May 12, 1970 F. MIRO 3,511,700

ELECTRO-SENSITIVE MARKING BLANK

Original Filed Oct. 21, 1964

Fig. 1.

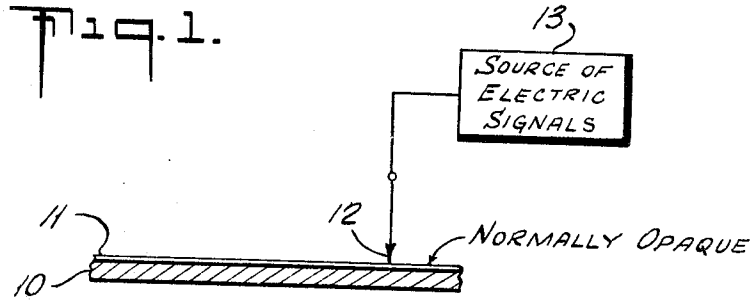
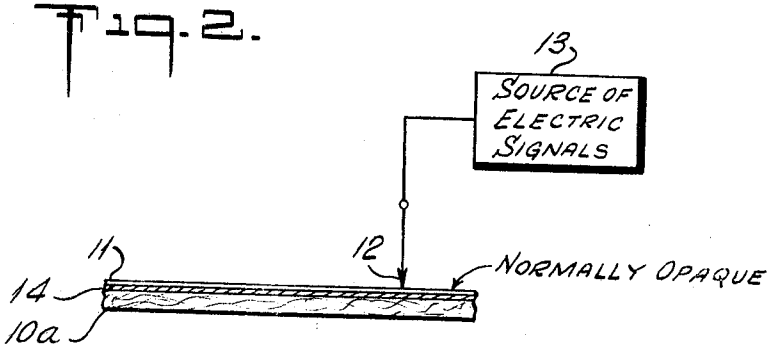


Fig. 2.



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ELECTRO-SENSITIVE MARKING BLANK

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Int. Cl. G03g 5/00
U.S. Cl. 117—201 6 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to an electro-sensitive recording blank in which a blush coated conductive substrate has incorporated therein sufficient conductive pigment to render the blush coating capable of allowing passage of electric current.

This application is a continuation of my copending application, Ser. No. 405,405 filed Oct. 21, 1964 and now abandoned and assigned to the same assignee as the present invention.

This invention relates to marking blanks and more especially to blanks of the electro-sensitive or electrically inscribable kind.

A principal object of the invention is to provide an improved electro-sensitive recording blank of the kind which has a coating that is removed or disintegrated in localized areas to which electric marking potentials are applied.

Another object is to provide an improved recording blank of the masked coating kind which is capable of producing tonal shade variations or markings in response to applied electric voltages.

A feature of the invention relates to an electro-sensitive or electrically inscribable record blank having an electrically conductive backing of one color or shade, and a contrasting masking coat which is selectively disintegrated or removed either partially or wholly in minute localized areas to produce record markings having optimum tonal variations and optimum line definition.

Another feature is to provide an electro-sensitive or electrically inscribable record blank of the kind having an electrically conductive backing and a contrasting masking coat whereby improved tonal variations and improved line definition can be obtained with a minimum of thickness of the masking coat.

A further feature relates to an electro-sensitive blank having a dark colored electrically conductive backing on which is applied a white masking coat which is formulated to increase the whitish contrast with the backing by embodying a whitish blushing action into the masking coat during its application and drying on the backing.

A further feature relates to a composite heat sensitive and electro-sensitive coated recording blank.

A further feature relates to the novel organization, arrangement and relative location and composition of parts which cooperate to provide an improved electro-sensitive blank.

Other features and advantages not particularly enumerated will be apparent after a consideration of the following detailed descriptions and the appended claims.

There is disclosed in U.S. Pat. No. 2,555,321 a recording blank comprising a non-conductive paper backing on which are applied two successive coats. The first coat is an electrically conductive coat consisting of powdered carbon dispersed in a binder such as a wax or gelatin. The second or top coat is applied as a whitish masking coat and consists of a mixture of a whitish pigment such as zinc oxide, zinc sulphide in a binder such as Methocel or cellulose derivative. In the prior known blank the contrast between the marked and unmarked areas is achieved substantially entirely by the presence of the whitish pigment in the masking coat. However, since that pigment consists of discrete physical particles, any microscopic spaces or pores between the individual particles detracts from the total masking effect and may decrease the total whitish appearance of the coat. Therefore, in order to achieve the maximum masking effect it was necessary to employ a masking coat which was not below a certain minimum thinness, for example of approximately 0.2 mil. Since the masking coat is the sensitive coat, in that it must be removed or disintegrated by the electric discharges applied thereto, either in the form of a minute arc, spark, or corona discharge, the heretofore increase in thickness to achieve the desired masking quality militates against its marking sensitiveness to the recording signals. It should be remembered that the electric discharge or recording current is usually applied by means of a needle-pointed electrically energized stylus. During the existence of the recording discharge or current the masking coat is disintegrated or removed by a quasi-explosive action. To achieve the required sensitivity of recording, therefore, a certain minimum amount of electric power must be used to achieve the desired explosion or disintegration of the masking coat beneath the stylus. While a certain amount of heat is engendered by the recording arc or discharge, the effectiveness of this heat on the recording action is lessened the greater the thickness of the masking coat. Therefore, the thinner the masking coat can be made consistent with its required masking properties the greater will be the effectiveness of this heat at the stylus in achieving disintegration at the localized areas to be recorded. The invention is not necessarily limited to the complete removal or the complete disintegration of the masking coat beneath the point of the stylus. In fact, according to the invention the masking coat can be formulated so that it has some of the properties of so-called heat-sensitive recording coatings. Such coatings are normally opaque but when subjected to recording heat they become at least partially transparent. Therefore, according to one phase of the invention the masking coat combines the characteristic of a heat-sensitive coating and an electro-sensitive coating. This means that even if the minute area of the coating beneath the stylus is not completely removed or disintegrated there will still be a tonal variation in the recorded points because of a change in the transparency of that coating as a result of its heat-sensitivity characteristics.

