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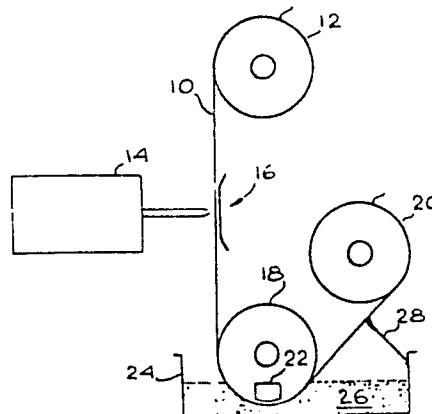
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54 **Magnetic jet ink printing.**

57 A method of depositing ink compositions by ink jet printing on metal, plastic, or paper surfaces to develop a tacky imprint surface and thereafter applying at least one magnetic pigment to give the printed pattern properties of opacity and a magnetic character readability.



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MAGNETIC JET INK PRINTING

This invention relates to jet ink recordings characterized by opaque properties in light. More specifically, this invention relates to ink recordings which are opaque in ordinary light and magnetically readable so as to render them particularly suitable as a means for marking various materials.

Ink jet printing is a recent development in the art of applying identifying and decorative indicia to a base. In general terms, a fluid ink is forced, under pressure, through a very small orifice in an orifice block which contains a piezoelectric crystal vibrating at high frequency (50 - 100,000 vibrations per second) causing the ink passing through the orifice to be broken into minute droplets equal in number to the crystal vibrations. The minute droplets are passed through a charging area where individual droplets receive an electrical charge in response to a video signal, the magnitude of the charge being dependent on the amplitude of the video signal. The droplets then pass through an electrical field of fixed intensity, causing a varied deflection of the individual droplets depending on the density of the charge associated therewith, after which the deflected drops are directed to the base medium

which is to receive the decorative or informative printed indicia.

In order to operate satisfactorily in an ink jet printing system, an ink must display a consistent drop breakup length, drop velocity and drop charge under set operating conditions. It has been determined that inks with viscosities of 25 cps. will perform satisfactorily depending upon the type of nozzle used. However, inks with lower viscosities perform much better. Resistivity of ink may range as high as 10,000 ohm-cm. for satisfactory operations.

The information recording process of the present invention includes jet printing by producing a fine jet of liquid droplets, directing the jet toward the recording medium and modulating the density of the jet with an electric field in accordance with information to be recorded. The information is recorded on the medium since the liquid or ink contacts the medium in a pattern determined by the modulation and adheres to the medium upon impact. The liquid may be colorless at this point, as it is subsequently contacted by a magnetic pigment to produce a magnetic image and to make the information opaque and visible. The magnetic pigment is applied to the medium before the ink is dried so that it adheres to the ink, and is preferably applied while the ink is in a tacky state. One method of applying the particles is to pass the medium over a magnetic surface, and thus draw the pigment to the medium by magnetic means. Another means of applying the pigment may be to pass the medium through a fluidized bed of magnetic pigment, the important consideration being the contacting of the medium by the magnetic pigment while the liquid is still sufficiently tacky to adhere

the appropriate amount of pigment. This would be determined by such factors as the temperature of the operation, the solvent content in the ink, the pigment selected, and the desired strength of the resulting magnetic image. In the preferred form,
5 a comminuted magnetic pigment is used and magnetic means of attraction are used to apply the pigment.

Printed ink images as developed by the invention include three basic components. The first is a magnetic pigment, added after the jet ink pattern has been established, for providing
10 visibility of the printed indicia. The second major component is the solvent which provides fluidity to the jet ink which is used and carries in solution or suspension the resin and the other components, as noted below. The third component is a resin or binder which remains on the substrate surface after printing and
15 serves to adhere and bind the comminuted magnetic pigment in position on the substrate surface. In addition to these three components, which are found in nearly all fluid printing inks, various other ingredients may be utilized, including drying, dispersing and wetting agents, plasticizers, diluents and the
20 like.

