

[54] **ELECTRICAL RECORDING MEDIUM AND PROCESS FOR RECORDING THEREON**

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[22] Filed: **Dec. 27, 1971**

[21] Appl. No.: **212,263**

[30] **Foreign Application Priority Data**

Dec. 29, 1970 Japan..... 45/126303
Dec. 25, 1970 Japan..... 45/129299

[52] **U.S. Cl.**..... **204/2, 8/2, 117/36.8**

[51] **Int. Cl.**..... **B44m 5/00, B44m 5/20**

[58] **Field of Search**..... **204/2; 8/2;**
117/36.8

[56] **References Cited**

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[57]

ABSTRACT

The electrical recording medium comprises a composite mounted on a base sheet, said composite comprises an electron-donative color reactant, an electron-acceptive material and an electric conductive material, the electron-donative color reactant and the electron-acceptive material being reacted thereby the color reactant coloring by itself, and said reaction brought about by multiplex effect of the electrolytic reaction and/or the exothermic reaction by applying the electric current. The recording process for recording on said electrical recording medium comprises the steps of mounting a composite comprising an electron-donative color reactant, an electron-acceptive material and an electric conductive material upon a base sheet, making a reaction between the electron-donative color reactant and the electron-acceptive material owing to an effect of or a multiplex effect of an electrolysis and/or an exothermic reaction, and thereby coloring the color reactant.

4 Claims, No Drawings

ELECTRICAL RECORDING MEDIUM AND PROCESS FOR RECORDING THEREON

FIELD OF THE INVENTION

This invention relates to an electrical recording process which is adapted to gain coloring images by applying an electric current and an electro-sensitive recording material which is employed on the recording process.

PRIOR ART

In the prior art, it is well known that there are two recording process employing an application of electric current, such as an electrolysis recording process and discharge-breakdown recording process.

The electrolysis recording process is carried out in such a manner as follows:

1. introducing as ion from an electrode into a recording sheet,
2. discharging the ion above the electrode contacted with the recording sheet,
3. making an oxidation-reduction reaction on a surface of the electrode contacted with the recording sheet,
4. making a change of P H on the surface of the electrode contacted with the recording sheet.

With reference to such recording sheet, various kinds of it have been proposed already. The conventional recording sheets, however, have some disadvantages. The recording sheets are needed to be wetted in a recording operation and the images recorded on the sheets react with an electrolyte or the like to be discolored. In a recording operation or process of discharge-breakdown recording process, there are bad odor and smoke due to electrical discharge, and at the same time the image is apt to be inferior in quality. Also a method for coloring or discoloring a heat sensitive material by means of electrical exothermic phenomena has been invented. But, the coloring or discoloring method needs to be applied to a special electro-conductive material.

It is well known in prior art that an electron-donative color reactant for example leuco compound and an electron-acceptive material is reacted so as to produce a visible colored image.

It is also well known that a thermal recording process comprising the steps of dispersing an electron-donative color reactant and an electron-acceptive material in a binder, making use of a visible coloring reaction, melting the electron-donative color reactant and/or the electron-acceptive material by means of heating out of the outer heat source or infrared ray radiation, and reacting the electron-donative color reactant and the electron-acceptive material so as to color the color reactant. Further, it is well known that leuco compound of an electron-donative color reactant, when it is electrolysed in an electrolyte solution, is anodic oxidized on a surface of an electrode to be colored.

We have examined and studied the facts and knowledge mentioned above and developed a recording process and an electro-sensitive recording material, wherein recordings are effected to gain visible colored images according to a multiplex effect of electrolysis and/or exothermic reaction of electric current, making use of electric signals.

The present invention essentially relates to an electrical recording medium comprising a composite mounted on a substrate or base sheet, said base sheet

comprising an electron-donative color reactant, an electron-acceptive material and an electric-conductive material so as to color the color reactant by an electrolytic reaction of said electron-donative color reactant and electron-acceptive material occurred by applying of electric current or multiplex eddect of the electrolytic reaction and the exothermic reaction owing to the electric current and a recording or coloring process of said electrical recording medium.

