United States Patent Office 3,446,619
Patented May 27, 1969

3,446,619

RADIATION SENSITIVE SILVER-DYE COMPLEXES

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No Drawing. Filed Nov. 16, 1964, Ser. No. 411,594
Int. Cl. G03c 1/40
U.S. Cl. 96—63 40 Claims

ABSTRACT OF THE DISCLOSURE

A radiation-sensitive composition which consists essentially of at least one reaction product of silver and a spectral sensitizing dye which upon exposure to radiation forms active sites for physical development. Typical sensitizing dyes include cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benzylidenes.

This invention concerns light sensitve photographic elements particularly those using a light sensitive coating containing a silver complex of a sensitizing dye.

Light sensitive coatings based on silver customarily used in photography are based on silver halide compositions carried in water permeable colloid layers. These silver halide emulsions are relatively expensive to prepare due to the amount of silver used. Moreover, they produce a photographic image which is limited in its resolving power due to the graininess of the silver halide particles. In addition, the silver halide emulsion normally requires chemical development including a fixing step in which the undeveloped silver halide is removed. The silver halide salts do not absorb beyond about 500 mμ and must be dyed with sensitizing dyes to produce sensitivity beyond that wavelength.

It is known that sensitizing dyes are effective with both slow and high speed photographic emulsions. The same sensitizing dyes may confer green or red sensitivity for both very slow emulsions or to the highest speed emulsions available. However, in the green or red region of the spectrum the silver halide acts only as an acceptor of the response produced by exposure of the sensitizing dye. The limit of photographic sensitivity possible is not limited by sensitizing dyes but by the substrate used to adsorb the dye.

The spectral sensitization of silver halide is based on the use of the sensitizing dye adsorbed to the silver halide surface. It is generally accepted that light energy absorbed by a mobile silver io nfrom the silver halide lattice to manner that an electron appears in the conduction band of the silver halide, the electron is trapped and neutralized by a mobile silver ion from the silver halide lattice to form a speck of silver. The silver halide acts as a medium through which the dye passes its energy so that ultimately a speck of silver is formed.

Spectral sensitization of silver halide by addition thereto of the reaction product of a sensitizing dye and a soluble silver salt is known. This reaction product, identified herein as the silver-dye complex, reacts with the silver halide to produce silver halide grains with the dye adsorbed thereon. The silver halide emulsion which is mixed withe such a silver-dye complex has its spectral sensitvity extended into the region of absorption of the dye.

To improve further the photographic sensitivities in the visible region of the spectrum, more effective photographic substrates must be devised or more direct ways found to detect or respond to the effect that an exposure to light produces in a sensitizing dye.

We have now found in the present invention a method of forming silver-dye complexes of sensitizing dyes which results in a photosensitive medium of which the sensitizing dye is an integral part, so that energy absorbed by the dye is not transferred but is used directly to form metallic silver as a result of the exposure of the silver-dye complex.

The silver-dye complexes, which may be highly colored, have the property of producing silver directly upon an exposure to light and may be developed by any method of physical development.

One object of this invention is to provide light sensitive silver complexes of organic sensitizing dyes. Another object is to provide light-sensitive coatings free from the usual graininess of silver halide emulsions, making possible higher resolving power images. An additional object is to provide light sensitive elements which require only very small amounts of the light sensitive material. A still further object is to provide a light sensitive system in which no fixation is required of the image. Another object is to provide a light sensitive system which can be processed using the simple diffusion transfer process for amplifying the initial photo effect. Another object is to provide light sensitive layers which need no secondary means of sensitization to produce visible sensitivity but depend only on the proper choice of dye to form a light sensitive species of any desired spectral sensitivity. Additional objects will be apparent from the following disclosure.

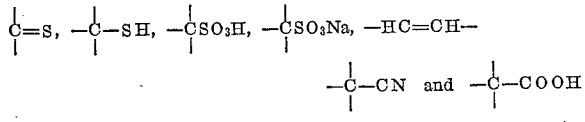
Our invention involves a reaction product (silver-dye complex) of a spectral sensitizer and silver ion, which product is dispersed in a colloid and coated on a support with any suitable water permeable colloid binder, preferably gelatin. Following exposure, this light sensitive coating is physically developed, for example, by contacting with a conventional photographic emulsion in the presence of a silver halide developer containing a silver halide solvent and then after a short time removing the silver halide emulsion in the light to reveal a silver deposit in the areas of exposure in the exposed silver-dye complex layer. A positive image will then be obtained in the silver halide emulsion when it is subsequently exposed, which can be suitably fixed if desired. It may not be necessary to fix the positive image, depending upon the time of transfer and the amount of silver halide present in the silver donor layer. As an alternative developing system, a physical developer solution may be used rather than the diffusion transfer method of development.

