United States Patent [19]

Huffman et al.

[11] **3,767,414**

[45] **Oct. 23, 1973**

[54] **THERMOSENSITIVE COPY SHEETS COMPRISING HEAVY METAL AZOLATES AND METHODS FOR THEIR USE**

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[22] Filed: **May 22, 1972**

[21] Appl. No.: **255,617**

[52] **U.S. Cl.**..... **96/114.6**, 96/114.1, 117/36.9, 250/65 T

[51] **Int. Cl.**..... **G03c 1/02**, G03c 1/72, B41n 5/00

[58] **Field of Search**..... 96/114.6, 114.1; 117/36.8, 36.9; 250/65 T

[56] **References Cited**

OTHER PUBLICATIONS

Chemical Abstracts, 1964, 733 b,c.

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[57] **ABSTRACT**

Copy-sheets containing heavy metal azolates, such as silver imidazolates, are imaged by heating with a reducing agent applied in image-forming pattern. Colored images are then produced in base-sensitive copy-sheets by heating the imaged azolate sheet thereagainst.

20 Claims, No Drawings

THERMOSENSITIVE COPY SHEETS COMPRISING HEAVY METAL AZOLATES AND METHODS FOR THEIR USE

This invention relates to the image recording art particularly as exemplified by the copying or reproduction of documents, designs, and similar graphic originals in making projection transparencies as well as hard copies. In one important aspect there are involved novel compositions and coated sheet materials.

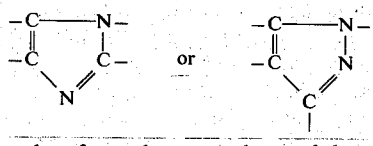
Heat-sensitive copy-sheets containing heavy metal salts, especially silver salts, of organic acids have been described, for example in U.S. Pat. No. 2,910,377. The present invention in one aspect likewise relates to heat-sensitive sheet materials containing organic silver or other heavy metal salts but employing specifically different materials and providing unexpected advantages.

Heat-sensitive copy-sheets containing organic silver salts have also been employed in conjunction with light-sensitive components, for example as described in U.S. Pat. No. 3,094,417. In another aspect the present invention similarly relates to the recording of light-images, again using novel materials and with advantageous results.

A particularly important aspect of the present invention relates to the formation of images in color, using the heavy metal salt copy-sheet in an intermediate process step.

It has now been found possible to employ heavy metal, particularly silver, azolates as components of primary copy-sheets having improved stability against backgrounding and which are further useful, e.g., in the preparation of secondary copies in color.

The azoles include the dinitrogen, five membered, unsaturated heterocyclic compounds having the skeletal structure



In its simplest form the copy-sheet of the present invention comprises a film or coating containing a silver imidazolate or pyrazolate dispersed in a polymeric binder. Amounts of the silver compound equivalent to from one-half to 14 grams of silver per square meter are useful. Imaging is accomplished by heating the coating in the presence of a suitable reducing agent, preferably together with other auxiliary components as will be further described. The reducing agent may be locally applied to the sheet, e.g., by inscribing with an ink containing the material or by transfer from a source sheet, and the entire sheet then heated. Alternatively, the reducing agent is supplied over the entire surface of the copy-sheet either as a separate coating or contained in a second sheet, and imaging is accomplished by localized heating, accomplished thermographically or with heated stylus or type, or by localized removal of the reducing agent followed by over-all heating.

Hindered phenolic reducing agents, e.g., butylated hydroxytoluenes, are useful but by themselves require undesirably high temperature for reaction with the silver salt in reasonable time and are therefore more effectively used in conjunction with at least minor proportions of more active reducing agents, e.g., non-hindered phenols such as methyl gallate or methoxyhydroxynaphthalene. In all cases, reduction of the silver salt occurs, accompanied by a visible change in the copy-sheet film or coating.

The copy-sheet showing a visible image obtained as just described is useful as a permanent record, showing substantially no loss of density at image areas or darkening of non-image areas during prolonged storage. The sheet is additionally useful in making further copies of the image areas in color. For the latter use the imaged sheet is promptly heated while in contact with a further sheet or stratum containing a base-sensitive color-producing system. The volatilizable azole compound released during formation of the silver image is transferred to the base-sensitive layer and there causes the formation of a colored image. Preferably the secondary colored image is formed in a separate sheet or film which is then removed, leaving the primary silver image in the first sheet. The base-sensitive sheet may itself carry a layer of reducing agent for reaction with the silver salt, in which event both images may be formed simultaneously.

