

[72] Inventor **John R. Manhardt**
Nashua, N.H.
[21] Appl. No. **697,319**
[22] Filed **Jan. 12, 1968**
[45] Patented **Dec. 28, 1971**
[73] Assignee **Itek Corporation**
Lexington, Mass.

944,362 12/1963 Great Britain
1,091,715 11/1967 Great Britain

Primary Examiner—George F. Lesmes
Assistant Examiner—John C. Cooper

Attorneys—Homer O. Blair, Robert L. Nathans and W. Gary Goodson

[54] **PHOTOGRAPHIC SYSTEMS AND PROCESSES
HAVING HEAT ALTERABLE SPECTRAL
SENSITIVITY**
32 Claims, No Drawings

[52] U.S. Cl. **96/27,**
96/1 R, 96/1.5, 96/1.7, 96/1.8, 96/102, 96/48, 96/88,
96/1.6, 260/576, 252/501, 250/65 R
[51] Int. Cl. **G03g 5/00,**
G03g 13/22
[50] Field of Search..... 96/1.5-1.8,
88, 102, 27, 48; 252/501; 260/576

[56] **References Cited**

UNITED STATES PATENTS

3,127,332	3/1964	Banrud.....	204/18
3,291,600	12/1966	Nicoll.....	96/1
3,380,823	4/1968	Gold.....	96/27
3,390,989	7/1968	Bermen et al.....	96/27

FOREIGN PATENTS

853,880 11/1960 Great Britain

ABSTRACT: Reproduction systems having broader spectral sensitivity are produced wherein certain classes of dyes are added to photosensitive materials which, when activated, are capable of producing chemical reaction when in contact with image-forming agents to produce a visible image. The dyes are those which undergo a color change when heated to elevated temperatures and thus alter the spectral sensitivity of the photosensitive materials after heating. The dyes include styryl dyes substituted on the vinyl group by a nitrogen-containing heterocyclic, which in their unaltered state, themselves alter the sensitivity of the reproduction system.

Improved processes using this improved reproduction system comprise selectively exposing the present systems to activating radiation after heating to the color transition temperature or alternatively first exposing and then heating to the said temperature. A preferred process is an add-on technique for addition of images to a reproduction system in which readable images are already present. The new reproduction systems of this invention have a built-in differential in spectral sensitivity by virtue of alteration of the dye by heating.

PHOTOGRAPHIC SYSTEMS AND PROCESSES HAVING HEAT ALTERABLE SPECTRAL SENSITIVITY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the field of photographic reproduction systems and, more specifically, to a photographic system utilizing an improved copy medium comprising a dye-sensitized photosensitive material which, when activated by suitable means, is capable of producing a visible image.

2. Description of the Prior Art

Data or image storage media comprising radiation sensitive materials such as titanium dioxide are described in detail in U.S. Pat. Nos. 3,152,903; 3,052,541; French Pat. Nos. 345,206 and 1,245,215 and in commonly owned copending U.S. Applications Ser. No. 199,211 filed May 14, 1962 in the names of Elliot Berman et al., now abandoned. In the aforementioned U.S. Patent Application, radiation-sensitive titanium dioxide functions as a photosensitive component of the media and exposure of said media to activating means such as radiant energy, electron beams or the like results in the storage of a reversible latent image pattern therein. The reversible latent image pattern exists for a limited time during which said pattern can be converted to an irreversible form and read out visually by contacting said pattern with a suitable image forming material, such as a chemical redox system. In the aforesaid U.S. and French Patents, the radiation-sensitive material is combined with at least one component of an image-forming material prior to exposure to activating means. For example, U.S. Pat. No. 3,152,903 describes a photosensitive material such as titanium dioxide in combination with a reducible metal ion such as silver nitrate. This copy media is exposed to activating means and then contacted with a reducing agent to produce a visible image. U.S. Pat. No. 3,152,903 also discloses a system wherein the photosensitive material is used in combination with both an oxidizing agent such as silver nitrate and a reducing agent, such as Metol (1,4-methyl paraminophenol sulfate). Upon exposure to suitable activating means, a visible image is formed. One of the limitations of the above-mentioned data or image storage systems is that they lack the photographic speed of systems such as silver halide.

Commonly owned copending U.S. Application Ser. No. 633,689 filed Apr. 26, 1967 describes a method to expand the possible uses of these photographic systems described in the above-mentioned Patents and Application, by increasing the photographic speed of these systems by use of cyanine and hemicyanine dyes with the photosensitive materials, including styryl dyes as described therein.

SUMMARY OF THE INVENTION

It has now been unexpectedly found that the spectral sensitivity of reproduction systems may be altered by incorporating into the reproduction system a dye which undergoes color change when heated to elevated temperatures, thus altering the spectral sensitivity of the system. The contemplated dyes include styryl-substituted nitrogen-heterocyclic dyes, especially those of the formula: $A-CR_3=CR_4-C_6H_4-NR_1R_2$ in which substituent A is a nitrogen-containing heterocyclic nucleus; and substituents R_1 , R_2 , R_3 , and R_4 are each selected from the group consisting of hydrogen, alkyl, aryl, aralkyl and alkaryl groups. The preferred dyes of this formula are those in which the heterocyclic nucleus contains at least one nitrogen heteroatom and may include other hetero atoms such as oxygen and sulfur such as those derived from thiazole, isoxazole, quinoline, benzimidazole, indole, benzothiazole, thiadiazine, or similar such heterocyclics and the substituents R_3 and R_4 are hydrogen while R_1 and R_2 are lower alkyl, especially methyl or ethyl. In the said dyes, the heterocyclic nucleus is most commonly in the form of a salt such as a quaternary ammonium salt or acid addition salt by virtue of the nitrogen in the heterocyclic ring. As is appreciated by those in the art, the heterocyclic nucleus may be substituted for example by vari-

ous groups such as hydrocarbon radicals as previously enumerated, or alkoxy groups, without affecting the dye property of the compound.

The present invention provides image reproduction systems comprising the aforesaid dyes in the heat transformed color and a photosensitive material which, when activated, is capable of producing chemical reaction when in contact with image-forming agents to produce a visible image.

It will be understood that the copy media of this invention may optionally include imaging material such as above described. Therefore, one of the preferred embodiments of this invention is where an oxidizing agent is present on the dyed photosensitive substrate of this invention at the time of exposure. Another preferred embodiment is wherein the dyed photosensitive substrate includes not only an oxidizing agent but additionally, a reducing agent at the time of exposure to suitable activating means.

DESCRIPTION OF PREFERRED EMBODIMENTS

The photoconductor or photocatalyst preferred in this invention are metal-containing photoconductors. A preferred group of such photosensitive materials are the inorganic materials such as compounds of a metal and a nonmetallic element of group VIA of the periodic table* (*Periodic table from Lange's HANDBOOK OF CHEMISTRY, 9th edition pp. 56-57, 1956.) such as oxides, such as zinc oxide, titanium dioxide, zirconium dioxide, germanium dioxide, indium trioxide; metal sulfides such as cadmium sulfide (CdS), zinc sulfide (ZNS) and tin disulfide (SnS_2); metal selenides such as cadmium selenide (CdSe). Metal oxides are especially preferred photoconductors of this group. Titanium dioxide is a preferred metal oxide because of its unexpectedly good results. Titanium dioxide having an average particle size less than about 250 millimicrons and which has been treated in an oxidizing atmosphere at a temperature between about 200°C. and 950°C. for from about 0.5 hours to about 30 hours is especially preferred and, more especially, that titanium dioxide produced by high temperature pyrolysis of titanium halide.

Also useful in this invention as photoconductors are certain fluorescent materials. Such materials include for example, compounds such as silver activated zinc sulfide, and zinc activated zinc oxide.

While the exact mechanism by which this invention works is not known, it is believed that exposure of photoconductor or photocatalysts of this invention to activating means causes an electron or electrons to be transferred from the valence band of the photoconductor or photocatalyst to the conductance band of the same or at least to some similar excited state whereby the electron is loosely held, thereby changing the photoconductor from an inactive form to an active form. If the active form of the photoconductor or photocatalyst is in the presence of an electron accepting compound a transfer of electrons will take place between the photoconductor and the electron accepting compound, thereby reducing the electron accepting compound. Therefore a simple test which may be used to determine whether or not materials have a photoconductor or photocatalytic effect is to mix the material in question with an aqueous solution of silver nitrate. Little, if any, reaction should take place in the absence of light. The mixture is then subjected to light, at the same time that a control sample of an aqueous solution of silver nitrate alone is subjected to light, such as ultraviolet light. If the mixture darkens faster than the silver nitrate alone, the material is a photoconductor or photocatalyst.

It is evident that the gap between the valence and the conducting band of a compound determines the energy needed to make electron transitions. The more energy needed, the higher the frequency to which the photoconductor will respond. It is known to the art that it is possible to reduce the band-gap for these compounds by adding a foreign compound as an activator which either by virtue of its atomic dimensions or by possessing a particular electronic forbidden zone struc-

ture or through the presence of traps as donor levels in the intermediate zone between the valence and the conduction band stresses the electronic configuration of the photoconductive compound, thereby reducing its band-gap and thus increasing its ability to release electrons to its conduction band.

The phenomenon observed with respect to the increased speed of the photosensitive material containing the dye, prior to permanent color change or subsequent to color change, is not necessarily understood. However, color change of the dye during heating is gradual over a range of temperature up to the permanent color transition temperature and, until permanent transition is generally found to be thermoreversible, since cooling the dye results in change back to the original color. Further, this thermoreversibility of color change and the rapidity with which color change occurs indicate that a simple physical change is responsible for the color change and extension of spectral sensitivity. This behavior of the specified dyes cannot be explained by mechanism involving thermal decomposition of the short chain dyes followed by recondensation as a longer chain dye.

The foregoing theoretical explanation is not intended to be binding on the applicant but rather is offered to permit a better understanding of the invention.

Regardless of the theory, the present invention comprises the process of altering the spectral sensitivity of a reproduction system by contacting the system with a dye which undergoes a color change at elevated temperatures and heating the system.

The operability of any dye in the present process can be routinely determined by simply coating a suitable photosensitive medium as hereindescribed and then heating the medium to elevated temperatures. If color change occurs, then the dye is suitable for the process. For example, in general, the preferred dyes undergo color change at temperatures in the vicinity of about 200° F. Usually evidence of color change manifests itself on first heating the medium, and the color change is usually thermoreversible up to the permanent color transition temperature.

Photosensitive media containing the preferred dyes of this invention are sensitive to light of maximum wavelength of about 500 to below 600 millimicrons, but, after heating, the sensitivity is extended to light of longer wavelength, e.g. extending into the region of red sensitivity. When the permanent color transition temperature is reached, the extended sensitivity is made permanent.

Advantage of this extended sensitivity can be taken by utilization of the differential spectral sensitivity of the photosensitive medium. For example, where the initial dye-containing medium is not sensitive to red light prior to heat treatment but is sensitive thereafter, red light may be used to register an image on the photosensitive medium and, after registration of the image, the medium is heated to obtain a latent image when the medium is rendered red light-sensitive. Such flexibility in reproduction systems is fully appreciated by those skilled in the art. For example, with media which have the possible extended sensitivity of the present invention, the registration of an image on the medium must be followed by a long wait period to permit loss of the activation created by impingement on the photosensitive surface, e.g. by dark storage, or alternatively, the medium must be deactivated before forming the desired registered latent image. The present process obviates the need for long wait period between registration and formation of the desired registered latent image. With media which lack the means of extending the spectral sensitivity of the present invention, a movable colored filter or second light source must be provided as a source of actinic light for latent image formation after the registration is completed. This aspect of the present invention is of particular importance where it is desired to add additional information to photosensitive media on which is already present visible information or images, i.e. as "add-on" process. For example, in data storage systems based on photosensitive media, it is possible to add distinct information utilizing the add-on technique.

For instance, an information storage tape comprising titanium dioxide can be provided with an area for "add-on" information. This add-on area can already contain a dye as described herein, or the dye can be added as needed to specified areas. The information to be added can then be registered in the desired position by the method described and, after registration, the registered latent image formed by the mere expedient of heating the medium. The latent image is rendered visible by contact with an image-producing agent, as desired.

The use of red light for registering and imaging on the medium presupposes the use of a dye which, at the color transition temperature, is converted to a color which is sensitive to red light. Particularly effective in this use are the dyes in which substituent A is a thiadiazole nucleus or a thiazole nucleus.

It is intended that the add-on process also embraces the use of dyes which do not necessarily extend light sensitivity of the photosensitive medium to the red region, since it follows that the initial registration of image on the medium can be effected with visible light (not necessarily red light) of wavelength to which the medium is not sensitive prior to color change by heating but to which the heated medium is sensitive. The use of red light and the specified dyes merely represents the preferred form of the invention.

The dyes of this invention may be used in solution to treat the photosensitive materials prior to their incorporation into a copy medium. These dyed photosensitive materials can then be deposited on a substrate, or incorporated into a substrate such as a fibrous web of paper. Alternatively, the dye can be combined with the photoconductive materials in the copy medium, as for example, by dispersion of the dye in the binder for the photosensitive material. In addition, it is possible to dip-dye the photosensitive substrate by merely immersing a substrate containing the photosensitive material into a solution of the particular dye. In coating a transparent film such as cellulose triacetate, particular problems arose when applying a dyed photoconductor in a gelatin binder to a transparent plastic film such as cellulose triacetate. This problem was overcome by first forming an aqueous slurry of the photosensitive material with gelatin dissolved therein and then incorporating a solution of the particular dye desired. This slurry is then applied to the film substrate to form a uniformly dyed photosensitive substrate having the desired increased speed and other desirable properties of this invention.

The inert carrier sheet upon which the photoconductor and dye of this invention are deposited comprises any suitable backing of sufficient strength and durability to satisfactorily serve as a reproduction carrier. The carrier sheet may be in any form such as, for example, sheets, ribbons, rolls, etc. This sheet may be made of any suitable materials such as wood, rag content paper, pulp paper, plastics such as, for example, polyethylene terephthalate (Mylar) and cellulose acetate, cloth, metallic foil and glass. The preferred form of the carrier sheet is a thin sheet which is flexible and durable.

It is also useful to use a binder agent to bind the dye of this invention and photosensitive materials to the carrier sheet. In general, these binders are translucent or transparent so as not to interfere with transmission of light therethrough. Preferred binder materials are organic materials such as resins. Examples of suitable resins are butadiene-styrene copolymer, poly(alkyl acrylates) such as poly(methyl methacrylate), polyamides, polyvinyl acetate, polyvinyl alcohol and polyvinylpyrrolidone.

The photoconductor should be conditioned in the dark before exposure. Such conditioning is generally conducted from 1 to 24 hours. After conditioning, the photoconductor is not exposed to activating radiation prior to its exposure to activating radiation for recording an image pattern.

The period of exposure will depend upon the intensity of the light source, the particular imaging material, particular photoconductor, the type and amount of catalyst, if any, and like factors known in the art. In general, however, the exposure may vary from about 0.001 seconds to several minutes.

While this invention is concerned particularly with forming a negative image of a positive print, or vice versa, it will be understood that the invention described therein is also applicable to such positive processes as that described in commonly assigned copending U.S. Pat. No. 3,414,410. In this process, a photosensitive material is uniformly dye sensitized and then exposed to an image pattern of activating radiation to desensitize the dye-sensitized medium to activating radiation in those portions thereof which are struck by radiation during the initial exposure, and then subsequently this thus partially desensitized medium is exposed to activating radiation to activate those as yet unexposed areas of said medium which correspond with opaque areas of the original image. By contacting with image-forming material, as described in the prior art, a positive visible image of the original positive is produced.

It is also within the scope of this invention to heat imagewise the dyed photosensitive copy medium of this invention and then expose uniformly to radiation to which the heated areas are sensitive and to which the unheated areas are insensitive. In the alternative, the uniform exposure can be with radiation to which the unheated areas of the copy medium are sensitive, but to which the heated areas are insensitive. The activated areas of the copy medium in either case may then be developed to form a permanent image.