The following dyes are representative merocyanine dyes which may be used in this process and the region of their spectral response is indicated:

(a) 3-carboxymethyl-5-[(3-methyl-2-thiazolidinylidene)-ethylidene]rhodanine 420–560 mμ
(b) 5-[(3-methyl-2-thiazolidinylidene)ethylidene] rhodanine 460–570 mμ
(c) 5-[(3-methyl-2-thiazolidinylidene)ethylidene]-2-thio-2,4-oxazolidinedione 400–560 mμ
(d) 3-ethyl-5-[(3-methyl-2-thiazolidinylidene)ethyl-idene]-2-thio-2,4-oxazolidinedione 430–540 mμ
(e) 1-methyl-5-[(3-methyl-2-thiazolidinylidene)ethyl-idene]-2-thiobarbituric acid 430–530 mμ
(f) 3-carboxymethyl-5-[(3-ethyl-2-benzoxazolinylidene) ethylidene]rhodanine 420–580 mμ
(g) 5-(3-ethyl-2-benzoxazolinylidene)rhodanine 370–460 mμ
(h) 5-[(3-ethyl-2-benzoxazolinylidene)ethylidene] rhodanine 520–560 mμ
(i) 3-ethyl-5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1-phenyl-2-thiohydantoin 520–560 mμ
(j) 1-carboxymethyl-5-[(3-ethyl-2-benzoxazolinylidene) ethylidene]-3-phenyl-2-thiohydantoin 520–560 mμ

It has been found that a wide variety of dyes including sensitizing dyes have ability to enter into complexes of

varying strength with soluble silver salts such as silver nitrate. Representative functional groups which are useful for silver-dye complexing ability are



Sensitizing dyes with these functional groups appear to react with silver to form light sensitive species.

These silver-dye complexes are prepared by mixing the dyes with a water soluble silver salt. The resulting complex can be used in the reaction solution or colloidal suspension without being isolated. Theoretically an equimolar quantity of silver to dye is necessary to form the complex. However, it may be desirable to use an excess of silver depending upon the particular dye used and the concentration of the dye in solution.

The dyes utilized in the manner of our invention may be water soluble but in the event they are insoluble in water, solutions may be obtained by dissolving them in sufficient water miscible solvent. The water miscible solvent is not critical but may be chosen from those which are compatible with the colloid used as a binder or coating medium.

In the event a solvent soluble silver salt is used, the reaction to form the complex may be carried out in a suitable solvent.

Various dyes may be used to form the complex including known sensitizing dyes such as cyanines, merocyanines, oxonols, hemicyanines, styryls, hemioxonols, benzylidenes, etc. However, our invention is not limited to these dyes but includes any dyes which form radiation sensitive silver complexes which can be developed by physical development to form a visible image.

The following examples are intended to illustrate our invention but not to limit it in any way.

Example I

Under red safelight conditions a light sensitive emulsion was prepared in the following manner:

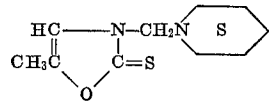
To 100 ml. of 5% gelatin were added 4 ml. of a 7½% aqueous saponin solution and 3 ml. of a 10% formaldehyde solution. To 10 ml. of the above solution were added 0.10 ml. of 0.10 molar silver nitrate solution and 0.20 ml. of a 1% methanolic solution of the merocyanine sensitizing dye, 3-carboxymethyl-5-[(3-methyl-2-thiazolinylidene)ethylidene]rhodanine, λ maximum 420–560 mμ.

Coatings having a 0.004 inch wet thickness were made on a cellulose triacetate film support.

After exposure, the coatings were developed by immersing a strip of unexposed fine grain silver chlorobromide film in a developer having the following composition:

DEVELOPER 1

Methylaminoethanol-SO_2 (18.9% SO_2)	g	190.0
Hydroquinone	g	11.6
Dimezone	g	1.0
Sodium thiosulfate pentahydrate	g	60.0
Potassium iodide	g	0.42
Water to	ml	1000.0
1% methanolic solution of 5-methyl-3-piperidinylmethyl-2-thiooxazolidine	ml	20.0



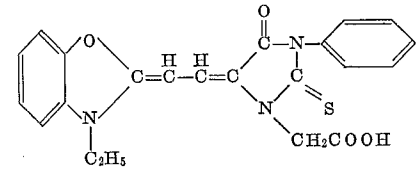
After 4 seconds, the unexposed fine grain silver chlorobromide film was rolled in contact with the exposed silver-dye layer. After a contact time of 2 minutes, the two layers were peeled apart in the light to reveal a negative image in the areas of exposure of the exposed silver-dye layer. The fine grain silver chlorobromide film was fixed in a solution of sodium thiosulfate, then washed and dried to reveal a positive image.

Example II

A light sensitive silver-dye coating was prepared as follows:

In a total of 380 ml. is contained:

10% gelatin solution	g	150
7½% saponin solution	ml	12
10% formaldehyde	ml	6
0.1 normal silver nitrate	ml	6
Solution containing 1 milligram of dye per ml. of solution	ml	2.5



The merocyanine dye used was:

1-carboxymethyl-5-[(3-ethyl-2-benzoxazolinylidene) ethylidene]-3-phenyl-2-thioyhdrantoin.

Coatings having an 0.004 inch wet thickness were made on cellulose triacetate film support.

After exposure processing was by immersion for 3 minutes in a solution physical developed of the following composition.

DEVELOPER 2

Part A:

Water	ml	800.0
Sodium sulfite	g	20.0
Sodium isoascorbate	g	20.0
Sodium carbonate·H_2O	g	50.0
Water to	liter	1.0
pH=11.0		

Part B:

Water	800.0 ml.
Sodium thiosulfate pentahydrate	30.0 g.
Silver chloride	5×10^{-2} moles.
Water to	960.0 ml.
5-methylbenzotriazole	40.0 ml. as 1% in dilute potassium hydroxide.

Mix Part A and Part B, 1:1.

The spectral response of this coating as determined by an exposure in a wedge spectrograph was from 460–560 mμ.