In the schematic figure of the accompanying drawing, recording medium 10 is provided on supply reel 12 and imprinted by jet printer 14 using backing 16. It then passes around reel 18 and on to take-up reel 20. Reel 18 is positioned in tray 24
25 so that magnetic particles 26 come in contact with the printed image. The particles stick to the tacky image surface and thereby render the printed information, characters or other format, magnetically readable. The recording medium continues along a path to the take-up reel 20 where the excess particles

are brushed off by brush 28. A magnet 22, which may be an electromagnet if desired, is shown positioned within the reel 18 to draw the magnetic particles into the tacky imprint surface for better adhesion to the medium.

5 The inks utilizable in the process of the present invention are preferably opaque, as printed, and contain resins and polymers in concentrations of from 1 to 80 weight percent, alone or in blends. The resin or polymer is dissolved in a solvent such as an aliphatic alcohol. Other solvents utilizable
10 to produce the ink include ketones, aldehydes, ethers, esters, glycols, glycol ethers, hydrocarbons, and lactones. The preferred aliphatic alcohols are all monovalent, and include methyl alcohol, ethyl alcohol, etc. As a general rule, the solvent is also present in an amount of from 1 to 80 weight
15 percent of the liquid, and is a mixture of a lower aliphatic alcohol, and a ketone. The particular solvent would depend upon the character of the resin or polymer utilized, and would especially depend on whether a mixture of resins and polymers is utilized, as different resins and polymers have different
20 solubilities in various solvents. Generally, in order to properly print, the inks have a viscosity of from about 1.5 cps to about 25 cps at 25°C. Preferably, however, the viscosity varies between 1.8 and 7.5 cps. The resistivity of the ink may be as high as 10,000 ohm-cm, but is preferably from about 1,500
25 to about 4,000 ohm-cm. The viscosity and resistivity of the ink are selected, depending upon the particular jet printing process utilized. As noted above, different types of equipment exist for jet ink printing. Thus, the particular ink composition including the resin, the solvent, the viscosity of mixture, and the

resistivity of the mixture would be determined by the apparatus in use. The ink utilized, however, must have good adhesion on practically all substrates, and in the process of the present invention, must exhibit good adhesion on aluminum, paper, and
5 polymeric substrates. The after-applied magnetic pigment, on the other hand, may vary with the desired eventual use. However, it is preferred that a comminuted magnetic pigment be utilized, and in the most particularly preferred form, comminuted iron oxide is utilized as the magnetic pigment.

10 Additionally, the resin component of a jet printing ink suitable for printing on coated or virgin metal must also meet a variety of requirements. Of primary importance is the ability of the resin to adhere to the coated or virgin metal surface on which the ink is printed and to maintain this strong adhesion
15 under widely varying conditions of humidity and temperature. When the ink is applied to a metal surface, it must "wet" or adhere to a coated or virgin metal surface, even in the presence of some moisture, and should be moistureproof, not only to maintain adhesion to the metal but also to adhere to the magnetic
20 pigment. The resin component must also be very readily soluble in the solvent combination to form a stable, low viscosity solution so that effective amounts can be dissolved in the solvent without unduly increasing the viscosity of the composition.

25 Synthetic, semi-synthetic and natural resins, which is to say both polymerization as well as polycondensation and polyaddition products, are suitable. In principle, all resins customary in the printing ink and paint industry may be used. Exemplary resins are described in the lacquer raw material tables

of Karstne (4th edition, Hanover, 1967) and in Wagner and Sarx's work on lacquer resins (4th edition, Munich, 1959). The following are suitable resins: colophony and derivatives thereof, hydrogenated colophony, di- or polymerized colophony, as
5 calcium or zinc salt, with colophony esterified with mono- or polyvalent alcohols; with resinifiers such as acrylic acid and butanediol or maleic acid and pentaerythritol modified colophony resin; the soluble resins modified with colophony and resins based on acrylic compounds, maleinate resins, oil-free alkyd
10 resins, styrolated alkyd resins, vinyl toluene modified alkyd resins, alkyd resins with synthetic fatty acids, linseed oil alkyd resins, ricinene alkyd resins, castor oil alkyd resins, soy oil alkyd resins, acrylated alkyd resins, also oils and oil varnishes. Also suitable are terpene resins, polyvinyl resins
15 such as polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetals, polyvinyl alcohol, polyvinyl ether, copolymers and graft polymers with various vinyl monomers, polyacrylic resins, acrylate resins, polystyrenes, polyisobutylenes, polyesters based on phthalic acid, maleic acid.
20 adipic acid, sebacic acid, etc.; naphthalene formaldehyde resins, furane resins, ketone resins, aldehyde resins, polyurethanes (especially urethane primary-products that cure only at elevated temperature), epoxide resins (especially resin-curer mixtures that cure only at elevated temperature) and precondensates
25 thereof. Suitable too are primary products of unsaturated polyester resins, dialkylphthalate-prepolymers, polyolefines such as polyethylene wax or polypropylene wax, indene and cumaronindene resins, carbamide and sulphonamide resins, polyamide and polyester resins, silicone resins, rubber and

