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[54] **PHOTOTHERMOGRAPHIC MATERIAL CONTAINING A PHOTOSENSITIVE METAL OXIDE SEMICONDUCTOR OR BENZOPHENONE AND A FREE METAL GENERATING ALKANOLAMINE**

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[51] **Int. Cl.**.....**G03c 1/00,** G03c 5/32

[58] **Field of Search**.....96/48, 88, 48 HD

[56] **References Cited**

UNITED STATES PATENTS

1,939,232	12/1933	Sheppard et al.	96/88
3,259,494	7/1966	Schlein et al.	96/88 X

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Assistant Examiner—Won H. Lowe, Jr.
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[57] **ABSTRACT**

A photosensitive recording material comprising a metal-containing amino-alcohol reaction product yielding free metal on heating and in inter-reactive relationship with said product a photosensitive substance, which in photo-exposed state lowers the decomposition temperature of said product.

The preferred reaction product is a reaction product of yellow lead(II)oxide and tri-isopropanolamine. Preferred photosensitive substances are photoconductive lead(II)oxide, zinc oxide and titanium(IV)oxide.

8 Claims, No Drawings

PHOTOTHERMOGRAPHIC MATERIAL CONTAINING A PHOTOSENSITIVE METAL OXIDE SEMICONDUCTOR OR BENZOPHENONE AND A FREE METAL GENERATING ALKANOLAMINE

The present invention relates to photothermographic reproduction of information and to recording materials and substances used therefor.

In the U.S. Pat. specification No. 1,976,302 a method of making a photographic image has been described, which comprises exposing to a light image a photosensitive layer containing as its primary constituent a salt selected from the group consisting of the silver, lead, mercury and manganese salts of organic saturated dibasic and tribasic acids, silver formiate, lead formiate and lead thioacetate, whereby a latent image is formed, and then submitting the layer to heat alone so that a visible image is developed therein.

The materials used in said process have to be kept in the dark until their information-wise exposure. They require a relatively high amount of radiant energy in order to build up the latent image and need a rather long duration heating for development.

It is one of the objects of the present invention to provide an improved photothermographic recording material in which a visible image is formed in a recording element by the simultaneous action of overall applied heat and information-wise irradiation with activating electromagnetic radiation.

It is a further object of the present invention to provide a recording material that obtains print-out image-forming capacity at elevated temperatures and maintains its original color at room temperature when exposed, e.g., to daylight.

Other objects will become apparent from the embodiments described furtheron.

According to the basic concept of the present invention an organic compound yielding free metal on heating is used in interreactive relationship with a photosensitive substance that by exposure to activating electromagnetic radiation is capable to decrease the decomposition temperature of said compound. The photosensitive substance suited for the purpose of the present invention effects in exposed state preferably a decrease of the decomposition temperature of the organic metal compound of at least 20°C and more preferably of 50°C and more.

It has been found that an amino-alcohol compound that is capable to form a lead-containing reaction product with lead(II) oxide is a suitable reagent for the production of organometallic compounds that are thermolabile, i.e., splitt off free metal above a critical temperature.

The preparation of such organometallic compounds proceeds preferably by intimately contacting through mixing the amino-alcohol with (1) a finely divided basic metal oxide, or (2) a metal compound containing the metal of such oxide linked to at least one hydroxyl group, or (3) a metal compound wherein the metal of said oxide is present in an enolate group, or (4) a metal compound wherein said metal replaces the hydrogen atom(s) of the hydroxyl groups of an element that can form weak acidic, amphoteric or weak basic hydroxides, e.g., derived from the elements arsenic, antimony, bismuth, thallium and lead.

The reaction conditions are selected such that the decomposition temperature of the formed metal-containing amino-alcohol reaction product is not surpassed. A suitable reaction temperature range for the preferably used compounds is between room temperature and a temperature that is 20°C below the decomposition temperature.

The presence of an inert solvent and an intimate mixing of the reagents as effected by ball-milling or high speed stirring is advantageous for obtaining reproducible results very quickly.