Example III

A light sensitive silver-dye complex layer was prepared according to the procedure described in Example II. The exposed coating was processed by immersion in a solution containing in 100 ml. of water, 0.84 gram of silver nitrate and 1.1 grams of 4,5-(2,3-D-fructo pyrano)-2-oxazolidinethione. After an immersion of from 5 seconds to 4 minutes in the silver solution the exposed silver-type complex layer was immersed for 30 seconds to 3 minutes in an undiluted Kodak D–19 solution.

Other complexing agents which formed effective soluble silver salts were the following:

(1) 3,8-dithiadecane-1,10-bis-(N-methylpiperidinium-p-toluene sulfonate)
(2) 7,13-dithianonadecane-1,19-bis-(pyridinium-p-toluene sulfonate)
(3) 3,9-dithiaundecane-1,11-bis-(N-methylmorpholinium-p-toluene sulfonate)
(4) 7,18-diaza-6,19-dioxotetracosane-1,24-bis-(pyridinium perchlorate)
(5) 3,6,9,12,15,18,21,24-octoxahexacosane-1,26-bis-

(5-ethyl-2-methyl pyridinium methane sulfonate)
(6) 3,13-dithiapentadecane-1,15-bis-(N-methylpiperidinium-p-toluene sulfonate)
(7) 3,10-dithiadodecane-1,12-bis(methyldiethylammonium-p-toluene sulfonate)

The preferred processing solution is one that contains 50.0 g. of compound (2) and 10 g. of silver nitrate per liter of distilled water. The exposed strip is immersed in the above solution for 20 seconds, allowed to drain for 10 seconds then immersed in D–19 solution for one minute; a water rinse stabilizes the processed image.

Although the spectral response of the silver-dye complex coatings is governed by the absorption of the silver-dye complex, it has been found possible to prepare silver-dye coatings which are separately sensitive in the ultraviolet, blue, green and red regions of the spectrum. By blending the appropriate combinations of silver-dye preparations, panchromatic coatings may be obtained. Since silver dye coatings may be made which have separate sensitivity to various regions of the spectrum, multilayer color films may be constructed which do not need any filter layers and which result in very high resolving power in the underlayers because of the lack of scattering in the top layers.

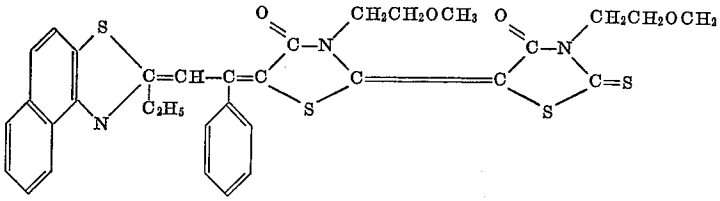
Example IV

A multilayer incorporated coupler color film may be constructed by mixing

(1)

10% gelatin solution	ml.	150
15% saponin solution	ml.	12
10% formaldehyde solution	ml.	6
0.1 normal silver nitrate	ml.	6
Red sensitizer	mg.	2.5

5-[(1-ethyl-2-(1)-β-naphtho-thiazolylidene)-α-phenylethylidene]-3-β-methoxy-thiazolidylidene-4-thiazolidone



4.4 g. of a cyan coupler of the type described in U.S. Patent 2,423,730.
385 ml. total volume.

This mixture was coated to yield 400 mg. gelatin per square foot and 2.6 mg. silver per square foot for the first layer.

(2) The second layer is the same as (1) above except that 2.5 mg. of green sensitizer 3-ethyl-5-(3-ethyl-2-benzoxazolinylideneethylidene)-1-phenyl - 2 - thiohydantoin was substituted for the red sensitizer and 5.25 g. of a magenta-forming coupler of the type described in U.S. Patent 2,600,788 was substituted for the cyan-forming coupler. Coating conditions were identical.

This coated material was exposed to a multicolored step chart and processed in a developer of the following composition:

Part A:

(1) Distilled water	ml.	750.0
(2) 2-amino - 5 - diethyl aminotoluene monohydrochloride	g.	3.8
(3) Sodium sulfite	g.	62.0
(4) Water to make 900 ml. total volume.		

Part B:

(1) Distilled water	ml.	80.0
(2) Silver nitrate	g.	5.0
(3) Water to make 100 ml. total volume.		

For use add 1 part of B to 9 parts of A.

After 5 minutes development in the above solution, a cyan image was produced in the red sensitive layer and a magenta image in the green sensitive layer. Bleaching of the physically developed silver image that was also produced in the exposed layers left a 2 color dye image containing a red and green record of the original test object.

Production of color in this 2 layer film could also be produced by placing the exposed layer in contact with an unexposed layer of a silver bromide emulsion which had been soaked for 30 seconds in a solution containing:

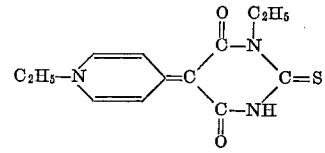
Distilled water	ml.	750
Sodium sulfite	grams	2
2 - amino - 5 - diethylaminotoluene monohydrochloride	grams	2
Sodium thiocyanate	do	10

Water to make 1 liter.
pH=11.5 with 20% sodium hydroxide.

After a contact time of 2 minutes the two layers were peeled apart to reveal a 2 color image in the exposed 2 layer silver-dye film. The silver image in the dye layers may be removed by bleaching to leave only the dye image.

Example V

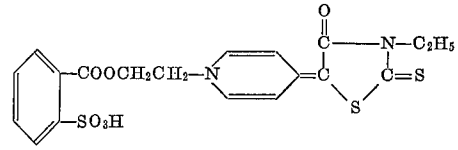
A silver-dye complex coating having only an ultraviolet sensitivity may be prepared as in Example II except that the dye



1 - ethyl-5-(1-ethyl-4(1H)-pyridylidene)-2-thiobarbituric acid is substituted for the dye used in Example II. The spectral sensitivity of this coating was from 378 to 420 mμ.

Example VI

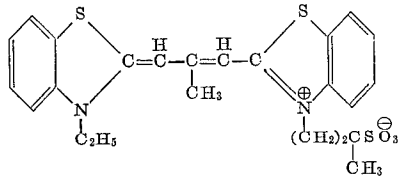
A silver-dye complex coating having only blue-green sensitivity may be prepared as in Example II except the dye



3-ethyl-5-(1-o-sulfobenzoyloxyethyl)-4(1H) - pyridylidene rhodanine is substituted for the dye used in Example II. The spectral response of this coating was from 420 to 530 mμ.

Example VII

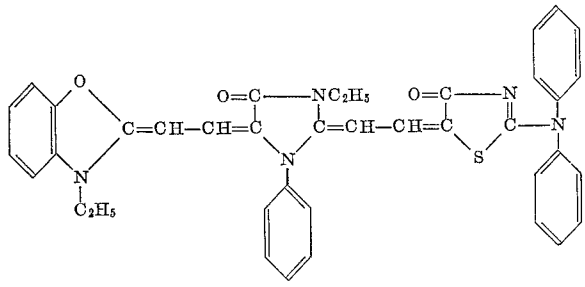
A silver-dye complex having only green-red sensitivity may be prepared as in Example II except the cyanine dye



Anhydro-3-ethyl-9-methyl-3'-(3-sulfobutyl) - thiacarbocyanine hydroxide is substituted for the dye used in Example II. The spectral response of this coating was from 500 to 630 mμ.

Example VIII

A silver-dye complex having red and infrared sensitivity may be prepared as in Example II except the dye



2[(2-diphenylamino-4-oxo-2-thiazolin-5-ylidene) ethylidene]-3-ethyl-5-[(3-ethyl-2-benzoxazolinylidene) ethylidene]-1-phenyl-4-imidazolidone is substituted for the dye used in Example II. The spectral response of this coating was from 500 to 720 mμ.

Example IX

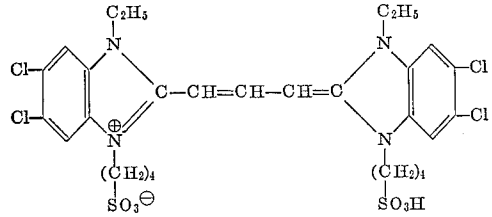
A silver-dye complex coating having a panchromatic response from 378 to 630 mμ may be prepared by blending the silver-dye complexes prepared as in Examples VI, VII and VIII.

The dyes used in Examples I through VI form silver-dye complexes which have rather broad absorption bands and correspondingly broad spectral sensitization bands. In some phases of photography it is desirable to have narrow, sharp spectral sensitization peaks. With silver halide emulsions, this desirable property is brought about by the use of dyes which aggregate to give very narrow absorption bands called J bands which can confer very narrow, sharp regions of spectral sensitivity on silver halide emulsions.

Example X

A silver-dye complex formed with an aggregating cyanine dye may be prepared as follows:

(1) Add 76 ml. of 10% gelatin to 160 ml. distilled water.
(2) Add 6 ml. of 7½% saponin solution.
(3) Add 3 ml. of 10% formaldehyde.
(4) Add 3.0 ml. of 0.1 N silver nitrate solution.
(5) Add 40 ml. of an ethanolic solution containing 1 mg. per 6 ml. of the cyanine dye, anhydro-5,5',6,6',-tetrachloro-1,1'-diethyl-3,3' - di - (3-sulfobutyl)benzimidazolocarbocyanine hydroxide

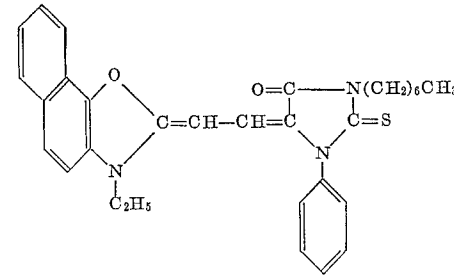


(6) A coating having a 0.004 inch wet thickness was made on cellulose triacetate film support. The spectral sensitivity of this coating showed a sharp peak from 570 to 590 mμ.

There are other sensitizing dyes which form aggregates but do not react directly with silver. It has been found that mixing dyes, which do complex with silver ions, with dyes that do not react with silver but do form aggregates results in a light sensitive coating having the sharp spectral response of the aggregate.

Example XI

(1) To 135 ml. of distilled water add 64 grams of 10% gelatin.
(2) Add 5.0 ml. of 7½% saponin solution.
(3) Add 2.5 ml. of 10% formaldehyde.
(4) Add 2.5 ml. of 0.1 N silver nitrate.
(5) Dilute total to 160 ml. with distilled water.
(6) To 40 ml. of the above mixture add 0.37 ml. of a solution containing 3.5 mg./380 ml. of the dye 1,1'-diethyl-2,2'-cyanine sulfate which forms an aggregate in the gelatin layer.
(7) Add 0.8 ml. of a solution containing .1 mg./3 ml. of the merocyanine dye 5[(3-ethyl-2-α-naphthoxazolinylidene)ethylidene] - 3 - n - heptyl-1-phenyl-2-thiohydantoin

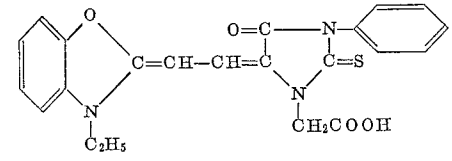


which reacts with silver to form a silver-dye complex. The spectral response of this coating showed a sharp peak at 565 to 590 mμ.

