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Poot et al.

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[54] **PHOTOTHERMIC MATERIAL CONTAINING A LIGHT-INSENSITIVE SILVER SALT AND AN INDANE-1,3-DIONE REDUCING AGENT**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **96/48 HD**, 96/50 R, 96/67, 96/114.1, 117/36.8, 117/36.9, 96/88

[51] **Int. Cl.** **G03c 5/24**, G03c 1/04, G03c 1/76

[58] **Field of Search** ..... 96/114.1, 67, 50; 117/36.8, 36.9, 48 HD; 250/65 T, 188

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

Photographic recording material with a light-sensitive layer comprising a substantially light-insensitive silver salt, an indane-1,3-dione compound acting as reducing agent and a light-sensitive heavy metal compound which upon exposure to activating electromagnetic radiation forms metal nuclei that upon heating of the material initiate a redox reaction between the light-insensitive silver salt and the reducing agent.

A preferred recording material for print-out reproduction contains silver behenate, 2-phenylindane-1,3-dione and traces of silver halide.

10 Claims, No Drawings

PHOTOTHERMIC MATERIAL CONTAINING A LIGHT-INSENSITIVE SILVER SALT AND AN INDANE-1,3-DIONE REDUCING AGENT

This invention relates to a method for recording information supplied in the form of information-wise modulated electro-magnetic radiation and to the photographic materials used in such process.

The present invention more particularly relates to a photographic process in which the development of a latent image proceeds in dry state and with the aid of heat.

In the United Kingdom Pat. Specification 1,110,046 a recording process is described, which comprises the steps of:

A. exposing briefly to a light-image a photosensitive material comprising (1) a substantially light-insensitive silver salt of an organic acid and (2) a catalytic amount of photolytically reducible silver halide, which has been prepared from said silver salt and stands in catalytic proximity to said silver salt, and

B. then heating said material in the presence of a mild reducing agent for said silver salt for a time and a temperature just sufficient to cause reduction of the silver salt and image-formation at light-exposed areas in contact with the reducing agent.

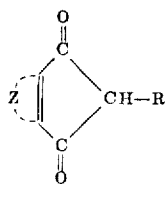
As useful mild reducing agents hydroquinone, methylhydroxy-naphthalene, methyl gallate, catechol, phenylene diamine, p-aminophenol, and 1-phenyl-3-pyrazolidone were mentioned explicitly.

The stability of said reducing agents is not as high as could be and therefore small amounts of acidic stabilizers are added that inhibit the oxidation and discolouration of the recording element under atmospheric conditions.

It is an object of the present invention to provide photographic materials, by means of which copies can be made according to a dry development process and which contain a fairly good oxygen stable reducing agent that is capable of reducing organic silver salts in a temperature range of 50° to 160°C in the presence of noble metal nuclei to metallic silver.

There has been found now a photographic recording material for the production of copies in a dry way, which comprises a substantially light-insensitive silver salt as oxidizing agent, a reducing agent, and a light-sensitive heavy metal compound, which upon exposure photolytically forms metal nuclei that initiate a redox reaction upon heating, a compound of the indane-1,3-dione series being used as reducing agent, which is capable of reducing the light-insensitive silver salt in a temperature range of 50° to 160°C in the presence of the photolytically formed heavy metal nuclei.

Reducing agents of the indane-dione-1,3 type that are suited for use according to the present invention correspond to the following general formula:



wherein:

Z represents the atoms necessary to close an aromatic ring or ring system including a substituted aromatic ring or ring system, e.g., a benzene ring including a benzene ring substituted with alkyl, halogen e.g., chlorine and bromine, nitro, amino, substituted amino, alkoxy, cyano or aryl, and

R represents hydrogen, an aryl group including a substituted aryl group e.g. phenyl, naphthyl, phenyl substituted with methoxy, dialkylamino, cyano, halogen, nitro, or azido (N_3).

The indane-1,3-dione compounds can be prepared according to methods known to those skilled in the art.

As mentioned before suitable oxidizing agents for the image-producing redox system are silver salts of organic acids that are insensitive or negligibly sensitive to light, e.g., silver saccharide, silver-5-chlorosalicylaldoxime, silver-5-nitrosalicylaldoxime or preferably a silver salt of a long chain fatty acid with at most 30 carbon atoms, such as silver stearate, silver palmitate or silver behenate or the silver salts of aliphatic carboxylic acids with a thioether group as described in the U.S. Pat. Specification No. 3,330,663.

