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SCREENING INKS WITH SUBLIMABLE SOLIDS

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9 Claims. (Cl. 106—26)

ABSTRACT OF THE DISCLOSURE

To a wet ink composition comprising metal powder pigment, vitreous binder, organic binder material and solvent, and which is adapted to be deposited in a given line pattern on a substrate, solidified on the substrate by drying and fused to the substrate by firing, is added a small percentage of a sublimable solid. The additive assures that the dry line has the same dimensions as the wet ink deposit.

This is a continuation of application Ser. No. 334,544 of Lewis F. Miller et al., filed Dec. 30, 1963, now abandoned.

This invention relates to inks and particularly to inks intended for printed image comopsitions and the like; and methods of preparing printed images, especially micro-miniature images.

Ordinary liquid inks when deposited on a substrate tend to spread, giving the "dry" ink lines a fuzzy outline; in the case of glossy substrates such as coated paper, metal, or ceramic, the ink may run. With low boiling solvents, it is not possible to maintain definition even at atmospheric temperature drying. For inks containing a low volatility solvent the problem is even more difficult because the elevated drying temperatures lower the ink viscosity and surface tension, and the inked line (print) flows beyond the deposited dimensions. For printed image compositions, in particular, either conductive or passive (resistors, capacitors, etc.), it is very desirable that the print maintain, essentially, the deposited ink dimensions. In the case of micro-miniature printed images it is essential that printed line definition be maintainnd.

An object of the invention is an ink which tends to maintain dimensional stability of the inked line (print) while the vehicle is being removed, i.e., while the wet ink is being dried. A preferred object is an ink for use in printed image composition, and especially micro-miniature images, which ink gives dry prints of essentially the same dimension as the wet print. Other objects of the invention will be apparent from the detailed description of the invention.

It has been discovered that dimensional stability of the ink lines (print) is attained when the ink composition consists essentially of pigment; liquid vehicle; vaporizable solid—which is removable at the temperature at which the print is held to dry the ink deposit; and binder material for retaining said pigment on the substrate after removal of said vehicle and said vaporizable solid.

The presence of a sufficient amount of vaporizable solid in an ink results in essential dimensional stability of the inked line (print), i.e., the dry line is essentially the same dimension as the wet line—line is used herein to include any inked configuration, line, letter or other shape. Vaporizable solid includes sublimable solids which are removed from the wet ink in the form of a vapor and solids which decompose to compounds or elements which pass off as gases—these may pass off completely or they may leave a residue which remains in the dry link.

These vaporizable solids may be organic or inorganic. Particularly good results have been obtained in printed image composition ink with sublimable organic solids.

Sublimable organic solids include certain organic acids such as terephthalic acid, furoic acid, 2,4-dischlorobenzoic acid and anthranilic acid; certain polynuclear hydrocarbons such as naphthalene and methyl-napthalene; certain quinones such as 2-methyl anthraquinone and 1,4-napthoquinone. Ammonium carbonate-carbamate sublimes at a suitable temperature. Many ammonium compounds decompose at moderate temperatures such as are used in ink drying, for example, ammonium carbonate and ammonium chloroplumbate. The above solids are illustrative only and do not limit the scope of the invention. Other suitable solids are readily located in the chemical handbooks.

The vaporizable solid is present in an amount sufficient to maintain dimensional stability of the inked line while the liquid vehile (solvent) portion of the ink is being removed. The amount present is dependent on the type of ink and the type of solid. In screening inks for printed images, the usage of sublimable organic solid falls in the general region of about 1–10 weight percent, based on ink composition.

The subliming solids can be added to present conventional formualtions to achieve dimensional stability. Solids which do not dissolve usually increase viscosity. When dissolvable solids lower viscosity the viscosity can be held constant by using dissolvable and non-dissolving solids e.g., such a mixture for metallic inks is three parts furoic acid to two parts terephthalic acid.

The ink composition includes a pigment which composes the dry ink line. The pigment type will be determined by the type of ink. For ordinary inks which are dried at moderate temperatures, the pigment may be carbon black, organic dyes, iron compounds and the like well known materials. For higher temperatures, metallic compounds and glass or enamel frits may be used as pigments. In printed images, the pigment can be electrically conductive and metal powders are used as pigments, such as platinum, gold, silver, palladium and the like. The amount of pigment present is determined by the type of ink. In the case of printed image inks, normally the ink composition includes about 60–80 weight percent of pigment.

Printed images for high temperature use require the presence of a fusible inorganic solid for bonding the metallic pigment to the substrate. These solids may be fusible metal oxides such as bismuth oxide, lead oxide, cadmium oxide; or a fusible metal compound such as lithium fluoride; or a glass or enamel frit. Since these materials remain with the pigment proper after the print has been dried and fired, herein these fusible solids are considered to be part of the defined pigment.

It has been observed that some metal oxide slowly react at ordinary temperatures with the organic acids and these compositions have a relatively short storage life. Reactive systems should be avoided where a long storage life is necessary.