- 10 The recording process of this invention will be still more fully described hereinafter. When an electron-acceptive material and an electron-donative color reactant are electrolysed under the existence of an electrolyte, both of them are reacted with each other and the color reactant colores by itself. When to a composite comprising an electron-acceptive material and an electron-donative color reactant mixed with an electric conductive material such as an electrolyte is applied electric current satisfactorily, the electron-donative color reactant or the electron-acceptive material is melted by the exothermic phenomena of electric current and reacted with each other in order to color the color reactant.

The present invention relates to an electrical recording medium comprising a composite mounted on a base sheet, said composite comprising an electron-donative color reactant, an electron-acceptive material and an electron conductive material, the electron-donative and the electron-acceptive material being reacted, thereby the color reactant coloring by itself and said reaction brought about, by electrolysis itself and/or by multiplex effect of the electrolytic reaction and the exothermic reaction caused by applying the electric current.

35 The present invention also relates to an electrical recording medium and to an electrolytic recording process, in which said recording medium comprising an electron-donative color reactant, an electron-acceptive material and an electrolyte, the electron-donative color reactant and the electron-acceptive material being reacted, thereby the color reactant coloring by itself and said reaction brought about by applying the electric current.

45 This invention further relates to an electric recording process, in which a composite mounted on a base sheet is used, said composite comprising an electron-donative color reactant, an electron-acceptive material and electric conductive material, the color reactant coloring by itself and reaction brought about, by the electrolysis itself and/or by multiplex effect of the electrolytic reaction and the exothermic reaction caused by applying the electric current.

The object of this invention is to provide a new recording process and a recording medium, wherein the recording process is carried out to obtain visible colored images of good quality by the use of an electric signal, and the recording sensitiveness is excellent and the images are preserved good enough.

60 The electron-donative color reactants employed in embodying the invention are leuco compound in the systems of triphenyl methane, fluoran, phenothiazine, auramine and spiropyran and the leuco compound is reacted with an electron-acceptive material to be colored.

65 The electron-acceptive materials in the present invention are phenolic compound (for example, see the Official Gazett of Japanese Patent Publication

No.14039/1970), or clay minerals of kaolin, acid-clay, silicic anhydride and aluminum oxide, etc.

The electric conductive materials in the invention are various electrolytes having any electrical conductivity in wet condition such as watersoluble salts of lithium, sodium, potassium, zinc, magnesium, aluminum, or water soluble polyelectrolyte of alginate and polyacrylate, electrical conductive polymer such as polymeric quaternary ammonium salt, antistatic agents such as anionic, cationic and non-ionic surface active agents, carbon black, and semiconductive pigment such as partially reduced oxide of metal or metal powder.

The steps of the process of this invention will be more fully pointed out below. One or a mixture of two or more of natural or synthetic polymer such as polyvinyl alcohol, polyvinyl acetate, polyacrylic acid ester, polystyrene, cellulose derivative, and synthetic rubber are prepared as a binder. Said electron-donative color reactant is added into the solution of the binder and powdered till the size of the particle is fined down to 3 micron by means of a ball mill. The powdered reactant is mixed with the solution of the binder. The resultant is called hereinafter liquid A.

Then, an electron-acceptive material is added into the binder solution. The resultant solution is called hereinafter Liquid B. The Liquid A and B are mixed and an electro-conductive material is added to the mixture to obtain coating color.

The liquid C prepared according to said way is applied or impregnated on suitable base sheet such as papers, fabrics, films or metal sheet, then dried for example in air the humidity of thereof being controlled so as to obtain electro-sensitive recording medium. Alternatively, a mixture of liquid A and B may be impregnated on the base sheet and dried, and then a electro-conductive solution such as electrolyte may be again applied or impregnated on the base sheet. When the reaction occurring between the electron-donative color reactant and the electron-acceptive material is very active, and a smudging because because of coloring before the application of electric current and the preserving quality is deteriorated, thereby it is effective that amine compound having a desensitizing function to electron-acceptive material such as cationic quaternary ammonium, polyamine or diamine is added, inhibitor, to the liquid B. To improve the tackiness upon a surface of the electro-sensitive recording material, talc or the like is effectively employed to mix with the liquid B.