The silver salt of imidazole is a preferred constituent of these novel copy-sheet materials. Various substituted imidazoles may also be used, benzimidazole being particularly useful. Mixtures of azolates may be used, a mixture of a major proportion of silver imidazolate and a minor proportion of silver benzimidazolate being particularly advantageous. Pyrazole forms a silver salt with which visible but weak primary images may be prepared. Azolates of heavy metals other than silver are somewhat less desirable for producing dense primary images but are frequently more useful in other ways. The copper salts, for example, produce low visual density primary images but which are electrically conductive, and whose conductivity may be enhanced by electroless plating in the preparation of printed circuit boards or for other purposes.

Heavy metal salts of various azoles have been reported in chemical literature. For example, Bauman and Wang, at page 370 of *Inorganic Chemistry*, Volume 3, (1964), describe the preparation of silver, zinc, copper, nickel and cadmium salts, (by them referred to as "complexes") of imidazole and N-methylimidazole, and the titration of silver imidazolate with sodium hydroxide. The silver salt of imidazole is represented by these authors as corresponding on ultimate analysis to the formula $Ag(C_3H_3N_2)$. However the compound has now been further found to have a molecular weight of the order of 20,000 and to have very low solubility, and is therefore to be considered as polymeric in nature, a conclusion which is further supported by the results of infra-red analysis.

The methods of preparation of the metal azolates described in the publication by Bauman and Wang result in products which in many cases produce only marginally operable copy-sheets. Modifications of these processes which result in materials of much smaller particle size are believed to be well within the skill of the art and involve changes in temperature of reaction mixture, rate of addition of reactants, concentration of reactants, extent of agitation, and the like; and reduction in particle size of the azolates is found to give greatly increased efficiency in copy sheet applications. In a typical laboratory scale example, following the general procedure described by Bauman and Wang, silver nitrate solution is diluted to 1/4 molar and the mixture is maintained at 2°–5° C. with vigorous agitation during addition of imidazole. 0.75 Molar sodium hydroxide

solution is added dropwise to a final pH of 10.50, and vigorous agitation is continued for an additional half hour prior to filtration. The particle size of the white powdery product obtained after washing and drying the precipitate is from about 3 microns to substantially less than 1 micron as determined with a "Quantimet 720" particle size analyzer using a scanning light beam. Weight loss on heating in hydrogen is 38.3 – 39.3 percent; theoretical for silver imidazolate is 38.3 percent.

For coating purposes the metal salt is well dispersed in a liquid vehicle, together with other components as desired, the degree of dispersion being sufficient to provide a uniform coating with good optical properties. For such purposes milling in a ball mill and in presence of an inert polymeric binder is effective. Vinyl resins, cellulosic derivatives and various other polymers are all useful; polyvinyl butyral resin is presently preferred.

Incorporation of hindered phenolic reducing agents in the coating containing the azolate lessens the amount of reducing agent which must be supplied at image areas and is usually desirable. Phthalazinone is a known toner for silver images and is found useful in the present compositions for such purposes. Pigments are sometimes used, e.g., to provide opacity or to lighten the background color and provide improved contrast; zinc oxide is one example. Plasticizers are sometimes helpful particularly where less flexible polymeric binders are to be used. It has been discovered also that catalytically small amounts of silver nitrate are particularly useful when added to the silver azolate coatings, which are thereby rendered more sensitive, and require less reducing agent and toner to provide a given image density.

Commercial diazo paper or film is one example of a secondary image sheet on which images in color may be formed by heating in contact with the imaged silver azolate sheet. Such papers contain an acid-stabilized diazonium salt in conjunction with an azo coupler. Transfer of imidazole, liberated at image areas from silver imidazolate, to the diazo sheet results in a coupling reaction between the diazonium compound and the coupler, with formation of an azo dye image. Proper selection of diazo and coupler components makes possible a variety of image colors.

Another form of color image sheet may be identified as containing in acid form an acid-base indicator which undergoes a visible change when exposed to the basic azole liberated at the primary image areas.

The following Examples, in which all proportions are in parts by weight unless otherwise indicated, will serve further to illustrate but not to limit the invention.

EXAMPLE 1

Silver imidazolate of minimal particle size is prepared as described hereinabove. The dry powder (4.5 parts) is mixed into a 12 percent solution of polyvinyl butyral in methylethyl ketone (30 parts) by prolonged milling in a ball mill. The resulting suspension is coated on both paper and film backing sheets using a coating bar held at an orifice of four mils (0.1 mm.) and the coatings are air dried, to provide primary copy-sheets.

