United States Patent

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[54] **HEAT AND LIGHT SENSITIVE LAYERS CONTAINING HYDRAZONES**
24 Claims, No Drawings

[52] **U.S. Cl.** **96/67,** 96/95, 250/65
[51] **Int. Cl.** **G03c 1/76**
[50] **Field of Search** 96/95, 107, 67, 102; 250/65

[56] **References Cited**

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P. S. & E., Vol. 7, 1963, p. 364– 370. D. W. Woodward, V. C. Chambers & A. B. Cohen.

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ABSTRACT: Certain ketone and aldehyde organic hydrazones exhibit utility in radiation-sensitive layers and elements as a spectral sensitizer for silver halide and as a selective reducing agent in photographic, thermographic and photothermographic layers.

HEAT AND LIGHT SENSITIVE LAYERS CONTAINING HYDRAZONES

This invention relates to the production of images, and more particularly, to the production of images by thermographic or photographic means or combinations thereof using heat or light-sensitive layers containing organic hydrazone compounds.

It is known in the photographic art to utilize certain hydrazone compounds in conjunction with the production of images. For example, U.S. Pat. No. 2,423,710, describes the use in photographic emulsions of p-dialkylaminocinnamic aldehyde phenylhydrazones as chemical supersensitizers for 2'-cyanine or oxacarbocyanine spectral-sensitizing dyes. However, the range and variety of utility of hydrazones heretofore known for image-forming operations are of limited scope.

Accordingly, it is an object of this invention to provide, for photographic image-forming purposes, new light-sensitive layers and elements which contain organic hydrazone compounds.

It is another object of the present invention to provide, for image-forming purposes, new heat-sensitive layers and elements which contain organic hydrazone compounds.

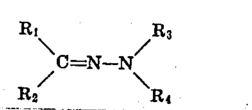
Yet another object of this invention is to provide new, spectrally sensitized photographic layers and elements.

Yet another object of this invention is to provide, for image-forming purposes, new layers and elements capable of reproducing images by thermographic and photothermographic means.

Another object of the present invention is to provide novel image-forming processes.

Yet additional objects will become apparent from a consideration of the following specification and appended claims.

The objects of this invention are accomplished with image-recording elements that have a support coated with a radiation-sensitive composition containing organic hydrazone compounds having the formula:



wherein:

R_1 and R_3 are each either a hydrogen atom, a lower alkyl radical or a carbocyclic aryl radical,

R_2 is either a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical or a heterocyclic radical, and

R_4 is either a lower alkyl radical, a carbocyclic aryl radical or a heterocyclic radical,

and an image-promoting component that includes radiation-sensitive silver salts, radiation-sensitive metal oxides and mixtures thereof.

As defined herein, lower alkyl radicals include straight and branched chain aliphatic radicals having from one to six carbon atoms and preferably from one to four carbon atoms. Typical lower alkyl radicals are methyl, ethyl, chloroethyl, isopropyl and the like. Carbocyclic aryl radicals of the subject invention are deemed to include mono- and polycyclic, carbocyclic aryl radicals, preferably having from six to 18 atoms in the aryl nucleus. Exemplary of aryl radicals are phenyl, anthracenyl, aminophenyl, diethoxyphenyl, triacetylphenyl, p-dimethylaminophenyl, p-sulfophenyl, etc. Aralkyl radicals are such radicals as phenethyl and include radicals having both an aryl moiety, such as the described aryl radicals, and an alkyl moiety which is preferably a lower alkyl radical as noted herein. Aralkenyl radicals include radicals like phenethenyl and additional radicals having an aryl moiety such as those aryl radicals mentioned herein and an alkenyl moiety that includes unsaturated aliphatic radicals having from two to four carbon atoms such as ethenyl and 1,3-butadienyl. Heterocyclic radicals useful herein include mono- and polycyclic heterocyclic radicals having from five to about 14 atoms and typically having from five to six atoms including hetero atoms in each cyclic nucleus. Exemplary of such heterocyclic radicals are pyridyl, quinolyl, julolidinyl, etc.