In accordance with the invention, the desired optimum masking is achieved with a minimum of thickness in the masking coat and at the same time a greater whiteness or contrast factor is obtained. This is achieved by formulating the masking coat so that it possesses the desired white masking effect by employing the combined whitish properties of a whitish pigment and which is incorporated in a continuous film-forming vehicle which when dried has the property of producing a whitish blush as distinct from the whitish hue of the pigment. Thus the blushing complements the white pigment in maintaining the contrast between the recorded and unrecorded areas. Furthermore, in accordance with the invention it is possible to obtain the desired white masking and optimum tonal response and line definition by using only a single coating on the backing. Thus the backing can be made of paper or other material which is conductive in itself including conductive paper, metal, plastic or the like which is dark or blackish in color, and to which is applied a single thin masking coat of the novel formulations to be described hereinbelow. However, it is to be understood that the invention in one of its aspects is not limited to a blank with a single coating.

Referring to the drawing,

FIG. 1 is a magnified cross-sectional view of a portion of the blank according to the invention and illustrating the chief method of recording thereon;

FIG. 2 is a modification of the blank of FIG. 1.

Referring to FIG. 1, the blank comprises a backing **10** which may be of paper, cardboard, metal foil, plastic, or other material which is conductive throughout a substantial portion of its thickness. Thus it may consist of any paper stock which has been rendered conductive by incorporating into the body of the paper a conductive filler such as powdered conductive carbon or gas black, powdered conductive metal, or in any other way rendered inherently conductive. Adherently attached to the backing **10** is a masking coat **11** which is white in color so that if the cooat **11** is removed in any area beneath the recording stylus **12**, the dark appearance of the backing **10** shows through the particular minute area of coating **11** which has been either wholly or partly removed or disintegrated by the electrically energized stylus **12**. The stylus **12** can be energized from any well-known source of electric voltages or signals schematically represented by the rectangle **13**.

In accordance with the invention the masking coat **11** is formulated so that it contains a certain percentage of whitish pigment such as zinc oxide, zinc sulfide, titanium dioxide, and the like, or a mixture of such pigments together with a film-forming binder or combination of binders together with a solvent for the binder and a plasticizer so that the coat can be applied to the backing **10** in a liquid or semi-liquid form. By reason of the composition of the coating batch, it is such that when it is dried in the open air and without the addition of any substantial amount of water to the coating batch, it assumes a whitish blushing effect. This whitish blushing complements the whitish appearance of the white pigment or pigments to increase the overall whitish character of the coating and thus increasing its contrast with the backing **10**.

While blushed coatings have heretofore been employed for various uses they have in general involved the use of a lacquer together with a substantial percentage of water in the coating batch to achieve the whitish blushing effect. However, in blanks of the kind shown in FIG. 1 and forming the subject of this invention, not only is it necessary to obtain a white blushing effect but it must be done in such a way that it does not weaken the continuous film resulting from the drying of the coat on the backing **10**. Therefore it is preferred, according to the present invention, to prepare the coating batch for coating **11** so that it is substantially entirely free from water. In accordance with the invention the film-forming binders for the coat **11** are chosen so that they obtain their white blush from the normal moisture in the air when the coating is dried in situ on the backing **10**.

The following are typical examples of formulations of coating batch to make the coating **11**:

EXAMPLE I

Butvar D–512 (a polyvinyl butyral product of Shawinigan Resins Corp.)	30.0
Ketone Resin MR–74 (a ketone aliphatic polymer product of Mohawk Industries, Inc.)	10.0
Nitro cellulose 1/2 sec. SS	10.0
Tricresyl phosphate	12.5
H.C. Zinc Oxide 5826 (a high conductivity zinc oxide phosphor product of N. J. Zinc Co.)	45.0
Zinc sulfide	90.0
Methanol	300.0

The procedure in mixing and forming the coating batch according to Example I is as follows. Add Butvar, ketone resin, cellulose nitrate, plasticizer and methanol to a beaker and stir until a clear solution is obtained. Then add clear resin-plasticizer solution to ball mill containing zinc oxide and zinc sulfide. Pebble mill for 8 to 12 hours.

