 gr of solvent, such as commercially available Dowanol PM DOW by slow RPM mixer until clear solution obtained. 35.56 gr of BaSO₄ powder, e.g., commercially available Blank-Fixe micro by Sachtelben Chemie GMBH is admixed with prime particles smaller than 1 micron, and dispersed for 20 min using a high shear mixer. The slurry is transferred to rotavapor such that DICY was slowly precipitated onto BaSO₄ fine particles during evaporation of solvent. The resulted fine powder was analyzed for optimal curing level vs. epoxy resin having EEW of 190 and found optimal at 56 PHR. The latency was similar to that of original DICY. The DICY-BaSO₄ compound refers hereinafter in the term '6116/1'.

Similar procedure was used to deposit latent imidazole compound, such as commercially available Curezol 2MZ-A by Shikoku Japan onto BaSO₄: 16.19 gr of commercially available Curezol 2MZ-A and 1,237.58 gr of methanol were mixed by slow RPM mixer until clear solution obtained. 46.24 gr of BaSO₄ powder by commercially available Blank-Fixe micro by Sachtelben Chemie GMBH was admixed with prime particles smaller than 1 micron, and disperse for 20 min using a high shear mixer. The slurry was transferred to rotavapor and the imidazole was slowly precipitated onto BaSO₄ fine particles during evaporation of solvent. The latency was similar to that of original 2MZ-A. The DICY-BaSO₄ compound refers hereinafter in the term '6116/2'.
A solder mask having solids content of about 47 to 48%, that is latent at ambient so viscosity increase by less than about 5 cps within 4 weeks at ambient temperature, can be applied by DOD ink jet onto PWB board, gels under UV irradiation (so drop size is set) to a tack free film, cures within 0.5 to 1 hour at 150 °C, and has viscosity of about 15 to 17 Cps at 10 l/s at 47 °C degrees, surface tension of about 35 dyne/cm and meets all IPC SM840C requirements is formulated form the DICY-BaSO₄ and imidazole-BaSO₄ powders:

21.91 gr of epoxy novolac resin, for example commercially available Epon 161 by Resolution Performance Products, 30.94 gr of solid DGEBA epoxy, e.g., commercially available EPON 1001F by Resolution Performance Products, 10.31 gr of rubber-modified epoxy resin, e.g., commercially available HYPOX RF1320 by CVC Specialty Chemicals, 32.13 gr of liquid epoxy resin, e.g., commercially available Epalloy 8220 by CVC Specialty Chemicals, 36.01 gr of diacrylate monomer, e.g., commercially available SR238 by Sartomer, 42.02 gr of tetra-acrylate monomer, e.g., commercially available SR295 by Sartomer, 4 to 9 gr photo initiator for UV and/or UV-visible range, such as commercially available Darocur 1173 by Ciba, wetting and dispersing agents in amount sufficient for stabilization of filler, 42.60 gr of 6116/1 (the aforesaid DICY-BaSO₄) and 15.26 gr of 6116/2 (the aforesaid imidazole-BaSO₄) and pigments, such as Phthalocyanine green and TiO₂, 62.3 gr of ether-ester solvent, e.g., commercially available Dowanol PMA by Dow, 189.6 gr cyclic ester solvent, such as commercially available Propylene Carbonate by Lyondell.

The mixture was milled by means of Dynomill KDL horizontal mill, media size 0.4 to 0.5 mm; media type Zr-Y, residence time of 15 minutes. The resulted ink is easily filtered through 1 micron filter and has excellent storage stability, i.e., low sedimentation rate, soft cake.

The ink was printed by Printar LGB809 printer, printing at 45 °C, 100V, 2 KHz, 6 μs pulse width onto printed wire board (PWB) board having bare glass-epoxy laminate and copper conductors. The ink wets very well both materials and the propagation of ink was easily controlled by timed UV pulse that initiated the photo initiator, and cured the acrylate monomers so a tack free film was obtained. The film was the dried and cured in oven for 60 minutes at 150 °C. The cured film has excellent mechanical and physical properties and passes all requirements listed in IPC-SM 840 °C protocol for solder-resists for PWB. The ink has good latency for 1 to 2 weeks at ambient temperature, the viscosity raised by less than about 2 Cps at ambient temperature within 2 weeks and less than about 5 Cps within 4 weeks.
When ink was manufactured according same procedure but based on original Dyhard UR100 SF DICY and Curezol 2MZ-A imidazole, the ink had poor storage stability and was difficult to filter. Since filtration was poor, this composition was not applicable to ink jet application.
CLAIMS

1. A liquid thermosetting ink for ink-jet applications, comprising
   a. one or more epoxy resin;
   b. at least one solid latent curing agent characterized by a maximal particle size of less than about 5 microns;

   wherein said single-pack or two-pack ink is characterized by a viscosity lower than 50 Cps at application temperature at shear rate 0.1-100,000 1/s, surface tension lower than 50 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than 80 °C is obtained.

2. The liquid thermosetting ink for ink-jet applications according to claim 1, additionally comprising at least one solid latent curing accelerator characterized by a maximal particle size of less than about 5 microns.

3. A liquid thermosetting epoxy-based ink according to claim 1, comprising an epoxy-based resin, wherein said ink is characterized by a viscosity which is lower than 20 Cps at shear rate 0.1-100,000 1/s, at application temperature; surface tension ranging from 24 to 34 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than 80 °C.

4. The ink according to claim 1, wherein the curing agent is selected from compositions containing modified amines, imidazoles, dicyandiamide, inorganic boron salts or any mixture thereof.

5. The ink according to claim 1, wherein the curing accelerator is selected from compositions containing urea derivatives, imidazoles, metal salts, metal complexes or any mixture thereof.

6. The ink according to claim 1, especially adapted for solder mask in printed boards, PCBs or PWBs.

7. The ink according to claim 1, especially adapted for bonding devices or components in the electronic manufacturing.

8. The ink according to claim 1, especially adapted for printing electronic manufacturing of passive component capacitors and/or resistors.
9. The ink according to claim 1, especially adapted for direct printing of conductive lines and features such as pads, bumps.

10. The ink according to claim 1, wherein the major portion of the epoxy comprising polymers selected from epoxy compound selected from bisphenol S epoxy resins, diglycidyl terephthalate resin, heterocyclic epoxy resins, bixylenol epoxy resins, biphelenol epoxy resins, tetracyclidyl xyleneol ethane resins, bisphenol A epoxy resins, hydrogenated bisphenol A epoxy resins, bisphenol F epoxy resins, brominated bisphenol A epoxy resins, Novolak epoxy resins, Novolak epoxy resins of bisphenol A, chelate epoxy resins, glyoxal epoxy resins, amino group-containing epoxy resins, rubber-modified epoxy resins, dicyclopentadiene phenolic epoxy resins, silicone-modified epoxy resins, heterocyclic ring containing polyepoxide such as tris (2, 3-Epoxy propyl) isocyanurate and epsilon-caprolactone-modified epoxy resins, or a mixture thereof.

11. The ink according to claim 1, additionally comprising impact modifiers and/or flexibilizers having rubbery moieties or blocks in their chain.

12. The ink according to claim 11, wherein the impact modifiers and/or flexibilizers are selected from elastomeric, oligomers comprising side or end groups, selected from amines, carboxyl, anhydride, epoxies, hydroxyls; wherein said functional terminated rubbers or rubber-like compositions comprising polybutadienes, acrylonitrile-butadiene, styrene-butadiene, styrene-acrylate, ethylene-acrylate, hydrogenated polybutadienes, polyisoprenes, ethylene-propylene copolymers, polydimethyl siloxane elastomers, polysulfide, polyester, polyether, polyurethane, polyetheramide or any mixture thereof.

13. The ink according to claim 1, additionally comprising adhesion promoters.

14. The ink according to claim 13, wherein the adhesion promoters are organometallic compounds selected from siloxane, zirconate, titanate, aluminate or any mixture thereof.