Particularly preferred organic hydrazone compounds of this invention include ketone and aldehyde hydrazones such as:

benzaldehyde phenylhydrazone
benzaldehyde methylphenylhydrazone
2-thiophenaldehyde phenylhydrazone
2-pyridylaldehyde phenylhydrazone
4-pyridylaldehyde phenylhydrazone
3-pyridylaldehyde phenylhydrazone
4-aminobenzaldehyde methylhydrazone
salicylaldehyde phenylhydrazone
diethoxybenzaldehyde phenylhydrazone
glyoxal diphenylhydrazone
cinnamaldehyde phenylhydrazone
cinnamylideneacetaldehyde methylphenylhydrazone
triacetylbenzene triphenylhydrazone
4-aminobenzaldehyde methylphenylhydrazone
anthracenealdehyde phenylhydrazone
dimethylaminobenzaldehyde-4-sulfophenylhydrazone
dimethylaminocinnamaldehyde-4-sulfophenylhydrazone
julolidine aldehyde-4-sulfophenylhydrazone
4-(dimethylamino)benzaldehyde 2-quinolylhydrazone

The hydrazone compounds of the general formula noted above can be prepared by known procedures. They are generally obtained in a simple manner by the condensation of equimolar quantities of a hydrazine with compounds containing a carbonyl function, for example, aldehydes, ketones and quinones, in an organic solvent such as ethanol.

As noted herein, the subject hydrazone compounds are utilized in the presence of or in combination with certain radiation-sensitive, image-promoting components. The term radiation-sensitive, as used herein, refers broadly to electromagnetic radiation and includes both heat and light rays. Advantageous electromagnetic waves are, for example, gamma rays, ultraviolet radiation, visible light and infrared radiation.

The types of hydrazones suitable for use in the present invention can also be utilized as photoconductors in electrophotographic systems; this is particularly true for the compound 4-aminobenzaldehyde methylphenylhydrazone. Alternatively, the hydrazone compounds of this invention can be used in conjunction with a polyhalogen compound such as iodoform or carbon tetrachloride to produce printout images.

The radiation-sensitive silver salts of the present invention are those silver salts that can be reduced to metallic silver by exposure to electromagnetic radiation, typically heat or light rays. More particularly, the radiation-reducible silver salts of this invention comprehend primarily heat-sensitive substantially water-insoluble silver salts of monocarboxylic and dicarboxylic acids having from two to about 22 carbon atoms such as silver oxalate, silver stearate and silver behenate. Additionally, light-sensitive silver halides are advantageously employed herein, as are light-sensitive, water-soluble silver salts like silver nitrate, silver acetate and silver lactate. Other silver salts useful in the practice of this invention, that are reduced to metallic silver by the impingement of electromagnetic rays are known to those skilled in the art.

Radiation-sensitive metal oxides useful in this invention are those metal oxides, both photoconductors and nonphotoconductors, which will transfer and donate electrons when activated by exposure to suitable electromagnetic radiation, typically rays of shorter wavelengths like X-rays as well as ultraviolet and actinic radiation. Typical such oxides are aluminum oxide, zinc oxide, titanium dioxide and antimony trioxide, but still additional radiation-sensitive metal oxides are known to those skilled in the art. In the radiation-sensitive compositions and elements described herein, mixtures of radiation-sensitive silver salts and metal oxides are advantageously employed.

As mentioned previously, the subject hydrazones are advantageously admixed with a light-sensitive silver halide salt. More particularly, in photographic elements having a support coated with at least one light-sensitive layer comprising a silver halide emulsion and a sensitizing amount of at least one of the hydrazone compounds described herein. The silver halide is spectrally sensitized to longer wavelengths by the organic hydrazone. Preferred as a spectral sensitizer for silver halide, such as silver chloride, silver bromide, silver bromoiodide, silver chloroiodide and the like, is the hydrazone 4-(dimethylamino)benzaldehyde quinol-2-yl-hydrazone.

A wide variety of silver halide emulsions are spectrally sensitized in this fashion, such as gelatinosilver halide emulsions and silver halide emulsions containing other hydrophilic colloid binders such as polyvinyl alcohol, cellulose acetate and the like binder materials. Additionally, other addenda such as hardeners, antifoggants. coating aids and other typical ingredients can be present in the silver halide emulsions that are spectrally sensitized as described herein.