Although for most purposes a polymeric binder is used as a vehicle to coat the silver-dye complex, it has been found possible to sensitize aluminum plates with the silver dye complex in the complete absence of any binder.

Example XII

(1) A grained aluminum plate was immersed for one minute in a water solution containing 1 mg./ml. of the merocyanine dye

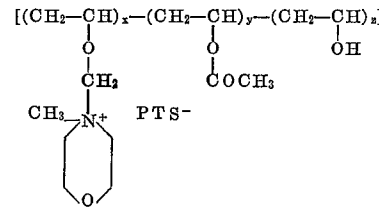


1-carboxymethyl-5-[(3 - ethyl - 2 - benzoxazolinylidene)ethylidene]-3-phenyl-2-thiohydantoin
(2) The excess dye solution was then rinsed off with distilled water
(3) The dyed plate was soaked for one minute in .01M silver nitrate to form the silver-dye complex, then the excess silver was rinsed off
(4) The plate was then dried, exposed to a line image, and physically developed with the developer of Example II to give a silver image in the areas of exposure

Because of the small size and low number of nuclei that are created by low levels of exposure to light of the silver dye complex, it is desirable that there be as little as possible of any inhibition or restraining action of physical development. Although it is well known that gelatin is an excellent protective colloid, it was found possible to decrease the protective action of the gelatin by adding polymeric compounds which allowed the physical development to take place at lower levels of exposure than with pure gelatin so that a doubling of the photographic speed results.

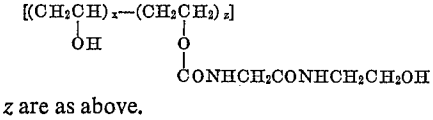
Example XIII

A light sensitive silver-dye complex coating was prepared in a manner identical to that described in Example II, except that from 5 to 50 ml. of an 8% water solution of copolymer (vinyloxymethyl methyl morpholinium p-toluene sulfonate) (vinyl acetate) vinyl alcohol



(X, Y, and Z can be whole integers of varying values) was added to the preparation to be contained in the 380 ml. of total emulsion.

A doubling of the emulsion speed was also obtained in a similar manner by adding to the gelatin in place of the above copolymer another copolymer of vinyl alcohol-vinyl N-β-hydroxyethyl carbamoylmethylcarbamate.



x and z are as above.

Example XIV

A light sensitive coating was prepared on a paper support containing 2.6 mg. silver nitrate per square foot, 400 mg. gelatin per spuare foot and 0.065 mg. of the sensitizing dye 3-ethyl-5-(3-ethyl-2-benzoxazolinylidene ethylidene)-1-phenyl-2-thiohydantoin per square foot. The light sensitive sheet was exposed to a line positive for 2 seconds to a No. 2 Photoflood lamp at a distance of 18 inches. After exposure the sheet was covered with a viscous activator solution of the following composition:

Water	ml	750.0
Sodium sulfite	grams	10.0
p-N-methylaminophenol sulfate (Elon)	do	12.0
Sodium carbonate·$1H_2O$	do	50.0
Sodium iso-ascorbate	do	40.0
Potassium iodide (0.1% aqueous solution)	ml	50.0
Potassium bromide	grams	2.0
Sodium thiosulfate·$5H_2O$	do	15.0
Hydroxyethyl cellulose	do	15.0
Mercaptoacetic acid	ml	5.0
Water to make pH=11.0	ml	1000.0

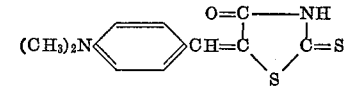
A sheet of a low speed, high resolution silver chlorobromide emulsion coated to yield a silver coverage of 432 mg. per square foot and gelatin coverage of 320 mg. per square foot was pressed in contact with the viscous solution on the exposed sheet. The "sandwich" was together for one minute. Silver was deposited in the exposed areas of the silver-dye layer to form a positive print of the line image.

Example XV

The light sensitive layer of the preceding example was prepared and exposed in the manner described. Processing was carried out with the materials described except that the viscous processing solution was contained in a rupturable pod between the two sheets. When the sandwich was drawn between two closely spaced rollers, the viscous solution was spread evenly between the two layers. Results similar to those described in the preceding example were obtained.

Example XVI

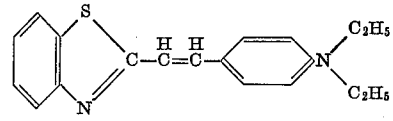
A light sensitive silver-dye coating using a benzylidene dye may be prepared as in Example II except that the dye



p-dimethylaminobenzylidene rhodanine is substituted for the dye used in Example II. The spectral sensitivity of this coating was from 460 to 590 mμ.