When a voltage is impressed or applied on the electro-sensitive recording material, an electric current easily runs through the composite comprising an electron-donative color reactant, an electron-acceptive material and an electric conductive material, owing to the function of the electric conductive material. If the electro-conductivity of the composite is low, it is necessary to raise the voltage to be impressed. Thus the volume of the electric conductive material to be employed is appropriately determined. So as to drop the voltage to be impressed or applied into readily applicable one.

It is preferable that said composite comprises an electrolyte so as to react the electron-donative color reactant and the electron-acceptive material by means of the application of electric current and the function of electrolysis and color the color reactant. Therefore, it is desirable that said electrolyte is used as one of an electric conductive material. It is also desirable that an

electric conductive material such as polyelectrolyte is employed in the binder.

It is preferable that the base sheets have electro-conductivity and are made of papers, fabrics, plastics and films, electric conductive material being applied thereto, or metal sheets, metal foils and metal evaporated sheets so as to improve the electro-conductivity of the electro-sensitive recording medium.

Alternatively, it is possible that the base sheets are given an electric conductivity when the composite comprising said electron-donative color reactant, said electron-acceptive material and said electric conductive material is applied or impregnated into the base sheets.

When an electrode is contacted with a surface of the composite of the electro-sensitive recording medium and the electrode is connected with a positive pole and the base sheet is connected with a negative pole so as to impress a voltage on the recording medium, the portions of the electron-donative color reactant and the electron-acceptive material where the electric current passes through are reacted and colored.

We made some experiments and examined on the coloring mechanism of the composite comprising said electron-donative color reactant, said electron-acceptive material and said electric conductive material due to the application of the electric current, and found many facts mentioned below.

When the electric current is applied to the composite, the humidity in the composite causes the ionization of circumference of the electron-donative color reactant and the electron-acceptive material, and then the color reactant constitutes the ionized or excited latent image. The latent image is reacted with the electron-acceptive material so as to reveal itself and color itself. Alternatively, when the composite is heated, the electron-donative color reactant or/and the electron-acceptive material are melted and reacted with each other so as to color the reactant. Therefore, when the electric current is applied to the composite and said composite is exothermically heated, the binder is softened or destroyed, or the electron-donative color reactant and/or the electron-acceptive material are melted and reacted with each other so as to color the color reactant.

It is desirable that an electrolyte is contained in the composite in order to constitute a latent image of the electron-donative color reactant ionized or activated by means of the application of the electric current, but the volume of the electrolyte is not important. A very small amount of water is needed to color the reactant electrolytically and the amount of the moisture produced in the hydrophilic binder under normal conditions is sufficient to color the reactant. A wetting agent such as glycerine and ethylene glycol may be contained in the composite to stabilize the moisture contained.

When the moisture contained is, however, too much, in spite of said electrolytic coloring being easily brought about. The coloring phenomena due to the exothermal heating from the application of the electric current does not readily occur and therefore the practical value of the finished products is deteriorated. There are created the tackiness on the surface of the electro-sensitive recording medium, the colored and smudged condition on the surface before the application of the electric current and the deterioration of the preservability or wetness of the recording medium.

In case the electron-donative color reactant is electrolyzed in an electrolyte solution, the coloring due to the anodic oxidation is brought only at the portion contacted with anode or at the very proximate portion thereof.

According to the present invention, the electrolysis occurs between the electron-donative color reactant and the electron-acceptive material. The coloring phenomena is brought about not only on the surface of the portions contacted with the anode but also within the interior portion of the current applied section, thus the density of coloring is considerably obtained.

In accordance with the present invention, the recording sensitivity is good enough because of the coloring reaction being brought about as set forth due to the multiplex effect of exothermic and electrolytic phenomena and a visible recording image of clear and stable is obtained by the electric signal.

EXAMPLE 1

1. preparation liquid A:

crystal violet acetone . . . 10 parts

The composite is added to 30 parts of polyvinyl alcohol 5 percent aqueous solution, ground so as to make the size of the particles less than 3 micron by means of ball mill to mix with the aqueous solution.