The subject hydrazones are typically added to silver halide emulsions in extremely small sensitizing amounts, generally varying between about 1 mg. and about 3 3 per gram of silver. More highly varying amounts can also be employed in accordance with conventional practice without detrimental effects. To produce a composite, sensitized photographic element, a silver halide emulsion containing at least one of the organic hydrazone compounds of this invention is coated on a support material and dried. Coating thickness is susceptible of somewhat wide variation, but typically wet thicknesses of from about 0.001 inch 3 mg. 0.006 inch are employed. More extensive variations can be used where desired for particular coating techniques or sensitometric characteristics.

The method of coating can be any of those known in the coating art, including such means as dipping, whirler coating and flow coating, except that hopper-coating or doctor blade coating means are preferred since they offer a higher degree of precision as regards coating thickness. Support materials which are advantageous in preparing these spectrally sensitized silver halide photographic elements are susceptible of extensive interchange and typically include cellulose esters such as cellulose acetate, cellulose butyrate, cellulose nitrate and cellulose acetate butyrate as well as other polymeric materials like polystyrene and poly(ethylene terephthalate). Additionally, papers including polyethylene and polypropylene coated paper are advantageous supports, as is baryta pigmented and other pigmented papers. Other support materials are well known in the art.

Subsequent to drying the silver halide containing layer, the composite photographic element can be imagewise exposed and processed to yield a visible photographic silver image. Since the hydrazone spectrally sensitizes the silver halide emulsion to visible light rays, the exposing means can be either a source of actinic radiation or a source of longer wavelength visible light to which the emulsion is sensitized by the subject organic hydrazone.

After an imagewise exposure, a spectrally sensitized silver halide photographic element as described herein can be processed in a conventional silver halide photographic developing composition to produce a silver image. Such developing compositions incorporate a silver halide developing agent, typically a hydroxylated aryl compound, such as dihydroxybenzenes like hydroquinones, catechols and pyrogallols, as well as other polyhydroxylated compounds such as ascorbic acid. Additional developing agents include aminophenols, p-phenylene-diamines and 3-pyrazolidones. Exemplary of silver halide developing agents that are advantageously used herein are compounds like 2-methyl-3-chlorohydroquinone, bromohydroquinone, catechol, 5-phenylcatechol, pyrogallol monomethylether(1-methoxy-2,3-dihydroxy benzene), 5-methylpyrogallol monomethyl-ether isoascorbic acid, N-methyl-p-aminophenol, dimethyl-p-phenylene diamine, 4-amino-N,N-di(n-propyl)anilene and 6-amino-1-ethyl-1,2,3,4-tetrahydroquinoline. After image development, the image is stabilized by treatment with a photographic fixing agent. Conventional fixing agents or silver halide solubilizing agents include water-soluble thiosulfates, and thiocyanates, and mercaptans, such as ammonium thiosulfate sodium thiocyanate, and the disodium salt of 2-mercapto-4-hydroxy-5-aminopyrimidine. hydroxy-5-aminopyrimidine. A particularly preferred fixing agent is sodium thiosulfate. Stabilization is generally accomplished by treatment with a composite fixing bath that incorporates a fixing agent such as those mentioned hereinabove.

In another aspect, the subject hydrazones function as heat and light activated selective reducing agents for metal ions, silver ions for example, in photographic, thermographic and photothermographic image-forming systems. Selective photo or photothermal reduction advantageously occurs subsequent to the formation of a metallic or other latent image which catalyzes the reduction of metal ions by the organic hydrazone compounds of this invention to form a visible image. Illustrative of this capability is an alternative development procedure for an imagewise-exposed silver halide element such as is described hereinabove and containing at least one of the organic hydrazones of this invention. A visible photographic silver image can be produced on such an imagewise-exposed element merely by treatment with a conventional fixing agent and simultaneously exposing the element to visible light radiation. Although the particular reaction mechanism is not unequivocally known, it is speculated that the overall exposure of the incorporated hydrazone produces a reducing agent in the coating which selectively reduces the silver ions of the solubilized silver halide onto the latent image specks produced by the first, imagewise exposure of the silver halide photographic element. Continued exposure of the silver halide layer when it is immersed in the fixing bath produces no additional latent image.

Advantageous selective reduction is also accomplished with thermographic elements having a support such as those described herein coated with at least one of the hydrazones described herein and at least one substantially water-insoluble silver slat, typically of monocarboxylic and dicarboxylic acids having from two to about 22 carbon atoms, such as silver cinnamate, silver behenate, silver stearate and silver oxalate. Coating techniques can be any of those noted hereinabove. The amount of hydrazone included in such element need only be sufficient to advantageously reduce the silver salt to metallic silver upon a suitable exposure, and in like fashion the silver salt need only be present in an amount that provides a reduced silver image of a desirable density for viewing purposes. Typically, the hydrazone and silver salt are included in weight ratios of from about 1:2 to about 1:4, but wider ratios can be used if desired. Although the water-insoluble silver salts are primarily heat sensitive and do not exhibit an excessive sensitivity to light radiation, exposure to ultraviolet and actinic light radiation can produce discoloration, and a suitable stabilizer such as a difunctional alkylene imine like N,N'-bis-1,2-ethyleneisophthalimide can be included in the heat-sensitive layer to prevent undesired photoreduction of silver. In a solely thermographic element such as this type, an imagewise thermal reduction is obtained without a preexisting latent image by effecting an imagewise concentration of heat radiation to selectively trigger the reduction reaction in only image areas. Such a pattern is typically produced by contacting the image-forming element, during the application of heat by such means as infrared radiation, with an original bearing an imagewise distribution of a heat-absorbing material like an infrared-absorbing carbon base printing ink. Such images can be stabilized against further printing out by suitable treatment with a conventional fixing bath such as those described above. Other means of image stabilization can be utilized if desired.

Additionally, at least one water-soluble silver salt such as silver nitrate, silver acetate and silver lactate, or any other light-sensitive, water-soluble silver salt, can be advantageously incorporated into the element already having a hydrazone compound and a water-insoluble silver salt in the radiation-sensitive layer. The water-soluble silver salt renders the element desirably light sensitive, and after an imagewise exposure to activating light radiation such as actinic light and the simultaneous formation of a metallic silver latent image by photoreduction of silver ions of the water-soluble silver salt, a visible metallic silver image can be produced by treatment with either heat or light radiation. Upon suitable exposure to either heat rays or an imagewise pattern of light exposure such as intense tungsten radiation, the latent image catalyzes the hydrazone's reducing action a metallic silver image is produced by selective reduction in only those areas corresponding to the latent image area. Such a water-soluble silver salt need only be present in an amount sufficient to provide a metallic silver latent image that will promote the reduction of the water-insoluble silver salt upon development. Typically, amounts by weight of from about 0.5 part to about two parts per part of hydrazone are used.

Alternatively, selective reduction produced by the subject hydrazone compounds can be encouraged or catalyzed by latent images obtained from the irradiation of photosensitive species other than silver halide, photoactivatable metal oxides for example, such as those described hereinabove. An element incorporating a support having coated thereon a light-sensitive layer including a hydrazone compound of this invention and a photoactivatable metal oxide can be imagewise exposed to light radiation and treated with a water-soluble silver salt solution such as aqueous silver nitrate to produce a visible metallic silver image in those areas corresponding to the imagewise exposure. A preferred light-sensitive metal oxide is titanium dioxide. The light-sensitive layer can also contain components like a hydrophilic colloid binder material such as gelatin or polyvinyl alcohol as well as other typical emulsion addenda such as spectral-sensitizing dyes, hardeners, coating aids and the like. The light exposure can be to actinic light rays or to longer wavelength visible light radiation if the titanium dioxide or other photoactivatable metal oxide is spectrally sensitized to such longer wavelengths. Additionally in the preparation of a light radiation sensitive element containing a metal oxide like those noted herein, the choice of both a support material and a coating technique can be any of those described elsewhere herein. The respective amounts of metal oxide and hydrazone need only be sufficient to effect an adequate reduction of metal ion in the processing medium, and typically, ratios of from about 20 parts to about 40 parts by weight of metal oxide per part of hydrazone compound are used. Wider ratios can be employed if desired.