Examples of suitable basic metal oxides are listed in the following Table under the numbers 1 and 2. An example of a suitable hydroxyl-containing metal compound is compound 8. The metal compounds 3 and 4 are enolate compounds. The compounds 5 and 6 are examples of compounds wherein the hydrogen atoms of the hydroxyl groups of an element that can form weak acidic hydroxides have been replaced by a metal that can form a basic oxide. Compound 7 forms a hydroxy-lead compound in alkaline conditions.

Preferred amino-alcohol compounds are trialkanolamino compounds. The aliphatic carbon groups in said compounds have preferably from 2 to 5 carbon atoms.

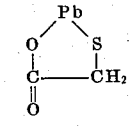
Very good results are obtained with metal-containing amino-alcohol compounds having a decomposition temperature above 100°C and wherein the metal is no stronger electron-donating than zinc, preferably no stronger electron-donating than lead.

The metal set free from the organometallic compound is preferably fairly stable to aerial oxidation and is, e.g., a metal of the class comprising lead, copper, silver, mercury, zinc and thallium.

Particularly suited for the purpose of the present invention are the reaction products of triisopropanolamine and one of the compounds listed in the following Table.

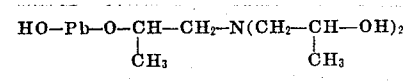
Table

1. yellow lead(II) oxide (massicot)
2. red to tan lead(II) oxide (litharge)
3. copper(II) acetylacetonate
4. zinc acetylacetonate
5. mercury(II) arsenite
6. thallium(III) arsenite
7.



8. $HO-Pb-S-CH_2-CH_2-OH$

Excellent results have been obtained with the reaction product of lead(II) oxide and triisopropanolamine. It has the following structural formula:



The preparation of the above cited reaction product may proceed by intimately mixing the reactants in an inert solvent, e.g., a chlorinated aliphatic or aromatic solvent such as toluene.

This can be done, e.g., by ball-milling, vibrating, high-speed-stirring, or boiling with complete reflux. The thermolysable lead compound of the above structural formula is prepared, e.g., as follows:

110 g of yellow lead(II) oxide are ball-milled with 100 g of tri-isopropanolamine dissolved in a mixture of 500 ml of trichloroethylene and 50 ml of toluene till the yellow color disappears. The thus obtained suspension is ready to be mixed with the elected photosensitive decomposition-promoting agent that is capable of lowering the decomposition temperature of the heat-decomposable metal-containing amino-alcohol compound by absorbing activating electromagnetic radiation.

Suitable photosensitive agents promoting decomposition can be found in the class of the photoconductive compounds, e.g., oxygen-containing photosensitive semiconductor compounds.

Particularly suited for being applied according to the present invention are inorganic photosensitive semiconductor substances such as titanium(IV) oxide, zinc oxide, yellow lead(II) oxide, and bismuth(III) oxide, or mixtures of said substances.

An organic substance that acts as a photosensitive semiconductor compound promoting the liberation of free metal from the heated organometallic compound is benzophenone. Excellent results are obtained therewith, e.g., when used in conjunction with the organometallic reaction product of triisopropanolamine and lead(II) oxide.

In a special embodiment use is made of photosensitive semi-conductor compound that by itself on exposure to activating electromagnetic radiation yields a free metal. This metal preferably is the same as that set free by the organometallic compound or should have a stronger electron-donating character.

Such a photosensitive semi-conductor compound is yellow lead(II) oxide, which is admixture with the thermolysable reaction product of tri-isopropanolamine and yellow lead(II) oxide produces lead metal on exposure to activating electromagnetic radiation.

The yellow lead(II) oxide may be replaced advantageously by other photosensitive semiconductor compounds such as photoconductive zinc oxide and titanium(IV) oxide.

Photoconductive zinc oxide and titanium(IV) oxide are inherently sensitive to ultra-violet radiation of wavelengths between about 360 nm and 420 nm; photoconductive yellow lead(II) oxide is inherently sensitive to radiation of wavelengths between about 360 nm and 460 nm.

The treatment of zinc oxide and titanium(IV) oxide by heating in vacuo will increase the photoresponse. The photoconductivity is raised by doping, e.g., with aluminium or chromium ions, and/or by dye sensitization.

The state of subdivision of the semiconductor particles is not critical, although very finely divided particles with a specific area as high as possible are preferred.

