

[72] Inventors **Paul B. Gilman, Jr.**
Rochester;
Charles A. Goffe, Brockport, both of N.Y.
[21] Appl. No. **744,733**
[22] Filed **July 15, 1968**
[45] Patented **Oct. 26, 1971**
[73] Assignee **Eastman Kodak Company**
Rochester, N.Y.
Continuation-in-part of application Ser. No.
244,456, Dec. 13, 1962, now abandoned.

[54] **SILVER IMAGES IN LIGHT SENSITIVE PRINT**
FORMING LAYERS
16 Claims, 4 Drawing Figs.
[52] U.S. Cl. **96/27,**
96/48 PD
[51] Int. Cl. **G03c 5/04,**
G03c 5/24

[50] Field of Search..... **96/1.5, 27,**
29, 50, 107, 48, 48 PD

[56] **References Cited**
UNITED STATES PATENTS
3,121,006 2/1964 Middleton et al..... 96/1.5
3,121,008 2/1964 Jones et al..... 96/1.5
Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard E. Fichter
Attorneys—W. H. J. Kline, B. D. Wiese and H. E. Beyers

ABSTRACT: Photographic elements and processes feature photoconductive, substantially silver halide free, inorganic particles and a photoreactive sulfur compound which will react with the inorganic particles upon exposure to light to form sulfur containing sites for physical development. Subsequent to exposure, the element is physically developed to produce a negative of the original.

FIG. 1

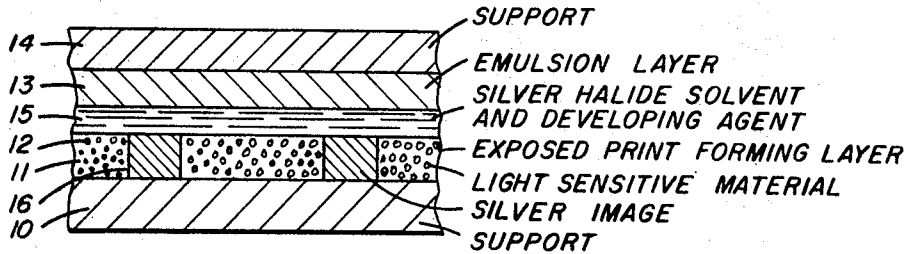


FIG. 2A

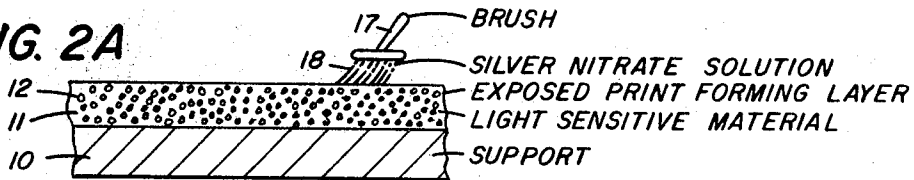


FIG. 2B

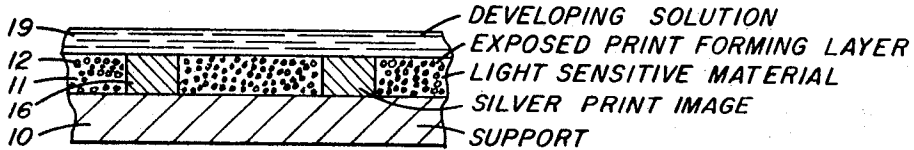
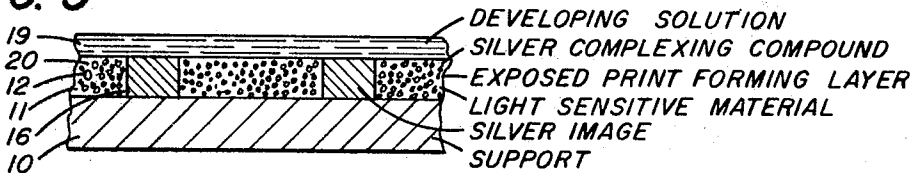


FIG. 3



PAUL B. GILMAN
CHARLES A. GOFFE
INVENTORS

BY *Henry E. Byers*

ATTORNEY

SILVER IMAGES IN LIGHT SENSITIVE PRINT FORMING LAYERS

This application is a continuation-in-part of U.S. Pat. application Ser. No. 244,456 filed Dec. 13, 1962 by Gilman and Goffe now U.S. Pat. No. 3,404,980.

BACKGROUND OF THE INVENTION

This invention relates to light sensitive photographic materials and in particular to materials which form a latent image comprising particulate centers capable of physical development to a visible silver or other metallic image and to the use of such materials.