The described elements containing a photosensitive metal oxide can also incorporate, in the light-sensitive layer, at least one reducible silver salt. The silver salt can be either a water-insoluble or a water-soluble salt like those described herein, and subsequent to an imagewise exposure to produce a photographic latent image a variable conductivity in the photoactivatable metal oxide, it can be developed by various techniques to produce a visible silver metal image. The reducible silver salt is present in an amount sufficient to provide a visible silver image of a density adequate for viewing purposes. Conventionally, amounts by weight of from about two parts to about four parts per part of hydrazone compound are used. Treatment with a photographic developing agent such as those described elsewhere herein produces a photographic silver image, but such processing does not utilize the advantageous selective reducing properties of the subject hydrazones. Alternatively, it can be processed as either a wholly photographic printout element or as a photothermographic element, since treatment with longer periods of intense light irradiation such as a 5-second exposure at a distance of 12 inches with a 500-watt tungsten lamp or heating to temperatures of about 190° F. effect advantageous selective reduction of silver ion to produce a dense metallic silver image in those areas corresponding to the latent image.

Although either type of reducible silver salt can be used advantageously, the substantially water-insoluble silver salts are preferred, however, since they exhibit both a susceptibility to advantageous reduction during image development and a higher resistance to undesired degradation during storage.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

To 100 ml. of 5 percent gelatin is added 2.0 ml. of 10 percent formaldehyde, 2.0 ml. of a 7½percent saponin solution, 20 ml. of a silver chloride emulsion which contains 1 mole of silver and 12 g. of gelatin in 0.52 kg. of emulsion. To separate 15 ml. portions of this mixture is added 1.0 ml. of a 1 percent acetone solution of the following hydrazones as spectral sensitizers for the silver halide.

1. 4-aminobenzaldehyde methylphenylhydrazone
2. anthracenealdehyde phenylhydrazone
3. diethoxybenzaldehyde phenylhydrazone
4. dimethylaminobenzaldehyde-4-sulfophenylhydrazone
5. dimethylaminocinnamaldehyde-4-sulfophenylhydrazone
6. julolidinealdehyde-4-sulfophenylhydrazone
7. dimethylaminobenzaldehyde quinol-2-ylhydrazone

Coatings of the above compounds are made at 0.004-inch wet thickness and dried. Wedge spectrograms show an extension of the spectral response as follows, when the strips are processed by immersion in a silver halide developing solution having the formula:

Water	500 cc.
Elon	3 g.
Sodium sulfite (desiccated)	45 g.
Hydroquinone	12 g.
Sodium carbonate (monohydrate)	80 g.
Potassium bromide	2 g.
Water to make	1,000 cc.

and immersion in a photographic fixing bath having the formula:

Water	600 cc.
Sodium thiosulfate	240 g.
Sodium sulfite (desiccated)	15 g.
Acetic acid (28% aqueous)	48 cc.
Boric acid (crystals)	7.5 g.
Potassium alum	15 g.
Water to make	1,000 cc.

after which they are washed and dried:

Material	Response
A. Control (silver chloride)	300–400 mμ
B. Control plus compound 1.	300–500 mμ with a peak at 420 mμ
C. Control plus compound 2.	300–540 mμ with a peak at 500 mμ
D. Control plus compound 3.	300–580 mμ with a peak at 540 mμ
E. Control plus compound 4.	420–600 mμwith a peak at 510 mμ
F. Control plus compound 5.	410–540 mμwith a peak at 450 mμ
G. Control plus compound 6.	410–530 mμwith a peak at 500 mμ
H. Control plus compound 7.	400–560 mμwith a broad peak over this entire range.

EXAMPLE 2

Photographic elements are prepared as in example 1. After an imagewise exposure as in example 1 to form a latent silver image, the elements are immersed in the fixing bath described in example 1 and simultaneously exposed to white light rays, whereupon a dense silver image is produced in the previously imagewise-exposed areas. The hydrazone compound functions as a selective reducing agent in those areas bearing a latent silver image.

EXAMPLE 3

A thermographic element is prepared by coating a paper support with a composition containing:

silver cinnamate	0.15 g.
anthracenealdehyde phenylhydrazone	0.05 g.
acetone	4.00 ml.
solution of 36 g. ethyl acetate 240 ml. acetone and 60 ml. alcohol (95:5 ethanol and methanol)	0.5 ml.