2. preparation of liquid B:

a. 4,4'-isopropylidene diphenol . . . 30 parts

b. Kaoline . . . 10 parts

c. talc . . . 160 parts

d. polyvinyl alcohol 2 percent aqueous solution . . . 500 parts

e. latex . . . 30 parts

The composites of (a) and (b) respectively were added to (d). They were ground to make the size of the particles less than 3 micron by a ball mill and then (c) and (e) were added to the ground composites and mixed enough with each other.

3. preparation of liquid C:

The liquid A and B were mixed and lithium chloride 20 percent aqueous solution 30 parts and polymeric quaternary ammonium salt 20 percent aqueous solution 20 parts were added to the mixture. In this way, liquid C was prepared.

4. Liquid C was applied and dried on a surface of an aluminum foil in order to produce solid matter 8 g/m on the surface by using Meier bar, and the surface was humidity controlled in the air of relative humidity 65 percent. A printing type electrode was pressed on the surface of the resultant recording medium and the aluminum foil was connected to the cathode and the printing type electrode was connected to the anode. Then, the voltage of 100v is impressed to the recording medium for 5 millisecond. A clean blue image was formed on the portion of the recording medium contacted with the printing type electrode.

EXAMPLE 2

1. preparation of liquid A:

3-diethylamino. 6-methyl. 7-chlorofluoran . . . 10 parts

The composition was treated in similar way to Example 1.

2. preparation of liquid B:

a. 4,4'-isopropylidene diphenol . . . 60 parts

b. talc . . . 160 parts

c. polyvinyl alcohol 4 percent aqueous solution . . . 250 parts

d. carboxy-methyl cellulose 2 percent aqueous solution . . . 250 parts

e. latex . . . 30 parts

The composite (a) was added to (c) and both were ground until the particle size of them becomes less than 3 micron. (b), (d) and (e) were added to the resultant mixed solution and mixed all of them fully.

3. preparation of liquid C:

The liquid A and B were mixed, then sodium polyacrylate 40 percent aqueous solution 120 parts was mixed with the mixture so as to prepare liquid C.

4. Liquid C was applied and dried on the surface of an aluminum vacuum evaporated paper by means of Meier bar so as to produce the solid matter of 8 g/m on the surface.

The surface was humidity controlled in the air of relative humidity 65 percent. The recording medium prepared by the process mentioned above was wound around an aluminum cylinder so as to earth the aluminum vacuum evaporated surface of the recording medium through the aluminum cylinder. When a tungsten stylus having a diameter of 100 micron was pressed on the surface of the recording medium under the pressure of 10 g and the voltage +120 v was impressed on the tungsten stylus revolving the cylinder at the circumferential speed of 1 meter per second, an electric current of about 1 milli ampere was flown and a clear red image was obtained.

EXAMPLE 3

1. preparation of liquid A:

a. 3-diethylamino. 7-dibenzylamino. 5-methylfluoran . . . 5 parts

b. 3-diethylamino. 6-methyl. 7-chlorofluoran . . . 3 parts

c. benzoin-leucomethylene blue . . . 4 parts

d. rhodamine B lactum . . . 2 parts

The composites mentioned above was treated by the similar way to Example 1.

2. preparation of liquid B:

liquid B was prepared in similar way to Example 2.

3. preparation of liquid C:

Liquid C was prepared in similar way to Example 2.

4. Aluminum vacuum evaporated Mylar film was employed as a base sheet and treated in similar way to Example 2 and a recording medium was obtained. The recording medium was treated by recording process in similar to Example 2 and a distinct and black image was formed.

EXAMPLE 4

1. preparation of liquid A:

crystal violet lactone . . . 10 parts

The lactone was added to polyvinyl alcohol 5 percent aqueous solution 30 parts and ground until the size of them become less than 3 micron by means of ball mill and then they were mixed.

2. preparation of liquid B:

a. Kaolin . . . 40 parts

b. talc . . . 120 parts

c. polyvinyl alcohol 3 percent aqueous solution . . . 300 parts

d. latex . . . 30 parts

The composites of (a) and (b) were ground enough until the size of them becomes less than 3 micron by a

ball mill and the ground composite was added to the mixed solution of (c) and (d) and they were mixed.

3. The mixed solution of liquid A and B were applied and dried on a paper of 30g of basic weight by Meier bar until the volume of solid matter on the surface of the paper becomes 8g/m. This paper was immersed into lithium chloride 4 percent aqueous solution and dried in the air of relative humidity 65 percent. The paper prepared in this was put on an aluminum plate with the applied face of the paper upward and further a printing type electrode was placed on them and pressed. The aluminum plate was connected to the cathode and the electrode to the anode. The voltage of 120v was impressed on them for 5 millisecond thereby obtained a distinct and blue image on the portion of the recording sheet contacted with the printing type electrode.

EXAMPLE 5

1. preparation of liquid A:
 - a. 3-diethylamino. 6-methyl. 7-chlorofluoran . . . 2 parts
 - b. 3-diethylamino. 7-benzylamino. 5.6-benzofluoran . . . 5 parts
 - c. benzoil leucomethylene blue . . . 4 parts
- All the said composites were treated in the same manner as Example 4 for preparing liquid A.
2. preparation of liquid B:
 - a. 4,4'-isopropyliden diphenol . . . 60 parts
 - b. talc . . . 160 parts
 - c. polyvinylalcohol 3 percent aqueous solution . . . 30 parts

The composite of (a) was added to (c) and ground sufficiently until the size of them becomes less than 3 micron. (b) and (d) were added to the resultant ground composite and they were mixed enough.

3. The mixed solution of liquid A and B were applied and dried on a paper of 30g of basic weight by Meier bar until the volume of solid matter on the surface of the paper becomes 10g/m, then the paper in this way treated was immersed into sodium chloride 4 percent aqueous solution and dried until the humidity contained of the recording sheet becomes about 25 percent. The paper treated as mentioned above was put around the aluminum cylinder and the tangsten stylus of diameter of 100 micron was put on a surface of the recording sheet under the pressure of 10g. The aluminum cylinder was connected with the cathode, the stylus with the anode and a voltage of 120 v was impressed on them revolving the cylinder at the circumferential speed of 1 meter per second, thereby about 2 milliamperes of the electric current occurred and a clean and black image was obtained.

EXAMPLE 6

1. preparation of liquid A:

- a. 3-diethylamino. 7-dibenzylamino. 5-methylfluoran . . . 5 parts
- b. 3-diethylamino. 6-methyl. 7-chlorofluoran . . . 3 parts
- c. rhodamine B lactum . . . 2 parts

All the composites mentioned above were treated in a similar manner to Example 4 to prepare liquid A.

2. preparation of liquid B:

It was prepared in the same manner as Example 5.

3. preparation of liquid C:

Liquid A and B were mixed and ammonium chloride 10 percent aqueous solution 100 parts and glycerine 10 parts were added, and they were mixed sufficiently.

4. Liquid C was applied on the surface of aluminum foil by Meier bar in order to form solid matter 10g/m on the surface and the surface was dried until the humidity in the liquid applied lay becomes about 25 percent.

The recording medium prepared by the process mentioned above was treated and recorded by the use of the voltage of 80v and 0.5 milliamperes in a similar manner to Example 5, thereby a distinct and black image was obtained.

What we claim is :

1. An electrical recording medium comprising a composite mounted on a base sheet, said composite comprising an electric-donative leuco compound, an electron-acceptive material and an electrically conductive material, the electron-donative leuco compound and the electron-acceptive material being dispersed in a hydrophilic binder, and forming a color upon being reacted with each other said reaction being brought about by applying an electric current to said medium.

2. An electrical recording medium as claimed in claim 1, wherein the electrically conductive material is an electrolyte.

3. An electrical recording medium as claimed in claim 1, wherein the base sheet is electrically conductive.

4. An electrical process for recording on an electrical recording medium comprising the steps of mounting a composite comprising an electron-donative color reactant, an electron-acceptive material and an electrically conductive material as defined in claim 1 upon a base sheet, applying an electric current to said recording medium thereby effecting a reaction between the electron-donative color reactant and the electron-acceptive material and thereby coloring the color reactant.

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