The ink composition includes a binder material in an amount sufficient to retain the pigment on the substrate when the vehicle and vaporizable solid have been removed. In addition to possessing adhesion for the substrate, the binder used herein must be chemically inert to the vehicle, pigment and vaporizable solid. The binder may be any of those conventionally used such as natural gums, glues, synthetic resins, cellulosics and the like. For printed images, it is preferred that the binder material be decomposed at firing temperatures to materials which do not affect the electrical properties of the fired image.

The ink composition also includes a liquid vehicle (solvent) in an amount sufficient to impart the desired

viscosity thereto. The vehicle is selected on the basis of the ink use and conventional solvents used in presently known inks are suitable for use herein. For printed image ink the vehicle may be any suitable high boiling organic solvent which can be removed by heating the inked line. The solvents commonly are the higher boiling paraffins, cycloparaffins and aromatic hydrocarbons or mixtures thereof; or are one or more of the Cellosolve or Carbitols or products thereof, such as butyl Carbitol acetate. Conventional inks using these high boiling solvents are difficult to handle where line definition is critical. The addition of the sublimable solid to such inks makes it simple to maintain definition of the inked line.

A preferred screening ink composition for use in printed image composition, on a non-conducting substrate, either thermoset resin or ceramic, consists essentially of metal powder pigment, about 60–80 weight percent; organic binder material, about 1–10 weight percent; sublimable organic solid, about 1–10 weight percent; and high boiling organic solvent, remainder.

A preferred screening ink composition for use in making fired printed images, on a ceramic substrate, consists of metal powder pigment, about 60–70 weight percent; fusible solid, about 5–15 percent; organic binder material, about 2–10 weight percent; sublimable organic solid, about 2–5 weight percent; and high boiling organic solvent the remainder.

ILLUSTRATIVE COMPOSITIONS

I

	Weight percent
Platinum black	65.0
Bismuth oxide	15.0
Furoic acid	2.0
Ethyl cellulose	3.0
Butyl Carbitol acetate	15.0

This composition produces prints on alumina substrates which dry well at temperatures of 90° C.–300° C. to give dry prints of essentially the same size as the screened wet print; this print was fired at about 800° C. to remove the cellulose and fuse the oxide—a durable fired circuit was obtained.

II

	Weight percent
Platinum black	60.0
Lead oxide	15.0
1,4-naphthoquinone	1.25
Resin (Piccolastic D–100)	9.0
Surfactant (Igepal CO 430)	0.75
Mixed paraffin-aromatic solvent	14.0

Wet prints on an alumina substrate dried dimensionally stable at 260° C.

III

	Weight percent
Platinum black	70.0
Glass frit	5.0
2-methyl anthraquinone	5.0
Polystyrene resin	2.0
Ethyl cellulose	1.0
Mixed paraffin-aromatic solvent	17.0

Wet prints on an alumina substrate dried dimensionally stable at 260° C.

Thus having described the invention, what is claimed is:

1. An ink composition consisting essentially of:

	Weight percent, about
Platinum black	65
Bismuth oxide	15
Furoic acid	2
Ethyl cellulose	3
Butyl Carbitol acetate	15

2. An ink composition consisting essentially of

	Weight percent, about
Platinum black	60
Lead oxide	15
1,4-naphthoquinone	1.25
Resin, thermoplastic	9
Surfactant	0.75
Hydrocarbon solvent	14

3. An ink composition consisting essentially of:

	Weight percent, about
Platinum black	70
Glass frit	5
2-methyl anthraquinone	5
Resin, polystyrene	2
Ethyl cellulose	1
Hydrocarbon solvent	17

4. A wet ink composition adapted to be deposited on a substrate, solidified on the substrate by drying, and fused to the substrate by firing, said composition consisting essentially of:

about 60–70 weight percent of electrically conductive metal powder pigment;

about 5–15 weight percent of vitreous binder for bonding the pigment to the substrate during firing;

about 2–10 weight percent of sublimable solid removable during drying;

about 2–10 weight percent of organic binder material for retaining the pigment and binder on the substrate until firing and being removable during firing;

and the remainder, organic solvent for imparting desired viscosity, being removable during drying.

5. A wet ink composition adapted to be deposited on a substrate, solidified on the substrate by drying, and fused to the substrate by firing, said composition consisting essentially of:

about 60–80 weight percent of pigment powders wherein said pigment powders comprise at least 60% electrically conductive metal and vitreous binder for bonding the pigment to the substrated during firing;

about 1–10 weight percent of organic binder material for retaining the pigment and binder on the substrate until firing, and being removable during firing;

about 1–10 weight percent of sublimable solid, removable during drying;

and the remainder, organic solvent for imparting desired viscosity, removable at drying temperature.

6. The composition according to claim 5 wherein said sublimable solid is terephthalic acid.

7. The composition of claim 5 wherein said sublimable solid is furoic acid.

8. The composition of claim 7 wherein said solvent is butyl Carbitol acetate.

9. The composition of claim 8 wherein said binder is ethyl cellulose.

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