After drying, the coated element is contacted to a typewritten page and while in contact, the two are heated to about 190° F. A dense deposit of metallic silver is produced in those areas of the element corresponding to the image areas of the typewritten page.

EXAMPLE 4

A silver oxalate-silver iodide precipitate is prepared as described in U.S. Pat. No. 3,143,419 by mixing:

A. Potassium oxalate monohydrate	54.2 g.
Distilled Water	200 ml.
B. Silver nitrate	13.5 g.
Distilled water	150 ml.
C. Potassium iodide	5.6 g.
Distilled water	150 ml.

The silver nitrate solution is added to solution A and the resulting silver oxalate precipitate is washed by decantation. Solution C is then added and the resulting mixed precipitate is washed by decantation. The wet slurry is then mixed 10:1 with a 1 percent acetone solution of cinnamaldehyde phenylhydrazone and the mixture is flow coated on filter paper. A photothermographic paper results. Exposure of the coating on a wedge spectrograph for 10 seconds at a 1-mm. slit width followed by thermal development at 120° C. for 5 seconds produces a heat-developed silver image in the exposed areas. Alternatively, the element can be developed to produce a silver image by printout techniques using higher levels of an imagewise light exposure.

EXAMPLE 5

A photographic element is prepared by coating a paper support material with a 0.004 wet thickness coating of a formulation having the composition:

A. Distilled water	25 cc.
B. Titanium dioxide	3 g.
C. 10% gelatin	20 cc.
D. 7½% saponin	2 cc.
E. 10% formaldehyde	0.5 cc.

After drying, the titanium dioxide element is flow coated with a 1 percent solution of 4-aminobenzaldehyde methylphenylhydrazone dissolved in 10 cc. of acetone. The dried coating is then exposed to a 500-watt tungsten photoflood lamp through a line image for a period of about 1 second. This exposure produces a latent image that is made visible by immersing the exposed layer in 0.5 percent aqueous silver nitrate, since the hydrazone compound functions as a selective reducing agent. The permanence of the image is improved by treatment with a sodium thiosulfate fixing bath to remove undeveloped silver salt.

EXAMPLE 6

A titanium dioxide photographic element is prepared according to the procedure of example 5, except that the flow coating contains 2 cc. of a 1 percent acetone solution of cinnamaldehyde phenylhydrazone, 2 cc. of a 1 percent aqueous silver nitrate solution and sufficient acetone to dissolve any precipitate. The composite photographic element is dried and then exposed through a line original for 5 seconds to the tungsten light of a 500-watt photoflood lamp at a distance of 12 inches from the exposing plane. A dense silver printout image is formed in the exposed areas directly upon exposure, since the hydrazone acts as a selective reducing agent in those areas bearing a latent image. A second element is prepared in like fashion, except that the exposure time is shortened to one-tenth of a second. No visible printout is observed; however, when the exposed coating is immersed in a black-and-white developer solution as in example 1, a dense silver image is produced in the exposed areas. A third element is also prepared in like fashion and imagewise exposed for one-tenth second as with the second element. Image development is obtained by heating the paper on a hot plate at 190° F., which produces a dense visible deposit of metallic silver in the exposed areas by photothermographic means.

EXAMPLE 7

A slurry of 0.15 g. of silver cinnamate is prepared in 3 ml. of acetone. To this slurry is added 0.05 g. of anthracenealdehyde phenylhydrazone in 1 ml. of acetone, followed by the addition of 5 drops of the following solution:

Ethyl acetate	36.0 g.
Acetone	240.0 ml.
Alcohol (95% ethanol, 5% methanol)	60.0 ml.

The resulting mixture is flow coated onto a titanium dioxide photographic element prepared as in example 5. The entire preparation is carried out under gold-colored fluorescent lamps. The composite element is exposed to produce a wedge spectrogram which shows a sensitivity from 280–560 mμ when the element is heated to 190°–200° F. over a hotplate. A similar element is exposed for 1½ seconds through a line original in a Photocopier (model 107 marketed by the Minnesota Mining and Manufacturing Company). A very faint tan image becomes visible in the exposed areas. The element is then heated by pressing it in contact with a hotplate at 190° F. for about 2 seconds whereupon a dark reddish-brown image appears in the exposed areas. The background remains the yellow color of the original coating. At high levels of exposure, coatings prepared in this way print out directly. Alternatively, the latent image can be intensified by photographic developing solutions, for example, by immersion in a black-and-white developer composition as in example 1. For permanence, the image may be fixed in thiosulfate solutions such as the fixing bath described in example 1.