Example XVII

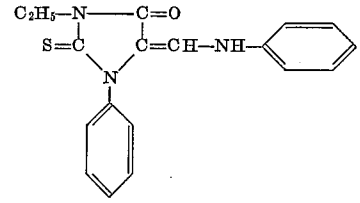
A light sensitive silver-dye coating using a styryl dye may be prepared as in Example II except that the dye



2-(p-diethylaminostyryl)-benzothiazole is substituted for the dye used in Example II. The spectral sensitivity of this coating was from 400 to 550 mμ.

Example XVIII

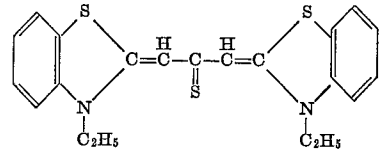
A light sensitive silver-dye coating using a hemioxonol dye may be prepared as in Example II except that the dye



5-anilinomethylene-3-ethyl-1-phenyl-2 - thiohydantoin is substituted for the dye used in Example II. The spectral sensitivity of this coating was from 460 to 560 mμ.

Example XIX

A light sensitive silver-dye coating using a thioacetone dye which becomes a cyanine dye upon reaction with silver may be prepared as in Example II except that the dye



Bis(3-ethyl-2-α-benzothiazolinylidene)thioacetone is substituted for the dye used in Example II. The spectral response was from 460 to 580 mμ.

Example XX

Physical development using an electroless copper plating bath may be used to deposit copper selectively on nuclei produced in an imagewise pattern by an exposure to light. When a coating of a silver-dye complex is prepared as in Example II and exposed to a Kodak Model 60 sensitometer, it may be developed by a 20-second immersion in a copper physical developer to produce a visible image in the exposed areas which contain 99.7 mg. copper per square foot in the maximum density.

By extending the time of development in the copper developer to 120 minutes, high neutral density images of 1.40 are obtained. Copper analyses of sensitometric strips indicate that over 150 mg. of copper per square foot exists in the image area.

The composition of the electroless copper plating bath used to deposit copper only on the photoproduced silver specks was

Cupric nitrate	grams	50
Ascorbic acid	do	40
2-Aminoethanol	ml	100
Sodium sulfite	grams	50
Water to	liter	1

Other silver compounds which may be used to form the silver-dye complex include water soluble silver salts such as silver acetate, silver benzoate, silver citrate, silver fluoride, silver lactate, silver laurate, silver p-toluenesulfonate, and the like. Since these are merely representative soluble silver salt compounds, it will be apparent to one skilled in the art that other soluble silver compounds may also be used within the scope of our invention.

When diffusion transfer physical development is employed, any of the known silver halide emulsions may be used in contact with the light sensitive, exposed, silver-dye complex emulsion, such as silver chlorobromide, silver chloroiodide, silver chlorobromoiodide, silver bromide, and silver bromoiodide.

The binder for the light sensitive silver-dye complex is not critical but may be any water permeable material such as the colloids known for use in silver halid photography including gelatin, carboxymethylcellulose, zein, various synthetic resins such as polyvinyl alcohol, acrylic resins, etc., collodion, albumin, cellulose derivatives, and the like.

Light sensitive silver-dye layers may also be made in the complete absence of a binder by coating a grained aluminum support with a solution containing a mixture of the silver-dye complex.

In preparing the light sensitive elements using a binder, the silver-dye complex is dispersed in a suitable binder and then the mixture is coated on a support using any of the known coating methods. Supporting materials can be any of the known materials for this purpose, such as film base (e.g., cellulose nitrate film, cellulose ester film, etc.), plastic supports (e.g., polyethylene, polyethylene terephthalate, etc.), paper, metal, glass, and the like.

The wet thickness of the coatings can be in the range from about 0.001 to about 0.01 inch with a preferred wet thickness in the range from about 0.003 to about 0.006 inch. Thicker coatings can also be employed without detracting from the invention.

Although the concentrations of the various components of the light sensitive composition of the invention can vary over a wide range, it has been found that quite useful coating compositions are prepared wherein the binder is present in the range up to about 10% by weight of the total coating melt and wherein the silver-dye complex is present in the range of from about .1% to about 10% by weight of the total coating melt.

Although the normal methods of physical development can be used, including swabbing with an aqueous silver solution such as a dilute silver nitrate solution and then immersing the swabbed layer in a photographic silver halide developing solution, followed by washing the developed print with water to stabilize it, other methods for development of the exposed layers of the invention comprise incorporating in the said layers a silver complex or salt, such as silver-thiosulfate complex or the silver salt of 4,5-(2,3-D-fructopyrano)-2 - oxazolidinethione, and the like. In processes where silver plus a complexing agent is incorporated in the sensitive layer, such layers are normally developed by treatment with a conventional silver halide developing solution.

The light sensitive layer of this invention when normally exposed to a positive image, results in a negative image. However, a reversal system can be employed wherein a positive image will be obtained. After exposure of the light sensitive coating, followed by a mild physical development, a mild bleach is used to remove the developed silver. By flashing to light or by similar fogging action followed by physical development, a positive image is obtained.

In the above examples, the images formed by physical development are silver. However, other metals are known for use in physical development and can be used for the same purposes as silver by the appropriate substitution of metallic salts. Metals which are members of the electromotive scale below hydrogen are those which are most commonly employed for this purpose and include copper, mercury, platinum, gold, silver, and the like. The use of these metals to form images according to our invention using solutions known as "electroless plating" baths is within the scope thereof.

At the instant of exposure the coated silver-dye emulsion is essentially grainless, since no particulate matter may be observed at the highest magnification available with the electron-microscope.