In general, commercially available photoconductive semiconductor materials having a particle size between about 0.03 and about 0.5 microns are employed. The larger the con-tact area between the photoactivatable agent promoting decomposition and the thermolysable organometallic compound, the higher the total photo- and heat-sensitivity of the system.

Preferably a mixture of a photosensitive semiconductor compound with a thermolysable metal-containing amino-alcohol compound formed in situ is used, since such a composition contains the agent promoting decomposition and the thermolysable organometallic compound in very intimately mixed state. However, the use of said reaction product in a layer being in intimate contact with a layer containing said agent promoting composition is not excluded.

Having in mind the preceding it is clear that the time needed to form a visible image will depend on the intensity of the exposure, the amount of effectively absorbed radiation and heat, the intrinsic photosensitivity of the semiconductor, the degree of effective contact with the thermolysable organic compound and its influence on the thermal decomposition thereof.

The ratio by weight of thermolysable organometallic compound to photosensitive agent promoting decomposition may vary within wide limits but preferably it is larger than 1.

A suitable ratio range of thermolysable compound to photosensitive agent is between 20:1 to 1:2 by weight.

A suitable coating according to the present invention contains approximately between 1 and 10 g of thermolysable organometallic compound per sq.m.

For the preparation of the recording material according to the present invention the thermolysable organo- metallic compound and photosensitive agent promoting decomposition are applied together to a suitable support from a solution or dispersion in an inert solvent containing a dissolved film-forming binding agent.

As binding agent for the photo- and heat-sensitive substances contained in the recording layer of the present invention all kinds of natural resins may be used, e.g., proteins such as gelatin, modified natural resins, e.g., cellulose esters and synthetic resins such as vinyl polymers. Best results, however, are obtained with film-forming binding agents that have a predominantly hydrophobic character, such as polyolefines, e.g., polyethylene, copolymers of butadiene and styrene, copolymers of acrylonitrile and butadiene, polyvinyl acetate, polyvinyl chloride containing a minor amount of chloro-sulphonyl groups, copolymers of butadiene and styrene containing a minor amount of unsaturated carboxylic acid such as maleic acid, a reaction product of polyethyleneimine and an aliphatic epoxide, and polyethylene containing in its structure a minor amount of carboxyl groups.

Suitable supports for the recording layer are, e.g., paper supports such as a glassine type paper support, and resin supports known from silver halide photography. It is also possible to apply the recording composition to glass, a metal support or a film base.

Advantages of the present invention are the completely dry processing and the fact that the recording material by a simple overall heat-treatment obtains a photosensitivity suited for copying purposes.

The following examples illustrate the present invention.

Example 1

110 g of yellow lead(II) oxide were ball-milled for 12 h in the presence of 100 g of tri-isopropanolamine, 500 ml of trichloroethylene and 50 ml of toluene till disappearance of the yellow color.

To the ball-milled composition 40 g of photosensitive semiconductive titanium (IV) oxide and 800 g of 20 percent by weight polyethylene solution in trichloroethylene were added. Ball-milling was continued for further 2 h.

The obtained suspension was spread onto a paper support in a ratio of 100 g per sq.m and dried at room temperature.

The obtained recording material was contact-exposed through a transparent original for 60 sec. while it was heated at 90°C. The exposure was carried out with a HPR lamp of 125 W (an ultra-violet lamp marketed by N.V. Philips Gloeilampenfabrieken, Eindhoven, Netherlands) placed at a distance of 5 cm from the recording layer.

A black print-out image having a maximum density of 1.4 in the image areas and a fog density of 0.1 in the background areas was obtained.

Examples 2–4

Analogous results were obtained by replacing the 40 g of titanium(IV) oxide by a same amount of one of the following compounds:

photoconductive zinc oxide;

photosensitive lead(II) oxide (massicot);

benzophenone.

Example 5

112 g of yellow lead(II) oxide were ball-milled for 2 h in the presence of 100 g of tri-isopropanolamine, 500 ml of trichloroethylene and 50 ml of toluene till disappearance of the yellow color.

49 g of the thus obtained dispersion were ball-milled for further 2 h in the presence of 41 g of a 20 percent by weight solution of polyethylene in trichloroethylene. Subsequently the obtained mixture was coated on a paper base at a coverage of 100 g per sq.m.

After drying, the coated layer was provided with a top-coating applied from a dispersion containing the following ingredients:

titanium(IV) oxide	4 g
EPIKOTE-162 (trade name of Shell Chemicals Inc. for an aliphatic polyepoxide binder)	17 g
polyethyleneimine	2 g
trichloroethylene	15 g

The thus obtained recording material was exposed for 15 sec. through a transparent silver image negative in a diazocopying machine ACTINA S (trade name of Regma N.V., Brussels, Belgium).

A black print-out image having a maximum density of 1.30 (measured reflectographically) and a fog density of 0.14 in the non-image areas was obtained.

When in said recording material the top layer containing titanium(IV) oxide was omitted, practically no image at all could be obtained in the same exposure circumstances.

Example 6

112 g of yellow lead(II) oxide were ball-milled for 2 h in the presence of 100 g of tri-isopropanolamine, 500 ml of trichloroethylene and 50 ml of toluene till disappearance of the yellow color.

49 g of the thus obtained dispersion were ball-milled for further 2 h in the presence of 17 g of EPIKOTE-162 (trade-name), 1 g of a mineral wax with melting point 70°C, 15 g of trichloroethylene, 2 g of polyethyleneimine and 4 g of epichlorhydrine.

The dispersion was coated onto a paper support bearing a white titanium(IV) oxide coating having 7 g of TiO_2 per sq.m.

The dried recording material was placed in a vacuum frame in contact with a metal plate heated at 100°C and contact-exposed for 60 sec. through a transparent silver image negative by means of a 2000 W mercury vapor lamp. A black print-out image with a maximum density 0.94 and a fog density 0.15 was obtained.

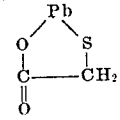
When the above dispersion was coated onto a paper support that had not been provided with a titanium(IV) oxide pigment coating the same exposure yielded an image with a maximum density of only 0.23 and a fog density of 0.13.

We claim:

1. A photosensitive recording material comprising an organometallic derivative of an alkanolamine yielding free metal on heating and in inter-reaction relationship with said derivative a photosensitive substance which in photo-exposed state lowers the decomposition temperature of said derivative, said photosensitive substance being benzophenone or at least one oxygen-containing inorganic semiconductive compound of lead, titanium, zinc or bismuth.

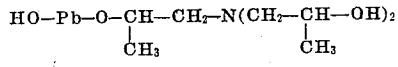
2. A photosensitive recording material according to claim 1, wherein the derivative alone is stable up to 100°C but above said temperature decomposes and yields free metal.

3. A photosensitive recording material according to claim 1, wherein said organometallic derivative is a reaction product of an alkanolamine and a metal compound selected from yellow lead(II) oxide (massicot), red lead(II) oxide (litharge), copper(II) acetylacetonate, zinc acetyl-acetonate, mercury(II) arsenite, thallium(III) arsenite,



and HO—Pb—S—CH_2—CH_2—OH.

4. A photosensitive recording material according to claim 3, wherein the reaction product has the following structural formula:



5. A photosensitive recording material according to claim 1, wherein the photosensitive substance and or-

ganometallic derivative are used in a same layer in admixture with a film-forming binding agent.

6. A photosensitive recording material according to claim 1, wherein the organometallic derivative and photosensitive substance are present in separate layers that are in intimate contact with each other.

7. A method of recording information comprising the steps of information-wise exposing to activating electromagnetic radiation a photosensitive recording material comprising an organometallic derivative of an alkanolamine yielding free metal on heating and in interreactive relationship with said derivative a photosensitive substance, which in photo-exposed state lowers the decomposition temperature of said derivative, and heating said recording material during or after exposure to develop a visible image in the unexposed areas thereof, said photosensitive substance being benzophenone or at least one oxygen-containing inorganic semiconductive compound of lead, titanium, zinc or bismuth.

8. A recording material according to claim 1 wherein the metallic atoms of said organometallic derivative are of the same metal as the semiconductive compound.

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