By "substantially light-insensitive" it is not meant that the organic silver salt must be completely insensitive to light, but that it should at least be resistant to darkening under indoor illumination to an extent sufficient to prevent destruction or deterioration of copies during several days of storage under diffuse sun-light conditions.

The preferred water-insoluble silver soaps of long chain fatty acids, e.g., silver behenate and silver stearate are fairly stable to light, even in the presence of moisture. The soaps are conveniently prepared by precipitation with silver nitrate solution from aqueous solutions of the alkali metal soaps of corresponding fatty acids and with or without co-precipitation of the fatty acid in any desired proportion. For transparent coatings the fatty acid content is restricted or omitted.

Suitable light-sensitive salts of heavy metals forming metal nuclei upon exposure, which are capable of initiating the image-producing redox reaction, are e.g., inorganic and organic salts of silver, mercury and gold. Heavy metals of the Ib group of the periodic table of the elements such as silver salts and particularly silver halide are preferred.

The light-sensitive heavy metal salt that is suited for a particular redox system can be determined by some tests. For instance the metal salt can be mixed in the form of an aqueous suspension with the components of the redox reaction. No modification should occur in the dark. If this mixture is then exposed to ultraviolet radiation it should change colour rather quickly. If these conditions are fulfilled, the heavy metal salt is suited for the redox system.

The light-senstive heavy metal salt is used in relatively small amounts comprised between approximatively 0.05 and 0.2 percent by weight calculated on the weight of the oxidizing agent. Such amounts of light-sensitive salt suffice for most systems. In certain cases, however, these amounts may be lower or higher.

The preferred photographic recording process according to the present invention comprises the steps of (1) forming silver nuclei in accordance with photographically exposed areas of a recording element containing:

A. a substantially light-insensitive silver salt of an organic acid, and

B. a photosensitive silver halide capable of producing photolytic silver in an amount sufficient to catalyse the reduction by heating above room temperature of said substantially light-insensitive silver salt by means of an indane-1,3-dione compound containing at least one hydrogen atom in the 2-position, and (2) heating the substantially light-insensitive silver salt in contact with said indane-1,3-dione compound for a time and at a temperature sufficient to cause reduction of said silver salt and a visible colour change in the light-exposed areas.

The light-sensitive silver halide should be present in such a low amount, that the photolytically formed heavy metal nuclei can initiate the redox reaction. Yet, the concentration of the silver halide should be so weak that no colour change of the copying material at all or but a negligible colour change is brought about by the metal nuclei formed.

The silver halide can be added to the coating solution for the layer containing the components for the redox reaction or it can be formed in situ in the coating solution e.g., by precipitation. In the latter case the silver ions needed for this precipitation of silver halide can essentially originate from the light-insensitive silver salt.

The halide ion (i.e., Cl^-, Br^-, I^-, or a mixture thereof) for the production of the photosensitive silver halide in situ can be supplied in different manners. One convenient procedure involves briefly exposing the surface of the silver salt particles or coating to the vapours of one or more halogen acids, the extent of the reaction being controlled by adjusting both the concentration of the vapour and the time of exposure.

The method of applying the halide ion from a liquid medium is particularly useful in the preparation of light-sensitive heat-developable recording materials. It permits the simultaneous efficient application of the reducing agent and of spectral sensitizing dyes or other components e.g., toning agents, pigments, e.g., titanium dioxide, silica, phthalazinone, or photoconductive compounds, e.g., photoconductive zinc oxide. In some cases the dye employed in spectrally sensitizing or otherwise modifying the sheet may itself serve as the source of halide ion.

The silver halide may alternatively be formed on the silver behenate or other organic silver salt prior to coating the latter on the paper or other carrier surface. As an example, the silver salt, dispersed in a volatile non-aqueous liquid medium, is treated with small amounts of HCl, HBr or HI prior to coating. The dry salt in finely divided particulate form may also, although less desirably, be treated with a source of Cl^-, Br^-, I^- or a mixture thereof in the dry state to provide in situ formation of silver halide at the surface of the particles.

Hydrogen chloride and hydrogen bromide are effective treating agents. Various water-soluble inorganic halides are somewhat more easily handled and are equally effective; ammonium bromide has been found particularly useful since the ammonium ion is subsequently readily removable, but halides of various metals, e.g., sodium, magnesium, cobalt and zinc, are also effective. Ionisable organic halogen compounds are also useful, examples being triphenylmethyl chloride, triphenylmethyl bromide, 2-bromo-2-methylpropane, 2-bromobutyric acid, 2-bromoethanol, and benzophenone dichloride.

The in situ formation of the silver chloride or bromide from an organic acid silver salt enhances the photosensitivity and imaging capability of the composition, more than added pre-formed silver halide.

For the manufacture of the material according to the invention the components for the redox reaction and the light-sensitive heavy metal compound are used together with an appropriate binding agent. Preferred binding agents are organic polymers such as copolymers of vinyl chloride and vinyl acetate or of butadiene and styrene, polyethylene, polyamide, polyisobutylene, polyvinyl chloride, polyvinylidene chloride, polyvinyl pyrrolidone, polystyrene, chlorinated rubber, polyvinyl butyral, polymers of acrylic or methacrylic acid esters or copolymers of derivatives of acrylic acid and methacrylic acid, derivatives of cellulose such as cellulose nitrate, cellulose acetates, cellulose propionate or mixtures thereof, e.g., cellulose acetobutyrate.

The light-sensitive layer may be a self-sustaining layer, but is preferably applied to an appropriate support. The support should be stable at the processing temperature comprised between 60° and 200°C. Suitable supports are e.g., sheets or foils of paper, cellulose acetate, polyethylene terephthalate, textile, metals foils or glass. Paper supports may be provided with the usual auxiliary layers such as e.g., baryta layers and polyethylene layers.

The concentration of the reducing agent and of the oxidizing agent in the layer may vary within wide limits.

A recording material according to the present invention preferably comprises the organic substantially non-light-sensitive silver salt and an indane-dione-1,3 compound in a molar ratio of 1:1 to 1:10.

Generally, the weight proportions of the components of the redox reaction and the binding agent vary between 4:1 and approximately 1:1.

The thickness of the light-sensitive layer may be adapted to the requirements of the specific reproduction process. A layer thickness between 5 and 100 μm appears to be sufficient in normal cases. The support has a thickness ranging between 0.1 and 0.8 mm.

The light-sensitive layers may be sensitized optically by the addition of dyes. Suitable optical sensitizing agents for common silver halide emulsion layers are e.g., cyanine dyes, merocyanines, oxonols or rhodacyanines of different nature such as those described e.g., by F. M. Hammer in the "The Cyanin Dyes and Related Compounds" 1964.

The image-wise exposure can be preformed with the light sources normally used in photographic techniques, e.g., mercury lamps, iodine quartz lamps or incandescent bulbs. The nature of the light source to be used depends on the spectral sensitivity of the heavy metal salt used. The common incandescent bulbs can be used advantageously in the case of silver halides, wherein the exposure takes only a few seconds.

The exposed material is heated uniformly to 60°–160°C. The time and temperature required for the heat treatment depends on the nature of the redox system. Generally a time varying between 3 and 80 seconds is sufficient. Dark brown to black images are formed mostly. They can be used immediately.

The following example, in which proportions are given by weight unless otherwise indicated, illustrates the present invention.

EXAMPLE

Preparation of the non-light-senstive silver salt

A mixture of equimolar parts of silver behenate and behenic acid is prepared by precipitation with silver nitrate from a solution of sodium behenate and behenic acid in alcohol and water. The precipitate is thoroughly washed and dried.