Since the light sensitive species is essentially of molecular size, the resolving power of these coatings is exceptionally high. No upper limit has been placed on the resolving power, but 800 lines per millimeter have been measured on a sample prepared according to Example I. Another unusual property that results from the physical development of these silver-dye coatings is the extremely high acutance which is greater than any silver halide material. Microdensitometer edge traces of sharply exposed lines yield results which indicate the physically developed silver dye materials have infinite acutance thus yielding photographic quality unobtainable with any other recording medium.

By radiation as used herein is intended visible light, infrared and ultraviolet, as well as X-rays, gamma rays, etc.

It will be appreciated that the light sensitive silver-dye complex can be prepared to be sensitive to a particular wavelength or wavelength band. However, these light sensitive silver-dye complexes may be further sensitized by having sensitizing dyes added thereto.

It will also be appreciated that the silver-dye complexes of our invention can be used in color processes with a para phenylenediamine type of silver halide developer whose oxidation products can couple with dye forming couplers as is used in conventional color photography. The dye forming coupler or couplers can be incorporated in the emulsion in one or more layers or may be present in the developing solution. Any of those known in the art for use in color photography may be used in our invention.

In a particular embodiment of our invention, a dye which is used as a precursor to release para phenylenediamine type silver halide developers may be used to form the silver-dye complex. In this situation, the dye cleaves under alkaline conditions to release the para phenylenediamine type silver halide developer. This developer then develops the exposed silver complex in conjunction with the soluble metal salt in the physical developer solution and forms an oxidized para phenylenediamine product which is capable of coupling with a dye forming coupler imagewise. By using a dye which is capable of cleaving as above, to form the silver-dye complex, it is possible to incorporate a para phenylenediamine developer as a precursor and the light sensitive coating.

When the light sensitive silver-dye complexes of this invention are used in one or more layers to form a color product, it is necessary to remove the silver image to obtain the dye image. This can be accomplished by normal bleaching operations which are used according to conventional color processes. Reversal may also be accomplished by conventional means, by developing the exposed image and bleaching, after which the remaining silver complex is exposed to a flash exposure and redeveloped.

The invention has been described in detail with particular reference to 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. A photographic emulsion comprising a radiation-sensitive material consisting essentially of a reaction product of silver ion with a spectral sensitizing dye selected from the class consisting of cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styrls and benzyl-

idenes which reaction product, upon exposure to radiation, forms an active site for physical development.

2. A photographic emulsion of claim 1 in which said dye is a cyanine.

3. A photographic emulsion of claim 1 in which said dye is a merocyanine.

4. A photographic emulsion of claim 1 in which said dye is an oxonol.

5. A photographic emulsion of claim 1 in which said dye is a hemicyanine.

6. A photographic emulsion of cclaim 1 in which said dye is a hemioxonol.

7. A photographic emulsion of claim 1 in which said dye is a styryl.

8. A photographic emulsion of claim 1 in which said dye is a benzylidene.

9. A photographic emulsion of claim 1 in which said dye is a 2-thiohydantoin spectral sensitizing dye.

10. A photographic emulsion of claim 1 in which said dye is 1-carboxymethyl-5-[(3-ethyl - 2 - benzoxazolinylidene)ethylidene]-3-phenyl-2-thiohydanion.

11. A photographic emulsion of claim 1 in which said dye is 5-[(3-ethyl-2-α-naphthoxazolinylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin.

12. A photographic emulsion of claim 1 in which said dye is 1-carbethoxy-5-[(3-ethyl-2-benzoxazolinylidene)-ethylidene]-3-phenyl-2-thiohydantoin.

13. A photographic element comprising a support having thereon at least one radiation-sensitive layer in which the radiation-sensitive material consists essentially of a reaction product of silver ion with a spectral sensitizing dye selected from the class consisting of cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benzylidenes, which reaction product, upon exposure to radiation, becomes an active site for physical development.

14. A photographic element of claim 13 in which said dye is a cyanine.

15. A photographic element of claim 13 in which said dye is a merocyanine.

16. A photographic element of claim 13 in which said dye is an oxonol.

17. A photographic element of claim 13 in which said dye is a hemicyanine.

18. A photographic element of claim 13 in which said dye is a hemioxonol.

19. A photographic element of claim 13 in which said dye is a styryl.

20. A photographic element of claim 13 in which said dye is a benzylidene.

21. A photographic element of claim 13 comprising a support having thereon at least one radiation-sensitive layer comprising a water permeable colloid containing said radiation-sensitive material.

22. A photographic element of claim 13 in which said layer has spectral sensitivity only in the region of absorption by said reaction product.

23. A photographic element of claim 13 in which said dye is a 2-thiohydantoin spectral sensitizing dye.

24. A photographic element of claim 13 in which said dye is 1-carboxymethyl-5-[(3-ethyl-2-benzoxazolinylidene)-ethylidene]-3-phenyl-2-thiohydantoin.

25. A photographic element of claim 13 in which said dye is 5-[(3-ethyl-2-α-naphthoxazolinylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin.

26. A photographic element of claim 13 in which said dye is 1-carbethoxy - 5 - [(3-ethyl-2-benzoxazolinylidene) ethylidene]-3-phenyl-2-thiohydantoin.

27. A process for forming a metallic image in an exposed radiation-sensitive layer in which the radiation-sensitive material consists essentially of at least one radiation-sensitive reaction product of silver ion with a spectral sensitizing dye selected from the class consisting of cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benzylidenes, comprising contacting said layer with a solution of a metallic compound and a reducing agent.