Image-forming materials which are useful in this invention are those such as described in U.S. Pat. No. 3,152,903 and in copending application Ser. No. 199,211. These image-forming materials include preferably an oxidizing agent and a reducing agent. Such image-forming materials are often referred to in the art as physical developers. The oxidizing agent is generally the image-forming component of the image-forming material. However, this is not necessarily true. Either organic or inorganic oxidizing agents may be employed as the oxidizing component of the image-forming material. Preferred oxidizing agents comprise the reducible metal ions having at least the oxidizing power of cupric ion and include such metal ions as Ag^+ , Hg^{+2} , Pb^{+4} , Au^{+3} , Pt^{+4} , Ni^{+2} , Sn^{+2} , Pb^{+2} , Cu^{+1} , and Cu^{+2} . Other suitable oxidizing agents useful in this invention as components of an image-forming material are permanganate (MnO_4^-) ion, various leuco dye materials such as disclosed in copending application Ser. No. 623,534 filed in the name of L. Case, and the like. Organic oxidizing agents include tetrazolium salts, such as tetrazolium blue and red, and diphenyl carbazone, and genarcyl red 6B (methine dye).

The reducing agent components of the image-forming materials of this invention include organic compounds such as the oxalates, formates, substituted and unsubstituted hydroxylamine, and substituted and unsubstituted hydrazine, ascorbic acid, aminophenols, and the dihydric phenols. Also, polyvinylpyrrolidone, alkali and alkaline earth metal oxalates and formates are useful as reducing agents. Suitable reducing compounds include hydroquinone or derivatives thereof, o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenyl, glycine, o- and p-phenylene diamine, and 1-phenyl-3-pyrazolidone.

Additionally, the image-forming materials or physical developers may contain organic acids which can react with metal ions to form complex metal anions. Further, the developers may contain outer complexing agents and the like to improve image formation and other properties found to be desirable in this art.

Additional stabilizing and fixing steps such as known to the art may also be added to the processes of this invention in order to increase the life and permanence of the final print.

The following examples further illustrate the invention.

EXAMPLE 1

A mixture of 4 parts by weight of titanium dioxide and 1 part by weight of an emulsion of polyvinyl alcohol resin containing about 50 percent of solids in water is used to coat paper sheets.

A sheet of the coated paper is then dipped into a solution containing 2-[p-(dimethylamino)stryryl]-4-methyl-thiazole methochloride in methanol and then dried. The medium contained 0.5 percent dye based on the titanium dioxide. The so-treated medium is heated on a hotplate and at about 200° F., the color of the coating (which is normally pumpkin orange) begins to change in hue to violet which becomes more intense as the temperature rises. Cooling of the paper caused a reversion in hue to the original color and this cycling of hue can be repeated over and over without apparent fatigue.

At a temperature of 500° F., the hue change becomes permanent with the purple color no longer reverting to orange upon cooling. A spectrogram of the heated medium shows a strong sensitization extending into the visible above 600 millimicrons. The original dye-sensitized paper showed sensitization extending into the visible to a maximum of less than 600 millimicrons.

The heated medium is then exposed at 400° F. to an image using a red light source and the latent image so formed is converted to a visible image by development using alcoholic silver nitrate, followed by Metol.

Alternatively, filled paper sheets containing about 20 percent of photoconductive ZnO and TiO_2 pigment are prepared in conventional paper making apparatus by addition of an aqueous slurry of the pigment to the beater and utilized in the above described procedure.

Finely divided water-insoluble photoconductive pigments are also dye sensitized by contacting the pigments with dilute solutions of sensitizing dyes. Excess dye solution is decanted, and the treated pigments are dried. The pigments can suitably be deposited without a binder on a substrate such as glass, or can be incorporated into a plastic or the fibrous web of a paper, or can be dispersed in a binder such as polyvinyl alcohol and used to coat rigid or flexible electrically insulating or conducting substrates.

EXAMPLE 2

A photosensitive copy medium as in example 1 is prepared containing 0.5 percent dye based on the titanium dioxide, the dye being 2-[p-(dimethylamino)stryryl]-3,5-dimethylthiadiazolium nitrate. The color change observed above 200° F. is more intense than that observed with the dye of example 1, although the hue also changes to purple. Similarly, above 500° F., the hue change is irreversible on cooling.