Preparation of the photosensitive material

A first coating composition containing the following ingredients was ball-milled for 12 hours

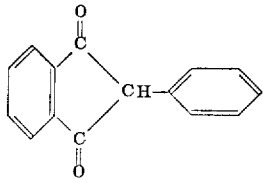
mixture of silver behenate and behenic acid mixture (molar ratio 1:1)	1.8 g
cellulose acetate (65 % of hydroxyl groups)	3 g
a solution of 1 g of calciumbromide in 100 ml of methanol	4.5 ml
mercury(II) acetate solution prepared by dissolving 1 g of mercury(II)acetate in a mixture of 1 ml of acetic acid and 100 ml of methanol	5.7 ml
acetone	55 g
1 % solution in ethanol of 1-ethyl-[3-ethyl-2(3H-benzoxazolylidene)-ethylidene]-3-n-butyl-2-thiohydantoin as spectral sensitizing agent	2 ml
colloidal silica	0.15 g
butyl acetate	20 g

The coating composition was applied to a glassine paper support at a ratio of 100 g a 200 g per sq.m and dried at 30°C.

This coating was covered with a second composition containing the following ingredients:

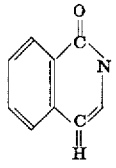
polyvinyl butyral (95 % of acetal groups) — 10 g

2-phenylindane-1,3-dione — 8 g



melting point: 150°C prepared according to C.A. 49, 6856e.

phthalazinone — 3 g



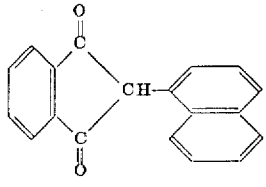
methanol — 100 ml

The second composition was coated in the ratio of 100 g per sq.m and dried at room temperature.

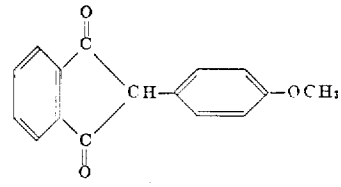
The thus prepared photosensitive sheet was exposed while in contact with a silver image transparency to a 40 W light exposure unit placed at a distance of 5 cm and used in the 3M dry-copying apparatus model M 179. The sheet was then developed at 95°C and a speed of 1 meter per 20 seconds.

A visible black negative reproduction of the original was obtained.

Similar results were obtained if the following indane-1,3-di-one compounds were used instead of the above-mentioned:



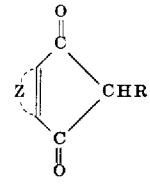
melting point: 206°C prepared according to J.Gen.-Chem. USSR 26, (1956) 657.



melting point: 154°C prepared analogously to the methods described in the J.Org. Chem. 25 (1960) 1860-5.

We claim:

1. Photographic recording material with a light-sensitive layer comprising a substantially light-insensitive silver salt of an organic acid, a reducing agent, and a light-sensitive salt of silver, gold, or mercury, which upon exposure to activating electromagnetic radiation photolytically forms metal nuclei, characterized in that said reducing agent is an indane-1,3-dione compound corresponding to the general formula:



wherein:

Z represents the atoms necessary to close a phenyl group, and

R is hydrogen or an aryl group.

2. Photographic recording material according to claim 1 characterized in that silver halide is used as said light-sensitive heavy metal salt.

3. Photographic recording material according to claim 1 characterized in that the heavy metal salt is used in amounts ranging between 0.05 and 0.2 percent by weight of the light-insensitive silver salt.

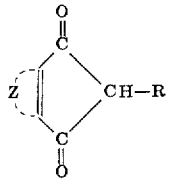
4. Photographic recording material according to claim 1 characterized in that a silver salt of a long-chain silver fatty acid is used as said light-insensitive silver salt.

5. Photographic recording material according to claim 1 characterized in that silver behenate is used as said light-insensitive silver salt.

6. Photographic recording material according to claim 1 characterized in that the material contains a polymethine dye as a spectral sensitizing agent.

7. Photographic recording material according to claim 1 characterized in that the material contains phthalazione as a toning agent.

8. A method of recording information-wise modulated electromagnetic radiation comprising the steps of: (1) imagewise exposing a photosensitive material containing a substantially light-insensitive silver salt of an organic acid and a photosensitive salt of gold, mercury or silver to electromagnetic radiation to photolytically release metal nuclei from said latter salt, and (2) heating the exposed photosensitive sheet while having said substantially light-insensitive silver salt in effective contact with an indane-1,3-dione reducing agent of the general formula:



wherein:

Z represents the atoms necessary to close a phenyl group, and

R is hydrogen or an aryl group.

9. The method of claim **8** wherein said light-sensitive salt is a silve halide.

10. The method of claim **8** wherein said light-insensitive salt is of a long-chain fatty acid.

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