In the above example the Butvar D–512 and the nitro cellulose are film-forming resins. The ketone resin is preferably, although not necessarily, added to give the coating batch a stronger bond to the backing **10** and is particularly desirable because of its high adhesion qualities and its relatively low melting point, for example 70–75° C. The tricresyl phosphate is added as a plasticizer but in the relatively high percent as indicated since it has the added advantage of lowering the melting point of the binder thus making the coating more sensitive to the heat generated by the recording current or discharge. The zinc sulfide aids in giving the coat a higher electrical resistance which in effect enables the recording current to increase the explosive or disintegrating action on the coating, thereby generating greater amounts of heat and having a greater recording effect on the heat-sensitive blush components of the coating, particularly of the resins. The zinc oxide is of relatively high conductivity and may, for example, be of the type disclosed in U.S. Pat. No. 2,887,-632. It is incorporated to control the electric arc or discharge during the recording operation and thus achieves better line definition or resolution. Furthermore, the line definition or resolution is enhanced by the melting or fusing of the resin binders which are in a blushed state before recording. Thus the coating **11** is a composite heat-sensitive coat which renders the blank more electrosensitive both as regards tonal definition and line definition.

In place of the above example, the following formulations may be employed in preparing the coat **11**:

EXAMPLE II

Butvar 76 (a product of Shawinigan Resins Corp.)	30.0
1/2 second butyrate	10.0
Cyclohexane	150.0
Methylene chloride	150.0
Santolite MHP (a product of Monsanto Chemical Co.)	10.0
Di-iso octyl phthalate	12.5
H.C. Zinc Oxide 5826	45.0
Zinc sulfide	90.0

EXAMPLE III

Ethyl cellulose	10.0
Butvar 72A (a product of Shawinigan Resins Corp.)	30.0
Methanol	300.0
Dioctyl phthalate	12.5
Pentalyn 255 (a product of Hercules Powder Co.)	10.0
H.C. Zinc Oxide 6505 (high conductivity zinc oxide, product of New Jersey Zinc Co.)	45.0
Zinc sulfide	90.0

The invention is not limited to the particular electrosensitive blush-forming resins and they can be used alone in any of the examples or in combination depending on the specific use for which the papers are intended and the type of solvent system desired.

An additional examples of electro-sensitive resins which have in common the property of blushing, the following may be mentioned: polyvinyl butyral, ethyl cellulose, cellulose acetate butyrate, cellulose nitrate, aliphatic ketone resin, rosin esters, sulfonamide formaldehyde resin.

The above coatings can be applied to the backing **10** for example by a 0.010 wire wound doctor, to a coating weight of 3.0# to 4.0# per 24 x 36 x 500 ream. After coating is dried by forced air the coated sheet is heated in an oven at approximately 150° F. for ½ minute to remove any remaining solvents.

As hereabove pointed out, the invention is equally well useful in connection with a blank such as shown in FIG. 2 wherein the backing **10***a* is of non-conductive material such as paper, cardboard, fibre, plastic, metal or the like.

The upper surface of the backing **10** is provided with a dark colored coating **14** which may include a powdered conductive material such as carbon or powdered metal, in a film-forming binder. For typical formulations for the coat **14** reference may be had to 2,555,321. Applied over the coat **14** is a masking coating **11** similar to the coat **11** of FIG. 1. The remaining elements of FIG. 2, namely elements **12** and **13** are the same as FIG. 1. In this embodiment the coat **11** is disintegrated or removed either wholly or partly beneath the point of stylus **12** in response to the signal voltages applied to that stylus, thus exposing the dark coating **14** to produce the required contrasting marking of the blank.

I claim:

1. An electro-sensitive recording blank having a conductive opaque substrate, a blushed coating on said blank, said blushed coating including a pigment and a film forming binder, said pigment being sufficiently conductive to allow passage of current through said blank, said coating being at least partially transparentized in localized areas when an electric disrupting voltage is applied thereto.

2. An electro-sensitive blank according to claim **1** in which the pigment is chosen from the group consisting of zinc oxide, zinc sulfide and titanium dioxide.

3. An electro-sensitive marking blank according to claim **1** in which the resin is chosen from the group consisting of polyvinyl butyral, ethyl cellulose, cellulose acetate butyrate, cellulose nitrate.

4. An electro-sensitive blank according to claim **1** in which the resin portion includes a film-forming mixture of at least two resins chosen from the group consisting of polyvinyl butyral, ethyl cellulose, cellulose acetate butyrate, cellulose nitrate, aliphatic ketone resin, rosin esters, sulfonamide formaldehyde resin.

5. An electro-sensitive marking blank according to claim **1** in which the film-forming material constitutes approximately 25% and the pigment constitutes approximately 70%.

6. An electro-sensitive marking blank according to claim **1**, said coating including a plasticizer for the purpose of controlling the melting point of said film forming binder.

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WILLIAM L. JARVIS, Primary Examiner

U.S. Cl. X.R.

117—215, 36.7; 204—2; 346—1