The spectral sensitivity of the unheated medium determined by exposure in a wedge spectograph for 1 minute, ceases at about 580 millimicrons whereas, after heating to 500° F., the spectral sensitivity extends to 620 millimicrons.

Thus, heating to 500° F. changes the medium from a green-sensitive orthochromatic medium to a green and red sensitive short panchromatic medium. Heating to the intermediate temperatures between 200° and 400° F. renders the medium both orthochromatic and panchromatic sensitive and reversible in spectral sensitivity.

The medium is imaged by exposure to red light and the image developed to obtain a visible image as described in example 1.

EXAMPLE 3

This example illustrates the add-on feature of this invention. A dyed photosensitive medium as described in example 2, prior to heating, is exposed using a tungsten light source to a pattern of activating radiation. The exposed medium is developed by dipping into a saturated solution of silver nitrate in methanol and then into a solution of 5 g. of Phenidone, 40 g. of citric acid monohydrate in one liter of methanol. A visible negative image of the light pattern is obtained. After fixing, the medium is dark adapted and exposed to a second image of red light to which the medium is not sensitive. After registering the image on the medium, the medium is heated to 400° F. and the latent image corresponding to the second

image is formed on the medium. Development and fixing gives a medium containing the original image and the second image.

The procedure of examples 1, 2, and 3 are repeated with similar results using the following compounds:

- 2-(p-dimethylaminostyryl)benzimidazole methochloride. 5
- 2-(p-dimethylaminostyryl)-6-ethoxyquinoline methochloride.
- 6-dimethylamino-2-(p-dimethylaminostyryl) quinoline methochloride.
- 2-(p-dimethylaminostyryl)-6-methylbenzothiazole methochloride.
- 2-(p-dimethylaminostyryl)-3,5-dimethylthiadiazolium sulfate.
- 2-(p-dimethylaminostyryl)isoxazole methochloride.

I claim:

1. A method of altering the spectral sensitivity of a metal containing photoconductor which comprises contacting the photoconductor with a dye of the formula

$A-CR_3=CR_4-C_6H_4NR_1R_2$ in which substituent A is a nitrogen heterocyclic nucleus; and substituents R_1 , R_2 , R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl, aralkyl, aryl and alkaryl groups; and heating to at least the color transition temperature of the dye.

2. Method as in claim 2 wherein the substituent A is selected from the group consisting of a thiazole nucleus, isoxazole nucleus, quinoline nucleus, benzimidazole nucleus, indole nucleus, benzothiazole nucleus and thiadiazole nucleus, said dye being in the form of a quaternary salt or acid addition salt.

3. Method as in claim 2 wherein the heating is conducted at a temperature of at least about 200° F.

4. Method as in claim 2 wherein the dye is 4-methyl-2-[p-(dimethylamino)styryl] thiazole methochloride.

5. Method as in claim 2 wherein the dye is 2-[p-(dimethylamino)styryl]-3,5-dimethylthiadiazolium nitrate.

6. Method as in claim 5 wherein the heating is conducted at a temperature of about 400° F.

7. A method of forming an image in a photosensitive medium comprising a metal-containing photoconductor that is not sensitive to red light radiation and which has been contacted with a dye of the formula:

$A-CR_3=CR_4-C_6H_4NR_1R_2$ in which substituent A is a nitrogen-containing heterocyclic nucleus and substituents R_1 , R_2 , R_3 , and R_4 are each selected from the group consisting of hydrogen, alkyl, aralkyl, aryl, and alkaryl groups, comprising the steps of:

- a. exposing the medium to an image with red light;
- b. heating the medium to at least the color transition temperature of the dye to form a latent image corresponding to the original image.
- 8. Method as in claim 7 wherein step b is conducted before step a.
- 9. Method as in claim 7 wherein step a is conducted simultaneous with step b.
- 10. Method as in claim 7 wherein the latent image is rendered visible by contact with an image-forming agent which undergoes an oxidation/reduction type reaction upon contact with an exposed, activated photoconductor.
- 11. Method as in claim 10 wherein the image-forming agent comprises a solution of a metal ion which is at least as strong an oxidizing agent as copper ion.
- 12. A method as in claim 11 wherein the metal ion is silver ion.
- 13. Method as in claim 11 wherein the solution includes a reducing agent for the metallic ion.
- 14. Method of adding an image to a photosensitive medium comprising a metal-containing photoconductor already containing a visible image thereon which comprises the successive steps of:

- a. Contacting the photoconductor with a dye of the formula: $A-CR_3=CR_4-C_6H_4NR_1R_2$ wherein substituent A is a nitrogen-containing heterocyclic nucleus and substituents R_1 , R_2 , R_3 , and R_4 are each selected from the group consisting of hydrogen, alkyl, aralkyl, aryl and alkaryl groups;
- b. registering an image on the medium with red light;
- c. heating the medium after registering the image to at least the color transition temperature of the dye to form a latent image corresponding to the registered image.

15. Method as in claim 14 wherein the latent image is rendered visible by contact with an image-forming agent which undergoes an oxidation/reduction type reaction upon contact with an exposed, activated photoconductor.

16. Method as in claim 15 wherein the image forming agent comprises a solution of a metal ion which is at least as strong an oxidizing agent as copper ion.

17. Method as in claim 16, wherein the metal ion is silver ion.

18. Method as in claim 16 wherein the solution includes a reducing agent for the metallic ion.

19. Method as in claim 15 wherein the substituent A is selected from the group consisting of a thiazole nucleus, isoxazole nucleus, quinoline nucleus, benzimidazole nucleus, indole nucleus, benzothiazole nucleus and thiadiazole nucleus, said dye being in the form of a quaternary salt or acid additional salt.

20. Method as in claim 19 wherein the heating is conducted at a temperature of at least about 200° F.

21. Method as in claim 14 wherein the dye is 4-methyl-2-[p-(dimethylamino)styryl] thiazole methochloride.

22. Method as in claim 14 wherein the dye is 2-[p-(dimethylamino)styryl]-3,5-dimethylthiadiazolium nitrate.

23. Method as in claim 22 wherein the heating is conducted at a temperature of about 400° F.

24. A photosensitive medium comprised of a metal containing photoconductor and a dye of the formula: $A-CR_3=CR_4-C_6H_4NR_1R_2$ wherein substituent A is a nitrogen heterocyclic nucleus; and substituents R_1 , R_2 , R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl, aralkyl, aryl and alkaryl groups; the medium having been heated to at least the color transition temperature of the dye.

25. Medium as in claim 25 wherein the photoconductor comprises titanium dioxide.

26. Medium as in claim 24 wherein the photoconductor is titanium dioxide of an average particle size of 250 milimicrons or less and the dye is 4-methyl-2-[p-(dimethylamino)styryl] thiazole methochloride.

27. Medium as in claim 25 wherein the photoconductor is titanium dioxide of an average particle size of 250 milimicrons or less and the dye is 2-[p-(dimethylamino)styryl]-3,5-dimethylthiadiazolium nitrate.

28. Medium as in claim 25 wherein the substituent A is selected from the group consisting of a thiazole nucleus, isoxazole nucleus, quinoline nucleus, benzimidazole nucleus, indole nucleus, benzothiazole nucleus and thiadiazole nucleus, said dye being in the form of a quaternary salt or acid additional salt.

29. Medium as in claim 25 wherein the dye is 4-methyl-2-[p-(dimethylamino)styryl] thiazole methochloride.

30. Medium as in claim 25 wherein the dye is 2-[p-(dimethylamino)styryl]-3,5-dimethylthiadiazolium nitrate.

31. A method of recording a latent image which comprises heating imagewise a copy medium comprising a photosensitive metal containing semiconductor and a sensitizing dye which undergoes a color change upon such heating and then exposing the copy medium to radiation which will selectively activate the heated portions of the copy medium and wherein the dye is of the formula $A-CR_3=CR_4-C_6H_4NR_1R_2$ in which substituent A is a nitrogen heterocyclic nucleus; and substituents R_1 , R_2 , R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl, aralkyl, aryl and alkaryl groups; and heating to at least the color transition temperature of the dye.

32. A method as in claim 31 comprising additionally contacting with image forming materials comprising a solution of metal ions to form a permanent, irreversible image in the activated portions of the copy medium.

* * * * *

5

10

15

20

25

30

35

40

45

50

55

60

65

70

75