EXAMPLE 8

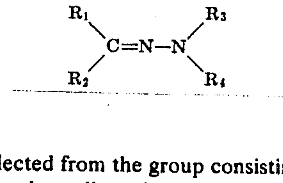
A paper support material coated with silver behenate is flow coated with a solution containing 2 cc. of a 1 percent acetone solution of cinnamaldehyde phenylhydrazone, 2 cc. of a 1 percent aqueous silver nitrate solution and sufficient acetone to dissolve any precipitate. The coating is then dried. Exposure and development by printout, photographic or photothermographic means as in example 6 produces a dense silver image in the exposed areas.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An element for recording image, said element comprising a support having coated thereon a radiation-sensitive composition comprising:

a. a hydrazone having the formula:



wherein:

1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and

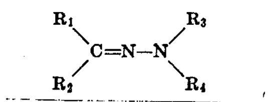
4. R_4 is selected from the group consisting of a lower alkyl radical, a carbocyclic aryl radical and a heterocyclic radical, and

b. an image-promoting component selected from the group consisting of:

1. a radiation-sensitive silver salt,
2. A radiation-sensitive metal oxide, and
3. mixtures thereof.

2. An element for recording images, said element comprising a support having coated thereon a radiation-sensitive layer comprising:

a. a hydrazone having the formula:



wherein:

1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and
4. R_4 is selected from the group consisting of a lower alkyl radical, a carbocyclic aryl radical and a heterocyclic radical, and

b. a reducible silver salt.

3. An element as described in claim 2 wherein the reducible silver salt is selected from the group consisting of substantially water-insoluble silver salts of monocarboxylic and dicarboxylic acids having from two to about 22 carbon atoms.

4. An element as described in claim 3 wherein said reducible, water-insoluble silver salt is selected from the group consisting of silver cinnamate, silver behenate and silver oxalate.

5. An element as described in claim 2 wherein the reducible silver salt is a water-soluble silver salt selected from the group consisting of silver nitrate, silver acetate and silver lactate.

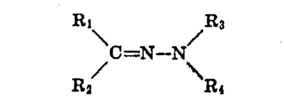
6. An element as described in claim 2 wherein said reducible silver salt radiation-sensitive component comprises the admixture of:

a. a silver salt selected from the group consisting of water-insoluble salts of monocarboxylic and dicarboxylic acids having from two to about 22 carbon atoms, and

b. a water-soluble silver salt selected from the group consisting of silver nitrate, silver acetate and silver lactate.

7. An element for recording images, said element comprising a support having coated thereon a light-sensitive layer comprising:

a. a hydrazone having the formula:



wherein:

1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and
4. R_4 is selected from the group consisting of a lower alkyl radical, a carbocyclic aryl radical and a heterocyclic radical, and

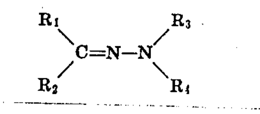
b. a silver halide.

8. An element as described in claim 7 wherein the hydrazone is selected from the group consisting of:

a. 4-aminobenzaldehyde methylphenylhydrazone,
b. anthracenealdehyde phenylhydrazone,
c. diethoxybenzaldehyde phenylhydrazone,
d. dimethylaminobenzaldehyde-4-sulfophenylhydrazone,
e. dimethylaminocinnamaldehyde-4-sulfophenylhydrazone,
f. julolidinealdehyde-4-sulfophenylhydrazone, and
g. dimethylaminobenzaldehyde-quinol-2-ylhydrazone.

9. An element for recording images, said element comprising a support having coated thereon a light-sensitive layer comprising:

a. a hydrazone having the formula:



wherein:

1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and
4. R_4 is selected from the group consisting of a lower alkyl radical, a carbocyclic aryl radical and a heterocyclic radical, and

b. a light-activatable metal oxide.

10. An element as described in claim 9 wherein said light-activatable metal oxide is titanium dioxide.

11. An element as described in claim 9 wherein the light-sensitive layer also contains at least one reducible silver salt.