15. The ink according to claim 1, additionally comprising monomers and/or oligomers selected from styrene, acrylic or methacrylic acid and esters thereof; acrylated or methacrylated epoxies; acrylated or methacrylated urethanes; more specific the unsaturated monomers are selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, N-vinylpyrrolidone, methoxytetraethylenglycol acrylate, methoxypolyethylene glycol acrylate, polyethylene glycol diacrylate, N,N-dimethyl acrylamide, N-methylol acrylamide, N,N-dimethylaminopropyl acrylamide, N,N-dimethylaminoethyl acrylate, N,N-
dimethylaminopropyl acrylate, melamine acrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polypropylene glycol diacrylate, phenoxymethyl acrylate, tetrahydrofurfuryl acrylate, cyclohexyl acrylate, glycerin diglycidyl ether diacrylate, glycerin triglycidyl ether triacrylate, isoborneolyl acrylate, cyclopentadiene mono- or di-acrylate; polyfunctional acrylates of polyhydric alcohols such as hexane diol, trimethylol propane, pentaerythritol, ditrimethylol propane, dipentaerythritol, and tris-hydroxyethyl isocyanurate and of ethylene oxide or propylene oxide adducts thereof; methacrylates corresponding to the acrylates enumerated above; and mono-, di-, tri-, and higher polyesters of polybasic acids with hydroxyalkyl (meth)acrylates, acrylated DGEBA epoxy, acrylated Novolac epoxy, acrylated polyurethane, acrylated polyester, acrylated polybutadiene, acrylated polyacrylate or any combination thereof.

16. The ink according to claim 15, additionally comprising photoinitiators and secondary thermal initiators adapted to initiate and cure unsaturated ingredients.

17. A method of controlling feature dimensions of ink jet printed ink by exposing ink as described in claim 16 to UV or visible light, in synchronization to jetting, so drop is cured adjacent to contact with substrate.

18. The ink according to claim 1 additionally comprising mineral fillers, having maximal particle size of about 5 micron in the final ink; wherein concentration ranges between about 1 to 70 % by weight.

19. The ink according to claim 18, wherein the mineral fillers are characterized by a maximal particle size of about 800 nm

20. The ink according to claim 1, additionally comprising additives selected from surface active agents and/or colloid stabilizers, rheology modifiers, pigments and dyes, matting agents, solvents; co-solvents, diluents or any mixture thereof.

21. The ink according to claim 20 wherein the solvents, co-solvents or diluents are volatile.

22. A method of producing a liquid thermosetting ink for ink-jet applications, comprising inter alia the steps of:
   a. dissolving at least one solid latent curing agent or catalyst or precursors thereof in a solvent to form a clear solution;
b. admixing an inert filler having potentially maximal particle size of about 2 microns after milling, with the solution obtained above to form a homogenized dispersion;
c. evaporating said solvent and simultaneously precipitating said curing agent as a layer or in the form of small crystals onto said filler surface and/or inside the internal porosity of said filler;
d. admixing the latent agent agglomerated fine particles with ingredients selected from the group of epoxy resins, solvents, fillers, wetting and dispersing agents, elastomeric modifiers, unsaturated monomers and oligomers, photoinitiators, pigments, adhesion promoters, rheology modifiers, photoinitiators and thermal stabilizers to a predetermined measure of ink composition; and,
e. milling said ink by means selected from the group of media mill, sand mill, attritor, or rotor-stator until slurry can be easily filtered through about 2 to 5 micron filter,
in the manner that ink characterized by a viscosity lower than about 50 Cps at application temperature at shear rate of about 0.1 to 100,000 1/s, surface tension lower than about 50 dyne/cm at application temperature, and glass transition temperature of cured ink of greater than about 80 °C is obtained.

23. A method according to claim 22, comprising dissolving a solid DICY curing agent.

24. A method according to claim 22, comprising dissolving a solid latent imidizole curing catalyst.

25. The method according to claim 22, wherein the ink is adapted for solder masks (solder resist), marking ink, electronic passive components printing, passive component, or adhesives applications in electronic manufacturing.