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[54] **ELECTROSENSITIVE RECORDING MATERIALS**

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[58] **Field of Search** ..... 346/135, 74 S, 74 SB, 346/74 SC; 117/201, 227, 213, 60

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[57] **ABSTRACT**

An electrosensitive recording material comprising a non-electrically-conducting support having a substantially uniform matt surface on which has been vapour deposited a coating, devoid of any overcoat, of a metal having the property of volatilising when contacted by an electrically energized stylus, the characteristics of the matt surface and the amount of metal deposited on the support being such that a visible image of good definition is produced upon application to the material of a stylus energized by A.C.

4 Claims, No Drawings

ELECTROSENSITIVE RECORDING MATERIALS

This invention relates to electrosensitive recording materials for use in recording data from an electrically energized recording member, for example for sonar recording, computer output recording, analogue and digital recording, facsimile recording and weather map recording.

Such recording materials comprise a support carrying a thin coating of vapour-deposited metal, for example of aluminium, zinc or cadmium, and in use for recording the material is traversed with respect to, and with the metal coating in contact with, a moving recording member which is usually a stylus, generally having a diameter of 0.003–0.010 inch, but sometimes a rotating helical blade which makes instantaneous point contact with different points of the material. When, and only when, current is supplied to the stylus or blade metal is vaporized from the minute zone of the material with which the stylus or blade is in contact to produce a visible image determined by the electrical signals applied to the stylus or blade. The thickness of the metal coating must be small since otherwise it would be necessary to apply an excessive voltage to the stylus to effect volatilization of the metal and in any event the thickness of metal which can be vapour-deposited is limited. The thickness of the metal coating must nevertheless be sufficient to mask the underlying support effectively in those areas from which it has not been removed by the stylus. Otherwise no observable image will be obtained.

When, as is preferred for cheapness, the support is of paper it is necessary to interpose between the paper and the metal coating a thin layer of resin to prevent the volatilised metal from penetrating into and being adsorbed by the paper during its application to the paper. Hitherto the resin used for this backing layer has been devoid of any matting agent and is present on the support as a smooth glossy film carrying the metal coating.

Some forms of apparatus in which such recording materials are used require application to the stylus of A.C.signals, which may range in voltage from 40–850 volts. Recording material with such a smooth backing layer of resin between the support and the metal coating is incapable of providing an image of good definition under these conditions, because the spark produced upon energization of the stylus tends to spread over the recording surface. This effect can be mitigated by providing another layer of resin as an overcoat on top of the metal coating but this expedient has the disadvantage of increasing the cost of the material.

This invention is based upon our discovery that it is possible to produce an electrosensitive recording material which will yield images of good definition when subjected to the action of a stylus energized by A.C. without the necessity of providing a resinous overcoat by applying the vapour deposited metal coating to a support having a matt surface. Thus it is possible to use as the support a film forming resin which has been given a matt surface by inclusion in the resin of a matting agent or by pressing the resin when softened, e.g. by heat or solvent, against a metal drum having a matt surface.

A matt surface exhibits minute protuberances, constituted in the case of the presence of a matting agent by individual particles of matting agent, and therefore

has a greater surface area than a smooth glossy surface having the same perimeter. When the metal coating is vapour deposited on a suitable matt surface, the surface coating of metal is no longer present as a smooth film and the effect of the protuberances is apparently to inhibit the spreading of the spark caused upon application of a stylus energized by A.C. and so ensure an image of sharp definition. This may, perhaps, be due to the matt surface effecting a discontinuity in electrical conductivity of the metal coating, forming it into contiguous areas of greater and lesser electrical conductivity. To achieve this result it is necessary that the characteristics of the matt surface having regard to the amount of metal deposited on the support should be such that the surface area of the support is increased sufficiently to ensure that the spark will not spread while nevertheless not so large as to result in inadequate masking of the support by the metal which has not been volatilised.

The invention accordingly provides an electrosensitive recording material comprising a non-electrically-conducting support having a substantially uniform matt surface on which has been vapour deposited a coating, devoid of any overcoat, of a metal having the property of volatilising when contacted by an electrically energized stylus, the characteristics of the matt surface and the amount of metal deposited on the support being such that a visible image of good definition is produced upon application to the material of a stylus energized by A.C.

Preferably the metal-receiving surface is a layer of resin containing a matting agent and deposited from solvent solution upon a base support. If desired, the base support may be of some other material from which the resin layer is subsequently stripped.

The thickness of the matt resin coating should be that corresponding to a weight of 0.5 – 10 grams/sq.metre (g.s.m.) and is preferably 3 g.s.m. The thickness of the vapour-deposited metal surface coating should be that conventionally used in recording materials of the type in question, and preferably corresponds to a weight of the metal coating of 0.2 g.s.m.

Any film forming resin can be used, for example polyvinyl chloride, polyvinyl chloride/polyvinyl acetate copolymer, cellulose acetate butyrate, cellulose acetate, polyvinyl butyral or nitrocellulose. Aqueous resin emulsions can also be used.

The particle size of the matting agent will normally be in the range of 0.01 – 25 microns and it may be present in the matt resin coating in an amount of 1 – 400% of the weight of the resin. The matting agent is normally incorporated in the resin by milling together the resin, the solvent, the matting agent and any other desired ingredients and the milling should be carried out until a spread layer of the milled mixture has a substantially uniform matt surface exhibiting no aggregates of matting agent particles. This can be readily determined by a simple test.

The matting agent is preferably finely divided silica, for example the materials sold under the Registered Trade Marks GASIL and AEROSIL. Successful results have been obtained with GASIL 200 which has a particle size of 7.5 microns and with GASIL 23 which has a particle size of 1–3 microns. The former may be present in an amount of 2–70 percent and the latter in the amount of 2–50 percent by weight of the resin.

Examples of other suitable matting agents are

Calcium silicate and other metallic silicates
Polyethylene waxes
Calcium carbonate
Zinc Oxide
Titanium dioxide
Metallic powders
Felspar
Mica
Clay

Indeed any finely divided solid which does not dissolve in the solvent used is suitable for the purpose.

The resin coating may contain plasticizers and will normally include a pigment or dye. It may, however, be colourless when the support is coloured. The base support is preferably paper but it may be of plastics film. The matting agent, and pigment if present, may be thoroughly mixed with the resin in a ball mill and the mixture applied to the support from solution in a solvent such as methyl ethyl ketone. Alternatively the resinous layer may be applied to the base support by calendering or extrusion and it is also possible to incorporate the matting agent in the resin during manufacture thereof.

The striking effect produced by the inclusion of a matting agent in the resin will be seen from the following. A conventional electrosensitive recording material having between a paper support and a vapour deposited coating of aluminium weighing 0.2 g.s.m. an undercoat of smooth and glossy polyvinyl chloride resin weighing 3 g.s.m. yielded an image which was hardly visible when subjected to the action of a stylus pulsed with 350 volts A.C. at a frequency of 18KHz. When this material was modified by including 15 percent by weight of GASIL 23 in the resin and used under the same conditions a strong image of excellent definition was obtained.

As will be understood the amount of metal deposited on the material controls the voltage at which maximum marking density occurs. This voltage is also affected by the speed of traverse of the material.

While the above-described electrosensitive recording material has the special advantage that it is capable of yielding a satisfactory image when used with a stylus energized with A.C. it has a further advantage of versatility in that it can also be satisfactorily used with a stylus energized by D.C. or pulsed D.C., even by D.C. voltages less than 1 volt. Moreover, it is cheap to produce, requiring only two coating layers, and it has been found to be less critical of stylus pressure than previously available materials.

The following are specific examples of materials according to the invention:

Example 1

Polyvinyl Chloride/Acetate Copolymer	10 parts by weight
Methyl Ethyl Ketone (MEK)	90 "
Carbon Black	1.0 "
Gasil 23	1.2 "

After matting, this mixture was coated onto white paper to give a weight of approximately 3 g.s.m. Aluminium was then vapour deposited onto the resinous layer to give a coating weight of 0.25 g.s.m.

When cut at 400 volts A.C. at a frequency of 18 KHz and a stylus to paper speed of 200 in/sec. the material gave a black image with good definition on a white background. This paper also gave a good black mark with voltages of less than 1 volt D.C. at slow speed and up to 60 volts D.C. at faster speeds.

Example 2

Cellulose Acetate Butyrate	10 parts by weight
Gasil 200	3 "
Carbon Black	1.0 "
MEK/Toluene	90 "

This mixture was coated on paper and metallised as in Example 1.

Example 3

Cellulose Acetate Butyrate	10 parts by weight
Gasil 23	1.5 "
MEK	90 "

This material was coated onto polyester film base to give a coating weight of 1 g.s.m. Aluminium was then vapour deposited to give a coating weight of 0.18 g.s.m. When cut at 250 volts A.C. at a frequency of 29 KHz with a paper to stylus speed 50 in/sec the material gave a transparent image. It also gave satisfactory results at low D.C. voltages.

Example 4

PVC/Polyvinyl Acetate Copolymer	10 parts by weight
Gasil 23	1.5 "
Fluorescent Yellow 61032	0.5 "

This material was coated onto transparent glassine paper using MEK as solvent and vacuum metallised as in Example 1. This paper gave a good yellow image on a white background with excellent definition. The image was also transparent.

Example 5

Paraloid AT/50 (Acrylic Resin)	100 parts by weight
Superfine Superflos	10 "
MEK	300 "
Irgalite Red Pigment	5 "

Coating and vacuum metallisation were as in Example 1. The material gave a red image on a white background.

Example 6

PVC/Polyvinyl Acetate Copolymer	10 parts by weight
MEK	90 "
Micronised Red Iron Oxide	3.0 "

Coating and vacuum metallisation were as in Example 1.

Example 7

As in Example 6 with 4.0 parts micronised Calcium Carbonate instead of Iron Oxide.
The material gave a transparent image.

Example 8

PVC/Polyvinyl Acetate Copolymer	10 parts by weight
MEK	90 "
Carbon black	20 "

Coating and metallisation were as in Example 1.

Example 9

Clear PVC film was softened with MEK and pressed against a matt steel drum. The film was then dried and metallised as in Example 1.

The back of this film can be coated with lacquers of different colours to give the desired contrast to the white background.

In the examples, the stylus was energized with A.C. at a voltage ranging from a low of 250 in example 3 to a high of 400 in example 1.

What I claim as my invention and desire to secure by Letters Patent is:

1. An electrosensitive recording material, capable of use with a stylus energized with A.C. at a voltage of 250–400 volts, comprising a base layer of non-electrically conducting material, a coating of film forming resin on said base layer and weighing from 0.5 to 10 grams/square metre, said resin coating having a non-smooth external surface impervious to vapour deposited metal and containing, in an amount of 2 to 70 percent by weight of the resin, a matting agent having a particle size in th range of 0.01 to 25 microns, and a layer of vapour deposited metal on the external surface of said resin coating.

2. A material as claimed in claim **1,** wherein the base layer is a sheet of paper.

3. A material as claimed in claim **1,** wherein the matting agent is silica of particle size 1 – 3 microns and present in an amount of 2 – 50 percent by weight of the resin.

4. A material as claimed in claim **1,** wherein the matting agent is silica of particle size 7.5 microns and present in an amount of 2 – 70 percent by weight of the resin.

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