A desensitizable intermediate transfer sheet, prepared as described in U.S. Pat. No. 3,094,417 and containing dye-sensitized substituted α-naphthol, is exposed to a light-image to an extent just sufficient to cause complete desensitization of the sheet at non-image areas, leaving the α-naphthol reducing agent only at the image areas. It is then placed in face-to-face contact with the primary copy-sheet and the couplet is heated by passing around a metal roller maintained at 260° F. Upon separation of the sheets, a visible record of the light-image is observed on the copy-sheet in the form of brown images on a white background.

The light-sensitive intermediate transfer sheet may be replaced by a transfer sheet coated with methyl gallate as used in U.S. Pat. No. 2,910,377. The transfer sheet is held in face-to-face contact with the copy-sheet and the couplet is held in heat-conductive contact against a printed original which is then briefly exposed to intense infra-red radiation. A copy of the printed image is formed on the copy-sheet.

The copy formed in the latter instance is placed in face-to-face contact with a commercial "Ozalid" diazo sheet and the couplet is held for one-half minute between metal platens maintained at 120°–125° C. A copy of the image areas appears in color on the surface of the diazo sheet.

EXAMPLE 2

The procedures of Example 1 are duplicated except that silver benzimidazolate is substituted for the silver imidazolate. Substantially identical results in terms of image formation and appearance are obtained, along with improved stability of background against darkening during prolonged storage in an office file cabinet.

EXAMPLE 3

Silver imidazolate	4.5
12% Polyvinyl butyral in MEK	30
Phthalazinone	1.25
Reducing agent	0.3
Silver nitrate	0.045

The reducing agent, a hindered phenol consisting of butylated hydroxytoluene available under the trademark designation "CAO-3," is added to the ball milled mixture of the several other components under brief mixing and the composition is promptly coated on paper and film backings, and dried. The resulting primary copy sheets are imaged as described under Example 1 except that in the second procedure the coating of methyl gallate is applied directly to the unprinted surface of the printed original instead of on a separate source sheet. Dense black images are obtained on the primary copy-sheet in all cases. The sheet both before and after imaging has high thermal stability.

A secondary sheet is prepared by coating a transparent film backing with a solution of

4% solution of nitrocellulose in 1:3 alcohol:ether	30.0
1-diazo-2,5-dibutoxy-4-morpholino-benzene sulfate	0.75
3-hydroxy-2-naphthol-phenetide	0.25
3-hydroxy-2-naphthol-toluidide	0.25

applied at a wet thickness of about 3 mils, and dried, in absence of light. The film backing is a polyester film which has first been subbed with "duPont 49,000," a soluble polyester of glycols, phthalic acids and sebacic acid, applied from solution in trichloroethane, or alternatively has been subjected to a surface treatment by corona discharge. A freshly imaged primary copysheet is placed in face-to-face contact with the secondary sheet and the couplet is heated at 260° F. A faintly yellowish projection transparency is produced which

when used with an overhead projector rapidly bleaches to a water-white appearance in the non-image areas and projects a blue image on a white background.

EXAMPLE 4

Polyester film base is coated with a 4 mil layer of a solution of 0.01 part of o-cresolphthalein and ten parts of polyvinyl butyral in 90 parts of acetone and the coating is dried.

A freshly imaged primary copy sheet prepared and processed as described under Example 3 is heated for one-half minute at 120° C. in contact with the coated film. A red image is formed, corresponding to the image of the printed original when viewed through the transparent film.

Incorporation of zinc oxide in the film coating produces a white-appearing film on which the red image appears with good contrast.

EXAMPLE 5

Component	A	B
silver imidazolate	0.5	2.0
reducing agent of Example 3	0.5	0.5
phthalazinone	0.5	0.5
binder (polyvinyl butyral)	2.0	0.5
solvent (MEK)	18.0	10.0

Mixtures A and B are separately prepared and coated on paper substrates, and the dried primary copy-sheets are imaged by heating in contact with a reflex exposed light-sensitive intermediate transfer sheet as described under Example 1 and under identical conditions. Sheet A produces a dense visible image on a substantially unchanged background; sheet B produces an image of still greater density but with some background darkening.

EXAMPLE 6

A receptor sheet is prepared by coating polyester film at a coater bar setting of four mils, with a solution containing

vinyl chloride-acetate copolymer	40
N-(bis(4-dimethylaminophenyl)methyl)pyrrolidine	1
salicylic acid	0.2
methylethyl ketone	160

The dried sheet is a dense cyan color. It is placed against a freshly imaged primary copy-sheet prepared and processed as described under Example 3. The couplet is heated briefly. The color is discharged at image areas, forming a substantially colorless clear image against a cyan background. On an overhead projector the thus imaged sheet projects a white image on a blue-green background.

EXAMPLE 7

Copper (I) imidazolate is prepared by mixing cupric chloride in 0.05 molar solution with an excess of imidazole, adding ascorbic acid and sodium sulfite to reduce the copper (II) to copper (I) as shown by conversion from blue to straw color, adding molar sodium hydroxide solution to cause precipitation, filtering, and washing and drying the resultant white powder.

A mixture of 10 parts of the powder with 100 parts of 10 percent solution of polyvinyl butyral in a mixture of methylethyl ketone and toluene is applied at 6 mils to a polyester film and dried. A printed sheet having on the reverse surface a coating of methyl gallate is placed against the coated film in face-to-face contact and the printed surface is briefly exposed to intense infra-red radiation, causing heating of the imaged areas and the formation of a corresponding copper image on the coated film. The copper image is intensified by dipping the film in an electroless copper plating solution. The image areas are found to be electrically conductive.

EXAMPLE 8

A primary copy-sheet prepared as described under Example 3 is first overcoated with a minimal continuous barrier coating of vinyl chloride-vinyl acetate copolymer and then with a photo-sensitive overcoat of dye-sensitized 4-methoxy-1-naphthol. The resulting integral sheet is first exposed to a light-image to densensitize the photosensitive layer at the light-struck areas and is then heated to cause an image-forming reaction at the unexposed areas, the substituted naphthol diffusing through the very thin separating layer for reaction with the silver imidazolate.

EXAMPLE 9

A commercial "Ozalid" diazo sheet as used in Example 1 is first overcoated with a photosensitive layer of dye-sensitized substituted α-naphthol as also employed in Example 1. The sheet is exposed to a light-image sufficient to desensitize the coating at the light-exposed areas. It is then placed in face-to-face contact with a primary copy-sheet prepared as described in Example 3 and the composite is heated. A dense black image forms on the primary copy-sheet; a colored reverse image appears on the diazo print sheet. There is involved first a transfer of the residual α-naphthol from the diazo sheet to the copy-sheet where it reacts with the silver salt to form a silver image, followed by transfer of the liberated imidazole from the copy-sheet to the diazo sheet where it neutralizes the acid stabilizer component and permits the diazo and coupler components to unite with formation of an azo dye image.

What is claimed is as follows:

1. Method of imaging comprising subjecting a first sheet material having a stratum containing a polymeric heavy metal azolate to heat at least at image areas and in the presence of a reducing agent to provide on said sheet material a visible image.

2. Method of claim **1** wherein said metal is silver.

3. Method of claim **1** wherein said reducing agent is photosensitive.

4. Method of claim **3** wherein said reducing agent is supplied from a second sheet held in face-to-face contact with said first sheet material.

5. Method of claim **4** wherein said second sheet is first exposed to a light-image to an extent just sufficient to desensitize all of said reducing agent in the lighted areas.

6. Method of claim **1** including the further step of heating the imaged first sheet in face-to-face contact with a base sensitive print sheet.

7. Method of claim **6** wherein said print sheet contains an acid stabilized diazo.

8. Method of claim **6** wherein said print sheet contains a base-reactive acid-base indicator.

9. Method of claim **7** wherein said first sheet material includes at least in the image areas thereof a layer containing a said reducing agent which is Photosensitive.

10. Method of claim **1** wherein said stratum contains a catalytically small proportion of silver nitrate.

11. Sheet material including a paper-thin backing carrying an image-forming stratum comprising a heavy metal azolate.

12. Sheet material of claim 11 wherein said heavy metal iS silver.

13. Sheet material of claim 12 wherein said heavy metal azolate is silver imidazolate.

14. Sheet material of claim 13 wherein said stratum includes a hindered phenolic reducing agent for silver ion, and phthalazinone.

15. Sheet material of claim 12 wherein is included a catalytically small amount of silver nitrate.

16. Sheet material of claim 15 having over said stratum a coterminous vapor-transmissive polymeric barrier layer and an outer layer comprising a volatilizable reducing agent for silver ion.

17. Sheet material of claim 11 wherein said heavy metal azolate is a copper azolate.

18. A print sheet useful in a couplet with the sheet material of claim 15 in forming an image in color and comprising a base-reactive color-producing stratum and an outer stratum containing a photosensitive reducing agent for silver ion.

19. Print sheet of claim 18 wherein the color-producing Stratum comprises an acid-stabilized diazo and an azo coupler component and said reducing agent is a substituted α-naphthol.

20. A couplet of the sheet material of claim 16 and in face-to-face contact therewith a print sheet having a base-reactive color-producing stratum and an outer stratum containing a photosensitive reducing agent for silver ion.

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