28. A process of claim 27 in which said radiation-sensitive material is dispersed in a water permeable colloid.

29. A photographic process of claim 27 in which said dye is a cyanine.

30. A photographic process of claim 27 in which said dye is a merocyanine.

31. A photographic process of claim 27 in which said dye is an oxonol.

32. A photographic process of claim 27 in which said dye is a hemicyanine.

33. A photographic process of claim 27 in which said dye is a hemioxonol.

34. A photographic process of claim 27 in which said dye is a styryl.

35. A photographic process of claim 27 in which said dye is a benzylidene.

36. A process for forming a metallic image in an exposed radiation-sensitive layer in which the radiation-sensitive material consists essentially of at least one radiation-sensitive reaction product of silver ion with a spectral sensitizing dye selected from the class consisting of cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styrls and benzylidenes, comprising contacting said layer with a silver halide emulsion in the presence of a silver halide developing agent and a silver halide solvent.

37. A process of claim 36 in which said radiation-sensitive material is dispersed in a water permeable colloid.

38. A process for forming a silver image in an exposed light sensitive layer in which the light sensitive material consists essentially of at least one light sensitive reaction product of silver ion with a spectral sensitizing dye selected from the class consisting of cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benzylidenes, dispersed in a water permeable colloid, comprising contacting said layer with a solution of a silver compound and a reducing agent to form a silver image, bleaching the silver image, exposing to light and developing.

39. A process for forming a color dye image in an exposed light sensitive layer in which the light sensitive material consists essentially of at least one light sensitive reaction product of silver ion with a spectral sensitizing dye selected from the class consisting of cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benylidenes, comprising contacting said layer with a solution of a metallic compound and a primary amino aromatic silver halide developer in the presence of a dye forming coupler, capable of forming a dye by coupling to the oxidation product of said developer and bleaching the silver image.

40. A process for forming a color dye image in an exposed light sensitive layer in which the light sensitive material consists essentially of at least one light sensitive reaction product of silver ion with a spectral sensitizing dye selected from the class consisting of cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benzylidenes, and a color forming coupler, comprising contacting said layer with a solution of a metallic compound and a reducing agent whose oxidized form does not couple with the coupler to form a dye, bleaching the metallic image formed, exposing and developing with a primary amino aromatic silver halide developer containing a silver compound and bleaching the silver image.

References Cited

UNITED STATES PATENTS

2,735,766	2/1956	Hill	96—103
2,993,893	7/1961	Hunt	96—102
3,206,309	9/1965	Haist	96—94

(Other references on following page)

FOREIGN PATENTS

733,731 7/1950 Great Britain.
524,500 8/1940 Great Britain.

OTHER REFERENCES

Natunson, J., Phys. Chem. U.S.S.R., vol. 14, pp. 989–995, 1940.

Chemical Abstracts, vol. 40, 9926i, 9927a (1956).

Leukoev and S. V. Watanson, (Kino-Photo Inst., Moscow (Zhur. Fiz. Khim. 30, 161–71 (1956). K. I. Pokrovskaya I.I.).

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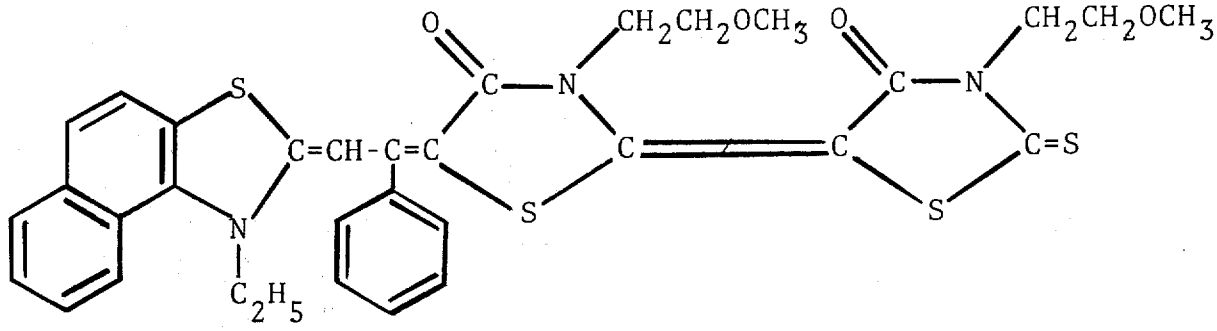
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,446,619 May 27, 1969

Paul B. Gilman et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 50, "by a mobile silver io nfrom the silver halide lattice to" should read -- by the dye is transferred to the silver halide in such a --; line 63, "withe" should read -- with --. Column 2, line 70, insert -- (k) 1-carbethoxy-5-[(3-ethyl-2-benzoxazolinylidene)-ethylidene]-3-phenyl-2-thiohyndantoin, 520-560 mμ --. Column 4, line 24, "thioyhdrantoin" should read -- thiohydantoin --; line 29, "developed" should read -- developer --; line 62, "silver-type" should read -- silver-dye --. Columns 5 and 6, lines 40 to 52, the formula should appear as shown below:



Column 12, line 75, "styrls" should read -- styryls --. Column 13, line 10, "cclaim" should read -- claim --; line 20, "thiohydanion" should read -- thiohydantoin --. Column 14, line 26, "styrls" should read -- styryls --.

Signed and sealed this 9th day of June 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents