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ELECTROSENSITIVE RECORDING MATERIALS AND THEIR MANUFACTURE

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2 Claims. (Cl. 117—216)

This invention relates to novel electrosensitive recording sheet materials, such as recording papers, and their manufacture. More specifically, it relates to improved recording papers which, under the localized action of an electrically signalling stylus, undergo chemical decompositon of the surface coatings thereon so as to provide a conspicuously contrasting show-through of the base material.

Electrosensitive recording papers are conventionally classified into two categories, namely, the so-called "wet" and "dry" electrosensitive recording papers. Presently available dry electrosensitive recording papers generally operate on the breakdown principle in which sufficient voltage must be supplied to break down the insulating barrier of the coating before the paper can be marked. The breakdown voltage in conventional dry electrosensitive recording papers usually exceeds seventy-five volts, which characteristic, of course, reduces their desirabilty and commercial feasibility for use in conventional recording instruments. On the other hand, wet electrosensitive recording papers are known in which lesser voltage may be applied. However, the wet electrosensitive recording papers are characterized by attendant physical disadvantages such as instability of the produced mark, and difficulties in manufacture, handling and storage. The novel electrosensitive recording material of the subject invention is designed to have the appearance and handling characteristics of dry electrosensitive recording papers while being markedly more sensitive to voltage signals. Thus, an electrosensitive recording paper produced in accordance with the features of this invention can be made to mark at signal voltages of as low as twenty volts. The paper thus exhibits the low voltage or sensitivity characteristics of a wet electrosensitive recording paper without the attendant physical disadvantages thereof.

Accordingly, it is an object of this invention to produce an electrosensitive recording paper which may be used in a dry state and which requires no moistening; which exhibits high sensitivity characteristics; which is extremely cheap to manufacture and easy to store and handle; which develops a permanent and stable mark in response to the presence of an electrically signalling stylus; which does not deteriorate with age or with significant variations in temperature or humidity conditions; which is non-toxic and non-flammable and which minimizes the presence of objectionable fumes in the recording process; which does not foul the stylus in operation; and which comprises only one coating of relatively low electrical impedance.

These and other objects, advantages, and features of the subject invention will hereinafter appear, and, for purposes of illustration but not of limitation, illustrative embodiments of the subject invention are hereinafter described in detail.

The novel electrosensitive recording material of the instant invention comprises a conducting sheet material of a given color and a moisturized coating thereon of a different color, whereby electrical current flow from an electrically signalling stylus though the coating to the sheet material chemically decomposes the coating such that the given color of the sheet material conspicuously shows through and contrasts with the different color of the adjacent coating materials thereon. Preferably, the sheet

material comprises a conventional paper stock to which carbon, graphite, or other conducting material, such as metallic powders, is added during manufacture so as to make the paper homogeneously conducting. The moisturized coating, which may be sprayed, dipped, or coated onto the conducting sheet material in any conventional manner, comprises a hygroscopic binding base having a conducting salt dispersed therein. Preferably, a metallic powder is also dispersed in the base along with the conducting salt so as to enhance the sensitivity of the composite recording material.

Thus, a typical formula for a moisturized coating in accordance with this invention includes a hygroscopic agent such as glycerol, and an alcohol diluent; a conducting salt such as sodium chloride or potassium iodide; a pigment, if desired, such as titanium dioxide; and preferably, where high sensitivity is desired, a finely powdered metal such as silver and/or aluminum. It has been found desirable, in order to obtain a smooth surfaced and properly functioning recording material, to ball mill or otherwise homogeneously blend the coating ingredients.

The coating may be applied to the paper base material by spraying, dipping or any other conventional coating techniques. After applying the coating to the paper, the composite is dried and is then ready for use in its dry state.

In order to more fully illustrate details in the practice of the instant invention, the following specific examples are given; however, it should be understood that the invention is not in any way to be limited or restricted to the specific recipes described.

Example I

A typical formula which has been found to yield a desirable high sensitivity electrosensitive recording material comprises the following coating ingredients:

Methyl alcohol	ml	100
Commercial shellac	ml	30
Glycerol	ml	15
Sodium chloride	ml	2
Sodium chloride	gm	2
Aluminum powder	gm	1.5
Titanium dioxide	gm	15

The glycerol and shellac are dissolved in the methyl alcohol diluent; of course, the hygroscopic glycerol always contains some residual water (as may the methyl alcohol), whereby a moisturized characteristic is imparted to the hygroscopic binding base of the coating material. The conducting salt is then dissolved or dispersed in the methyl alcohol-shellac glyceroil matrix, and the aluminum powder and titanium dioxide are correspondingly added. These ingredients are then ball milled for about twenty-four hours in order to obtain a homogeneous dispersion. The resulting composition is sprayed onto a homogeneously conducting carbonized paper sheet material to a thickness of about 0.5 mil. The composite paper is then passed through a drying oven at any convenient temperature below the scorching point of the paper whereby a dry appearing electrosensitive recording paper is provided.

The provision of shellac or conventional size as a binder without the utilization of flammable non-aqueous solvents is particularly desirable in the manufacture of recording papers since the paper is thus rendered non-flammable both in production and in eventual use. Alternatively, with the same view in mind, the shellac could be first dissolved in an alkali metal hydroxide solution (such as sodium or ammonium hydroxide) instead of the methyl alcohol diluent compound the remaining ingredients, so as to insure a completely non-flammable coating for the paper.

The resulting paper has a white opaque coating on a black base. Utilization of such a paper with a conventional electrically signalling recording stylus has been found to yield conspicuously sharp permanent markings of a black inscription on a white background nature.

While the invention is not to be restricted to any particular theory or mode of operation, the chemical reaction underlying the superior operating characteristics obtained by the subject paper are probably as follows:

The presence of the conductive salt in the moistened glycerol apparently makes the coating conductive. Of course, the conductivity and therefore the sensitivity of the paper is markedly enhanced by virtue of the presence of pure metallic powders therein. Upon the application of a stylus with a voltage applied to it, an electrolytic decomposition of the conducting salt occurs in the location of the positioned stylus, and water of crystallization is probably thereby released. Heat is generated by the passage of the electrolytic current, and the shellac in the binder melts, whereby the coating adhesion is destroyed so that the black base paper shows through to provide a conspicuous contrast with the adjacent white coating.

Apparently, the unique features of the subject recording paper are achieved by incorporating a small residual amount of water (by virtue of the presence of a hygroscopic agent and possibly also by virtue of the presence of water of crystallization) which moisture is sufficient to render the coating slightly conductive. Likewise, the interspersed metallic powder enhances the conductive characteristics of the coating. As the electrolytic action is thereby initiated upon the appropriate signal from the stylus, the resultant heat serves to melt the matrix of the complex base coating whereby a show-through color contrast is obtained.

Example II

As a further example, the following ingredients can be incorporated into a coating material in the same general fashion as described for Example I:

Methyl alcohol	ml.	500
Commercial shellac	ml.	150
Glycerol	ml.	75
Sodium chloride	gm.	10
Powdered silver	gm.	10
Powdered aluminum	gm.	5
Titanium dioxide	gm.	75

This composition is substantially the same as that described in Example I except that two powdered metals, namely, silver and aluminum, are utilized instead of just the one. However, in Example II, one and one-half parts metal powder per part conducting salt are utilized, as compared to three-quarters part metal powder per part conducting salt in Example 1. This range of the ratio of powdered metal to conducting salt and the attendant variation in the powdered metal content (i.e., utilizing two metallic powders instead of just the one) do not appear to have any appreciable effect upon the operating characteristics of the resultant papers.

It should be understood that various changes, modifications, and alterations may be made in the formulation described and in the processes for achieving the desired electrosensitive recording materials, without departing from the spirit and the scope of the instant invention, as defined by the appended claims.

What is claimed is:

1. In a heat-sensitive, electrically-conductive recording paper the combination of a conducting base sheet comprising a black paper sheet having conductive carbon particles dispersed therethrough with a moisturized cover layer coating one surface of said base sheet,

said moisturized cover layer comprising the following materials in the following relative proportions:

30 ml. of a commercial shellac solution,
2 grams of sodium chloride,
15 ml. of glycerol,
15 grams of titanium dioxide pigment, and
1.5 grams of aluminum conductive powder;

said sodium chloride, glycerol, titanium dioxide, and aluminum powder being dispersed substantially uniformly throughout said shellac solution to provide a a moisturized, white, opaque, conductive coating responsive to an electrically signalling stylus applied to selectable areas of said coating to exposure said base sheet therebelow to record conspicuously sharp permanent markings on said recording paper.

2. The method of preparing a heat-sensitive and electro-conductive recording sheet, which method comprises:

(A) dissolving about 15 parts by weight of glycerol 30 parts by weight of shellac in a solvent system selected from the group consisting of water-soluble alcohols and aqueous alkali solutions to provide a hygroscopic binding base,

(B) distributing about 2 parts by weight of sodium chloride, about 1.5 parts by weight of aluminum powder, and about 15 parts by weight of titanium dioxide in said base to provide a coating mixture,

(C) milling said mixture to provide a homogeneous dispersion coating composition, and

(D) applying said coating composition to one side of a graphite-impregnated paper base sheet and drying said composition on said sheet to provide a recording sheet comprising a dark colored base sheet having a light colored fusible moisturized cover layer uniformly coated thereon.

References Cited by the Examiner

UNITED STATES PATENTS

1,667,689	4/28	Grupe	117—3.3
2,141,975	12/38	Finch	204—2
2,294,146	8/42	Wise	204—2
2,294,150	8/42	Kline	204—2
2,310,946	2/43	Finch	204—2
2,317,789	4/43	Marriott	117—36.7
2,318,096	5/43	Quick	117—36.7
2,554,017	5/51	Dalton	204—2
3,048,515	8/62	Dalton	204—2
3,106,155	8/63	Eastman et al.	204—2
3,122,448	2/64	Hills et al.	117—36.7
3,142,562	7/64	Blake	204—2

JOHN H. MACK, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 68, for "though" read -- through --; column 2, line 41, strike out "sodium chloride-----ml-- 2"; line 70, for "compound" read -- compounding --; column 4, line 22, for "exposure" read -- expose --; line 28, before "30" insert -- and --.

Signed and sealed this 2nd day of August 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents