

United States Patent

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[54] **COMPOSITIONS FOR
ELECTROSENSITIVE RECORDING
MATERIAL**

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ABSTRACT

Compositions for electro-sensitive recording material used as recording paper for facsimiles etc., comprise zinc oxide doped with trivalent or tetravalent metal elements and a binder.

7 Claims, No Drawings

COMPOSITIONS FOR ELECTROSENSITIVE RECORDING MATERIAL

This invention relates to compositions for an electro-sensitive recording material and more particularly to electro-sensitive recording material comprising binder and zinc oxide doped with a donor impurity element and, if necessary, metallic soap of fatty acid.

It is known to us compositions to which electric conductivity has been bestowed by adding a conductive material as electro-sensitive recording materials. Metals, carbon black or graphite, or electrolytes such as metal chlorides, have been used as such additives. However, these have numerous defects such as being economically disadvantageous when a metal is used; a recording which has sufficient contrast cannot be obtained because the coated film is colored grey when carbon black or graphite is used; and the base material of the electro-sensitive recording material is eroded when electrolytes such as metal chlorides are used.

Furthermore, the previous electro-sensitive recording material had the defect of requiring a higher voltage, for example from 15 to 20 volts, in order to obtain a recording which has sufficient contrast.

The object of this invention is to eliminate such defects and provide compositions for electro-sensitive recording materials which can respond to recording signals at a lower voltage and faster than the previous electro-sensitive recording material, and also by a dry method.

This invention relates to the compositions of electro-sensitive recording material whose chief components are zinc oxide doped with a donor impurity element and a binder, and, if necessary, a metallic soap of fatty acid.

The impurity metal is doped to zinc oxide and made semiconductive. Metals used for this invention are elements which have a higher valence than the valence of zinc in the form of zinc oxide and generally, these are trivalent or tetravalent metallic elements and are doped to zinc oxide by heat energy. Elements which are to be doped to zinc oxide must have ionic radius which is smaller than the ionic radius of zinc (0.74A). Calcining with a higher temperature for a longer time is necessary for doping an element having larger ionic radius than that of zinc, and sintering takes place during calcination. Therefore, it is more difficult to pulverize the resulting material as compared with using zinc oxide doped with donor element having smaller ionic radius than the ionic radius of zinc in this invention. As a result, such materials are not suitable as compositions of this invention. Metallic ions which satisfy such condition are trivalent metallic ions such as Co^{3+} (ionic radius 0.65A.), Ga^{3+} (0.62A), Al^{3+} (0.50A), Fe^{3+} (0.60A) and Cr^{3+} (0.64A), and tetravalent metallic ions such as Si^{4+} (0.41A), Ge^{4+} (0.53A), Ti^{4+} (0.68A) and Sn^{4+} (0.71A), and normally, it is preferable to use transition elements. The quantity to be doped to zinc oxide is a range of from 0.005 to 10.0 percent by mole. It will be difficult for the zinc oxide to attain the objects of this invention if the quantity is smaller than 0.005 percent by mole or larger than 10.0 percent by mole.

In manufacturing zinc oxide doped with a donor impurity metal, the specified quantity of zinc oxide and compound of element having an ionic radius smaller than the ionic radius of zinc are mixed and blended,

calcined at a temperature of 800°-1,400° C in air and then pulverized. In the case of a calcining temperature lower than 800° C, a zinc oxide doped with a donor element which is suitable for this invention will not be obtained; it will not conductive. On the other hand, when the calcining temperature is higher than 1,400° C, it is difficult to crush the zinc oxide particles doped with donor element and it will be difficult to use it as fine powder such as in this invention.

The semiconductive zinc oxide obtained in this invention is dispersed into the binder in a range of from 150 to 1,000 per hundred resin (hereinafter referred in simply as "PHR"), preferably from 250 to 800 PHR. When the addition and dispersion concentration is less than 150 PHR, the hiding power of the compositions becomes very low. When the concentration is more than 100 PHR, the dry film obtained from coating said compositions is markedly brittle and has lower adhesive property.

It is not necessary to use special resin as binder in this invention because it is possible to use the general resins which have been used as vehicle for paints. For example, the binder may be one or more resins selected from urea resin (urea-alkyd resin), alkyd resin (oil-free, modified drying oil or modified semi-drying oil), melamine resin (melamine-alkyd resin), polyurethane resin, vinyl resin (vinyl chloride-vinyl acetate copolymer), epoxy resin, nitrocellulose lacquer, acryl lacquer and acryl resin.

A suitable resin selected from the binders above-mentioned is dissolved in a suitable organic solvent or mixture thereof to obtain the resin solution, the semiconductive zinc oxide is dispersed into the resin solution with a pebble mill or sand grinder, and then a suitable organic solvent is added for diluting to a viscosity which is suitable for coating on the base material.

It is not necessary to use a special organic solvent in this invention because it is possible to use the general solvent which have been used as solvents in the paint industry. If necessary, metallic soaps of fatty acids may be added.

Since smooth and flat coated film is obtained by using a metallic soap of fatty acid in the compositions according to this invention, a recording having favorable contrast is obtained easily, and it is not necessary to apply high voltage. As a result, in this invention, the film is prevented from break due to electric current and due to electric discharge. Furthermore, the soap improves the adhesive property of the film on the base material by its plasticizer-like action on the film and also improves flexibility. Soaps of fatty acids which can be used independently or as mixture are aluminum, copper, zinc, lead, iron, magnesium, cobalt, barium, nickel and lithium salts of palmitic acid, oleic acid, stearic acid, lauric acid and caprylic acid. The quantity of said soap used is a range of from 5 to 80 PHR, preferably from 10 to 60 PHR. When the quantity is smaller than 5 PHR, it is necessary to apply high voltage, and the dry film obtained is rough and has poor flexibility. On the other hand, when the quantity is larger than 80 PHR, it is also necessary to apply high voltage, and the adhesion of the dry film obtained is poor.

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EXAMPLE 1

500 g of zinc oxide doped with aluminum (1.0 mole as aluminum oxide), 40 g of Versamid No. 100 (polyamide resin manufactured by General Mills Co.), 150 g of isopropyl alcohol and 150 g of toluene were charged into a pebble mill and dispersed for 20 hours. Then the mixture was removed from the ball mill, and 60 g of Epon No. 1004 (epoxy resin manufactured by Shell Chemical Co.) and 40 g of methyl ethyl ketone were 10 mixed to prepare the composition. This composition was coated with a bar coater to a dry film thickness of about 10 microns on a conductive material laminated and vapor-deposited with tin. In two cases, 8 volts were applied while moving said coated material, and a mark 15 having favorable contrast was obtained.

EXAMPLE 2 - 9

Materials with compositions indicated in the following table were coated in a similar manner as in Example 1 on a conductive material laminated with aluminum. Each 500 g of zinc oxide was doped with each of the following donor impurities.

Ex. No.	Donor Impurity for Zinc Oxide	Binder Composition (As solid)	Voltage (V)
2	Co ₂ O ₃ : 2.5 mole	Epon No. 1001 70 g Versamid No. 100 30 g	10
3	Ga ₂ O ₃ : 1.5 mole	do.	9.5
4	Fe ₂ O ₃ : 0.8 mole	do.	8.0
5	Cr ₂ O ₃ : 2.0 mole	do.	8.5
6	GeO ₂ : 0.01 mole	do.	9.0
7	TiO ₂ : 0.05 mole	do.	8.0
8	SnO ₂ : 0.05 mole	do.	8.0
9	SiO ₂ : 0.03 mole	do.	10

EXAMPLE 10

Recordings were obtained from compositions obtained by altering the quantity of semiconductive zinc oxide in Example 1 from 500 g to various quantities. Otherwise the kind and quantity of other materials and the manufacturing process exactly the same. The quantities used are indicated below.

Example No.	Semiconductive Zinc Oxide (PHR)	Voltage (V)
10 - 1	300	9
10 - 2	500	8
10 - 3	750	6

EXAMPLE 11

500 g of zinc oxide doped with iron (0.8 mole as iron oxide), 70 g of Epon No. 1007 and 50 g of methyl ethyl ketone were charged into a pebble mill and dispersed for 20 hours. Then the mixture was removed from the ball mill; and 30 g of Versamid No. 100, 150 g of isopropyl alcohol and 150 g of toluene were added to prepare the composition.

This composition was coated with a bar coater to a dry film thickness of about 10 microns a conductive material laminated with aluminum. 8 volts were applied while moving said coated material and a mark having favorable contrast was obtained.

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EXAMPLE 12 - 19

Materials with compositions indicated below were coated in a similar manner as in Example 11 a conductive material laminated with zinc.

Example No.	Binder Composition (solid)	Voltage (V)
12	Beckosol J-557 (Note 1) 100 g Co 0.03 g Dryer Pb 0.3 g	8.5
13	Beckolite M-6402-50 (Note 2) 80 g Super Beckamine TD-126 (Note 3) 20 g	8.0
14	Beckurol G-1850 (Note 4) 45 g Beckosol J-579 (Note 5) 55 g Para-toluenesulfonic acid 2 g	8.0
15	Beckosol 1323 (Note 6) 70 g Super Beckamine J-820 (Note 7) 30 g Hitaloid 2405 (Note 8) 80 g	9.0
16	Melar # 20 (Note 9) 20 g Beckosol J-544 (Note 1) 50 g 1/4" Nitrocellulose (Note 10) 40 g	8.5
17	D.O.P. 10 g Lustrasol A-111-50 (Note 11) 65 g Cellulose acetate butylate 20 g	8.0
18	D.O.P. 15 g VYHH (Note 12) 42 g VMCH (Note 13) 42 g	8.0
19	D.O.P. 15 g Stabilizer (Note 14) 1 g	8.5

(Note 1) Trade name of safflower oil modified alkyd resin manufactured by Japan Reichhold Co.

30 (Note 2) Trade name of oil free alkyd resin manufactured by Japan Reichhold Co.

(Note 3) Trade name of butylated benzoguanamine resin manufactured by Japan Reichhold Co.

(Note 4) Trade name of butylated urea manufactured 35 by Japan Reichhold Co.

(Note 5) Trade name of tall oil modified alkyd resin manufactured by Japan Reichhold Co.

(Note 6) Trade name of coconut oil modified alkyd resin manufactured by Japan Reichhold Co.

40 (Note 7) Trade name of butylated melamine resin manufactured by Japan Reichhold Co.

(Note 8) Trade name of thermosetting acrylic resin manufactured by Hitachi Chemical Co., Japan.

(Note 9) Trade name of butylated melamine resin 45 manufactured by Hitachi Chemical Co., Japan.

(Note 10) Nitrogen content = 11.7 - 12.2 percent.

(Note 11) Trade name of polyacryl polyol manufactured by Japan Reichhold Co.

(Note 12) Trade name of vinylchloride-vinylacetate 50 copolymer manufactured by U.C.C.

(Note 13) Trade name of vinylchloride-vinylacetate-maleic acid copolymer manufactured by U.C.C.

(Note 14) Used mercaptodibutyltin maleate.

EXAMPLE 20

55 500 g of zinc oxide doped with titanium (0.05 mole as TiO₂), 100g of Lustrasol A-809 (Acryl resin manufactured by Japan Reichhold Co.), 130 g of butyl acetate and 70 g of toluene were charged into a pebble mill and dispersed for 20 hours, 10 g of aluminum oleate was added and mixed for 1 hour more, then the mixture was removed from the ball mill and a quantity of polyisocyanate, for example XDI (xylene diisocyanate) which is equivalent to the hydroxyl value of Lustrasol A-809 was added to prepare the composition.

60 65 This composition was coated with a bar coater to a dry film thickness of about 10 microns on a conductive

material laminated with aluminum. 6.5 volts was applied while moving said coated material, and a mark having favorable contrast was obtained.

EXAMPLE 21

A composition was prepared by the same procedure as Example 20 using 40 g of zinc stearate in place of aluminum oleate as the metal soap of fatty acid and 5 volts was applied through the film formed on the aluminum layer by the same method. A record having favorable contrast was obtained.

EXAMPLE 22

A composition was prepared by the same procedure as Example 20 using 60 g of copper palmitate in place of aluminum oleate as the metal soap of fatty acid and 6 volts was applied through the film formed on the aluminum layer by the same method. A record having favorable contrast was obtained.

What is claimed is:

1. A composition for an electro-sensitive recording material, which comprises zinc oxide doped with an oxide of a donor impurity metal having an ionic radius of less than 0.74 Angstrom units and selected from the trivalent or tetravalent metals, the zinc oxide doped component being dispersed in a binder in an amount from 150 to 1,000 parts by weight of the zinc oxide doped component per 100 parts by weight of the binder.

2. The composition of claim 1 wherein the donor impurity metal is a trivalent metal selected from the group consisting of cobalt, gallium, aluminum, mercury, iron

and chromium, and in which the zinc oxide is doped with the oxide of such metal in an amount of from 0.005 to 10.0 molar percent thereof.

3. The composition of claim 1 wherein the donor impurity metal is a tetravalent metal selected from the group consisting of silicon, germanium, titanium and tin, and in which the zinc oxide is doped with the oxide of such metal in an amount of from 0.005 to 10.0 molar percent thereof.

10 4. The composition of claim 1 further including as a plasticizer for the composition a metallic soap of a fatty acid having eight to 18 carbon atoms, in an amount of from 5 to 80 parts by weight per 100 parts of the binder for the composition.

15 5. The composition of claim 4 wherein the donor impurity is a trivalent metal selected from the group consisting of cobalt, gallium, aluminum, mercury, iron and chromium, and in which the zinc oxide is doped with the oxide of such metal in an amount of from 0.005 to

20 10.0 molar percent thereof.

6. The composition of claim 4 wherein the donor impurity metal is a tetravalent metal selected from the group consisting of silicon, germanium, titanium and tin, and in which the zinc oxide is doped with the oxide of such metal in an amount of from 0.005 to 10.0 molar percent thereof.

7. The composition of claim 4 wherein the metallic soap is an aluminum, copper, zinc, lead, iron, magnesium, cobalt, barium, nickel or lithium salt of a fatty acid selected from palmitic acid, oleic acid, stearic acid, lauric acid and caprylic acid.

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