derivatives thereof, for example, cyclorubber and chlorinated rubber.

A further requirement of resin is that it should have sufficient solvent release so that a desired slow rate of drying is obtained on a given substrate. In order to be effective in a formulation of a jet printing ink for a given substrate, the solvent medium must readily dissolve sufficient amounts of the resin component and any desirable optional components such as to achieve the desired level of tacky adhesiveness, conductivity and visual impact of the ink composition. Further, since some degree of evaporation of solvent will occur in the ink supply and ink return systems, thereby, increasing the solids concentration in ink and solvent should have sufficient power to prevent precipitation in this situation.

Depending upon type of substrate on which ink is to be printed, it is advantageous to use a solvent which will penetrate the wax or other coating on substrates to enhance adhesion and rub resistance of the ink. The jet ink normally contains a mixture of an aliphatic monovalent alcohol and at least one other solvent component. Typical aliphatic monovalent alcohols are methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, n-amyl alcohol, amylalcohol, isoamyl alcohol, hexyl alcohol, heptyl alcohol, octyl alcohol, or a mixture of same. Aliphatic monovalent alcohols with 1 to 8 carbon atoms are particularly preferred. The weight ratio of aliphatic monovalent alcohol to other solvents is preferably 1-99:99-1, especially 30-80:70-20, and particularly 40-80:60-20.

Solvents which form the mixture for these inks are

ketones, aldehydes, ethers, esters, hydrocarbons, glycol, glycol ethers and lactones. Suitable solvents are hydrocarbons, such as hexane, heptane, octane, decane, cyclopentane, cyclohexane, benzene, toluol, xylol, and ethylbenzene; hydrocarbon halides, 5 such as carbon tetrachloride, ethylene dichloride, trichloroethylene, tetrachloroethane, and dichlorobenzene; ether-type solvents, such as butyl ether, ethylene glycol-diethyl ether, ethylene glycol-monoethyl ether, ethylene glycol-monobutyl ether; ketone-type solvents, such as acetone, methylethyl ketone, 10 methyl propyl ketone, methyl isobutyl ketone, methylamyl ketone, cyclohexanone; ester-type solvents, such as ethyl formate, methyl acetate, propyl acetate, butyl acetate, phenyl acetate, ethylene glycol-monoethyl ether acetate, methylpropionate; other alcohol solvents, such as diacetone alcohol or such.

15 This invention uses jet printing inks which have excellent adhesion on various substrates. More particularly the invention uses printing inks which contain very high weight percentages of resin or blend of resins dissolved in a blend of solvents which are compatible with fatty oils and various oils, 20 resins, resinous varnishes, solvents, etc., conventionally used as printing ink materials. Further, if necessary, the ink may be prepared by milling and the addition of dispersing agents, extenders and/or auxiliary materials.

A binding agent and other additives, such as surface 25 active agents can be added to the ink. Suitable binding agents (vehicle) are dry oils, such as linseed oil, tung oil, safflower oil, soya oil, dehydrated castor oil; semidrying oils, such as cottonseed oil and beet oil; non-drying oils, such as castor oil and olive oil, aliphatic acids and esters of same, such as oleic

acid, linoleic acid, pelargonic acid, caprinic acid, ethyltridecanate and methyl laurate; dicarboxylic acid ester, such as dimethyl phthalate, diethyl phthalate, dibutylphthalate, butylbenzene phthalate, dioctylphthalate, dioctyladipate, 5 dioctylsebacate, dibutylsebacate, monomethyladipate and monoethylpimelate; polyvalent alcohols, such as ethylene glycol, polyethylene glycol, diethylene glycol, propylene glycol, glycerine, dipropylene glycol and esters and ethers of the same, such as diethylene glycol monobutyl ether, dipropylene 10 glycolemonoethyl ester or such.

Liquid resins with a molecular weight under 2000 can also be used, for example, polyester resins, epoxy resins and polybutadiene resins. Compared to commercial nonaqueous ink, the inks exhibit a high printing velocity, and, as a result, 15 excellent electrostatic deflection properties and increased stability are also available. The ink in accordance with the invention is suited for jet printing devices and electrical field type printers.

In practice the ink is selected in accordance with the 20 above parameters, provided to a piezoelectric crystal, and formed into very small droplets. It is then subjected to an electric field which is modulated or varied in accordance with a signal corresponding to an image that is to be placed upon a substrate. The resulting changed jet of ink is directed to a substrate or 25 record medium and impinged upon the medium and adhered thereto. The ink composition is selected in such a manner that it properly adheres to the medium, but does not dry completely before contact with the subsequently applied magnetic pigment. The magnetic pigment can be applied by, for instance, dusting, as is well

known in the art, or by dipping in a bath of magnetic particles. In addition, the pigment can be applied by magnetic means, or otherwise, as previously disclosed herein. The important consideration at this point in the invention is that the image
 5 produced by the ink, be it colored or colorless, is in a sufficiently tacky condition that the appropriate amount of magnetic pigment will adhere to the ink surface.

The invention is exemplified as follows:

Example 1

10	non-oxidizing polyester exhibiting a viscosity of S-X on the Gardner- Holdt scale and a melting point of 75 - 85 C sold as Archem 650 by Ashland Chemical Company, Columbus,	
15	Ohio	38.25
	diethoxyactophenone	22.00
	methanol	49.75
	para toluene sulfonic acid	1.30
	rhodamine B base	1.00
20	methyl ethyl ketone	<u>10.00</u>
		122.30

A 60% solution of Arochem 650 in methyl ethyl ketone exhibited a viscosity of less than 25 centipoises. A jet ink was formulated using Arochem 650 resin which was slow
 25 drying (which provides tack for pigment pick-up and adhesion) by using high boiling ketones, alcohols, etc. A magnetic iron-oxide is applied by a magnetic device over the printed ink to obtain opaque and visible prints. The pigment only adhered to the prior jet printed area

eliminating the jet ink tack. The conductivity is increased by adding sulphonic acid or any other compatible acid.

WHAT IS CLAIMED IS:

1. A process for information recording comprising producing a fine jet of liquid, modulating the charge density of the jet by applying an electric field in accordance with the information to be recorded, directing the jet of liquid to a recording medium to record said information, and subsequently applying at least one magnetic pigment to said recorded information on said medium, thereby rendering said recorded information magnetic, opaque and visible.
2. The process of claim 1 wherein comminuted iron oxide is used as the magnetic pigment to render the recording magnetic, opaque and visible.
3. The process of claim 2 wherein the information pattern is allowed to dry to a tacky state before adherence of the magnetic pigment.
4. The process of claim 3 wherein the magnetic pigment is applied to the tacky pattern by means of magnetic attraction.
5. The process of claim 1 wherein the jet ink has a viscosity of from 1.5 to 25 cps at 25°C and a resistivity of up to 10,000 ohm-cm.
6. The process of claim 5 wherein the viscosity is from 1.8 to 7.5 cps and the resistivity is from 1,500 to 4,000 ohm-cm.
7. A process for information recording comprising

producing a fine jet of a liquid containing a mixture of a resin dissolved in a solvent containing an aliphatic monovalent alcohol of from 1 to 8 carbon atoms, modulating the charge density of the jet by applying an electrical field in accordance with
5 information to be recorded, directing the jet of liquid to a recording medium to record the information, subsequently allowing the recorded information to dry to a tacky state, and thereafter applying a magnetic pigment to the recorded information on the medium.

10 8. The process of claim 7 wherein the jet of liquid is colorless, and is rendered opaque and visible by the application of the magnetic pigment.

 9. The process of claim 8 wherein the magnetic pigment is applied by contacting the surface of the medium with
15 comminuted magnetic particles.

 10. The process of claim 9 wherein the comminuted magnetic particles are comminuted iron oxide.

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