12. An element as described in claim 11 wherein the reducible silver slat is selected from the group consisting of water-insoluble silver salts of monocarboxylic and dicarboxylic acids having from two to about 22 carbon atoms.

13. An element as described in claim 12 wherein the silver salt is selected from the group consisting of silver cinnamate, silver behenate and silver oxalate.

14. An element as described in claim 11 wherein the reducible silver salt is a water-soluble silver salt selected from the group consisting of silver nitrate, silver acetate and silver lactate.

15. An element for recording images, said element comprising a support having coated thereon a light-sensitive layer comprising:

a. a hydrazone selected from the group consisting of:

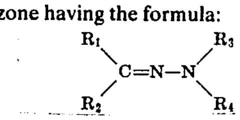
1. 4-aminobenzaldehyde methylphenylhydrazone,
2. anthracenealdehyde phenylhydrazone,
3. diethoxybenzaldehyde phenylhydrazone,
4. dimethylaminobenzaldehyde-4-sulfophenylhydrazone,
5. dimethylaminocinnamaldehyde-4-sulfophenylhydrazone,
6. julolidinealdehyde-4-sulfophenylhydrazone, and
7. dimethylaminobenzaldehyde-quinol-2-ylhydrazone.

b. titanium dioxide, and

c. a reducible silver salt.

16. A process for producing images on an element comprising:

a. a hydrazone having the formula:



wherein:

1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and
4. R_4 is selected from the group consisting of a lower alkyl radical and a heterocyclic radical, and

b. a reducible silver salt,

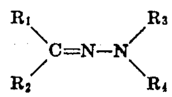
which process comprises imagewise exposing said element to electromagnetic radiation for a period of time sufficient to produce a metallic silver image in the irradiated areas.

17. A process as described in claim **16** wherein the electromagnetic radiation comprises heat radiation.

18. A process as described in claim **16** wherein the electromagnetic radiation comprises light radiation.

19. A process for producing images on an imagewise-exposed element comprising a support having coated thereon a light-sensitive layer comprising:

a. a hydrazone having the formula:



wherein:

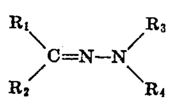
1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and
4. R_4 is selected from the group consisting of a lower alkyl radical, a carbocyclic aryl radical and a heterocyclic radical, and

b. a silver halide,

which process comprises treating said imagewise-exposed element with a processing medium selected from the group consisting of a silver halide developing composition and a silver halide fixing agent for a period of time sufficient to produce a metallic silver image in the exposed areas.

20. A process for producing images on an image light exposed element comprising:

a. a hydrazone having the formula:



wherein:

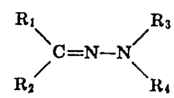
1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and
4. R_4 is selected from the group consisting of a lower alkyl radical, a carbocyclic aryl radical and a heterocyclic radical, and

b. a light-activatable metal oxide,

which process comprises treating said imagewise exposed element with a solution of a reducible, water-soluble silver salt for a period of time sufficient to produce a metallic silver image in the exposed areas.

21. A process for producing images on an imagewise light exposed element comprising:

a. a hydrazone having the formula:



wherein:

1. R_1 is selected from the group consisting of a hydrogen atom, a carbocyclic aryl radical and, when R_2 is an aralkenyl radical, a lower alkyl radical,
2. R_2 is selected from the group consisting of a carbocyclic aryl radical, an aralkyl radical, an aralkenyl radical selected from the group consisting of ethenyl and 1,3-butadienyl and a heterocyclic radical,
3. R_3 is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a carbocyclic aryl radical, and
4. R_4 is selected from the group consisting of a lower alkyl radical, a carbocyclic aryl radical and a heterocyclic radical, and

b. a light-activatable metal oxide, and

c. a reducible silver salt,

which process comprises treating said element with a developing means for a period of time sufficient to produce a metallic silver image in the exposed areas.

22. A process as described in claim **21** wherein said developing means comprises heat.

23. A process as described in claim **21** wherein said developing means comprises light irradiation corresponding to the original imagewise exposure.

24. A process as described in claim **21** wherein said developing means comprises a photographic silver halide developer.