In the photographic diffusion transfer process, silver precipitating nuclei or fogging agents are used as centers for physical development. These nuclei, however, are not themselves involved in the formation of the latent image, but merely offer convenient centers for a kind of electrolytic plating out of metal ions. The nuclei are under the control of a developing or developed image generated independently, for example, by exposure of a silver halide gelatin photographic image in the same or a juxtaposed layer. Such silver halide emulsions are usually opaque, relatively thick, and can be chemically developed. However, high image resolution in processes of this type has been difficult to obtain since lateral diffusion of solubilized silver halide usually occurs during transfer to the receiving layer from unexposed areas of a developed light sensitive contacting emulsion layer. Since a conventional silver halide emulsion must be used, much more silver halide is required in the sensitive layer than that which is actually used to form the silver image. Therefore, it has been desirable to obtain a metallic image which would require less metal, particularly less expensive silver, and which would have higher image resolution.

U.S. Pat. No. 3,052,541 discloses a method of using zinc oxide on a support in combination with various silver compounds to obtain a printout image. However, the coating must be moistened to render it light sensitive which may be inconvenient for many uses.

British Pat. No. 439,812 discloses the use of heavy metal compounds containing sulfur which upon exposure to light are decomposed into the corresponding metal sulfides. Metals which are suitable are those which yield dark metal sulfides. After exposure, the light sensitive material is chemically developed by treatment with a solution of a compound containing sulfur. However, the prior art has not solved the problem of obtaining a metallic image with a high resolving power or with a practical exposure speed.

SUMMARY OF THE INVENTION

According to the present invention, the aforementioned difficulties in connection with providing a light sensitive element having good image resolution which employ materials other than silver halide are met by using photo conductive, substantially silver halide free, inorganic particles such as zinc oxide,

zinc hydroxide and the like. These inorganic particles are combined with a sulfur compound which will react with the material upon exposure to light to form sulfur containing sites for physical development. Suitable compounds which will react with the inorganic particles include a wide variety of sulfur donor materials.

BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawing is illustrated a greatly enlarged cross-sectional view of a sensitive element comprising a part of our invention, illustrating methods by which light sensitive layers of our invention can be developed, for example;

FIG. 1 shows development by contact with an unexposed emulsion layer in the presence of a silver halide solvent and silver halide developing agent.

FIG. 2 shows development by treating with silver nitrate solution followed by treatment in a silver halide developer solution.

FIG. 3 shows development by treatment with a silver halide developer solution when a silver complex compound has been incorporated in the exposed print forming layer.

In particular, FIG. 1 shows a support 10 having a print forming layer coated thereon comprising a light sensitive material 11 contained in a binder 12 wherein after exposure the layer is contacted with an emulsion layer 13 and a support 14 in the presence of a solution 15 containing a silver halide solvent and a silver halide developing agent. By this process, a silver print 16 is produced in the exposed layer corresponding to the light exposed portions of said layer.

FIGS. 2A and 2B show the method of development comprising brushing a light sensitive layer of the invention after exposure with a brush 17 containing a silver nitrate solution 18 so that upon treatment of the layer with a developing solution 19, a silver image 16 is produced in said layer.

FIG. 3 shows development of an exposed layer in which a light sensitive material 12 and a silver complex compound 20 are contained in a binder 11 on a support 10 whereby a silver image 16 is produced in said layer, by treatment with a silver halide developing solution 19.

DESCRIPTION OF THE PREFERRED EMBODIMENT

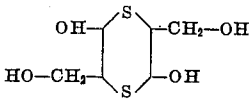
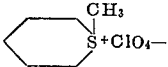
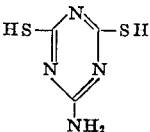
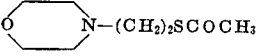
The photoconductive inorganic materials which are particularly useful in our invention include particles of zinc oxide, zinc hydroxide, lead iodide and the like. These photoconductive materials can be of colloidal size having an average diameter of 25-2500 A. units.

Sulfur compounds which are particularly useful comprise a wide variety of sulfur donor materials. These can be used by merely mixing the sulfur donor in a liquid coating composition prior to coating on a support. In other cases, where a gas is employed, such as hydrogen sulfide gas, the inorganic compound containing layers of the invention can be fumed in an appropriate manner. Suitable sulfur compounds for admixing with the inorganic materials of the invention include the following:

TABLE I

Name of compound	Structure	Sensitizing ability: None=0; best=5
Dithiooxamide	$\text{H}_2\text{NCSCSNH}_2$	4
1,4-diphospha-2,3-dithia-1,1,4,4-tetramethoxy-1,4-butanedithione	$\begin{array}{c} \text{S} \quad \text{S} \\ \parallel \quad \parallel \\ (\text{CH}_3\text{O})\text{P}-\text{S}-\text{S}-\text{P}(\text{OCH}_3)_2 \end{array}$	4
O,O-diethyl-S-methyl-phosphoro-thiolothionate	$\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{S}-\text{CH}_3 \\ \text{CH}_3\text{CSNH}_2 \end{array}$	3
Thioacetamide	CH_3CSNH_2	5
1,2-dihydroxy-3-mercaptopropyl, 2-oligoethylene-sulfide-4-oligo-hydroxymethylene-oxide-8.	$\begin{array}{c} \text{CH}_2\text{CHOHCH}_2\text{OH} \\ \diagup \quad \diagdown \\ \text{S} \quad \quad \quad \text{S} \\ \diagdown \quad \diagup \\ (\text{CH}_2\text{CH}_2)_4(\text{CHCH}_2\text{O})_8\text{H} \\ \quad \quad \quad \text{CH}_2\text{OH} \end{array}$	2

TABLE I—Continued

L-cystine.....	$\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}_2$ $\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}_2$	4
3,9-dithia-1,19-nonadecanediol.....	$\text{HO}(\text{CH}_2)_8\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_8\text{OH}$	3
Tetramethylene-bis(methyl-sulfone).....	$\text{CH}_3\text{SO}_2(\text{CH}_2)_4\text{SO}_2\text{CH}_3$	2
Di-isopropyl sulfoxide.....	$(\text{CH}_3)_2\text{CHSOCH}(\text{CH}_3)_2$	3
Di-n-hexyl sulfide.....	$\text{C}_6\text{H}_{13}-\text{S}-\text{C}_6\text{H}_{13}$	2
5-bromo-1-pentyl thioacetate.....	$\text{Br}(\text{CH}_2)_4\text{SCOCH}_3$	4
3-chloro-1-propyl thioacetate.....	$\text{Cl}(\text{CH}_2)_2\text{SCOCH}_3$	4
Evan acid 3CS.....	$\text{HOOCCH}_2\text{SCH}(\text{COOH})\text{CH}_2\text{COOH}$	3
Thioglyceraldehyde.....		5
Bis(2-isothiuroniummethyl) aminodichloride HCl.....	$\left[\begin{array}{c} \text{H}_2\text{N}^+ \\ \text{CS}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{SC} \\ \text{H}_2\text{N} \end{array} \begin{array}{c} \text{NH}_2^+ \\ \text{NH}_2 \end{array} \right] 2\text{Cl} \cdot \text{HCl}$	2
3,8-dithiadecane 1,10 bis (N-methylpiperidinium) p-toluene sulfonate.....	$\left[\begin{array}{c} \text{N}^+(\text{CH}_2)_2\text{S}(\text{CH}_2)_4\text{S}(\text{CH}_2)_4\text{N}^+ \\ \text{CH}_3 \end{array} \right] 2\text{pTs}^-$	2
L-cysteine (free base).....	$\text{HSCH}_2(\text{CHNH}_2)\text{COOH}$	2
Glutathione.....	$\begin{array}{c} \text{CH}(\text{CH}_2\text{SH})\text{CONHCH}_2\text{COOH} \\ \text{HN} \\ \text{CO}(\text{CH}_2)_2(\text{NH}_2)\text{CHCOOH} \end{array}$	2
2-mercaptoethyl amine HCl.....	$\text{HS}-\text{CH}_2-\text{CH}_2-\text{NH}_2 \cdot \text{HCl}$	2
Cysteine HCl.....	$\text{HSCH}_2\text{CHNH}_2\text{COOH} \cdot \text{HCl}$	2
Thiodipropionic acid.....	$\text{HOOCCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{COOH}$	2
Calcium thioglycolate.....	$\begin{array}{c} \text{O} \\ \text{O} \\ \text{S} \end{array} \text{Ca} \cdot 3\text{H}_2\text{O}$	4
2-hydroxyethyl isothiuronium trichloroacetate.....	$\left[\begin{array}{c} \text{HO}-\text{CH}_2-\text{CH}_2-\text{S}-\text{C} \\ \text{NH}_2 \\ \text{NH}_2 \end{array} \right]^+ \text{Cl}_3\text{CCOO}^-$	4
S-methyl tetrahydro thiapyran perchlorate.....		2
Dithioammeline.....		3
Sulfamic acid.....	$\text{NH}_2-\text{SO}_2-\text{H}$	2
Merapto acetic acid.....	HSCH_2COOH	3
Ethyl xanthic acid potassium salt.....	$\text{C}_2\text{H}_5\text{OCS}-\text{K}^+$	4
Sodium dithionate.....	$\text{Na}_2\text{S}_2\text{O}_4$	5
3-mercapto 1,2-propane diol.....	$\text{HOCH}_2\text{CHOCH}_2\text{SH}$	4
Sodium sulfide.....	Na_2S	5
β-Dithiocarbamyl propionic acid.....	$\text{H}_2\text{NCS}(\text{CH}_2)_2\text{COOH}$	5
β-Mercapto-propionic acid.....	$\text{HSCH}_2\text{CH}_2\text{COOH}$	2
4,4'-dithiodimorpholine.....	$\left[\begin{array}{c} \text{O} \\ \text{NS} \end{array} \right]_2$	5
Thioformanlide.....	$\text{C}_6\text{H}_5\text{NHCSH}$	4
β-Morpholino ethyl-thioacetate.....		3
Ethylene dithiocyanate.....	$\text{NCS}(\text{CH}_2)_2\text{SCH}$	3
Ammonium sulfamate.....	$\text{NH}_4\text{SO}_3\text{NH}_2$	3
5,5'-thiodisallylic acid.....	$(\text{HOCH}_2\text{CH}_2\text{COOH})_2\text{S}$	4
2,5-dithiobiurea.....	$\text{NH}_2\text{CSNHNHCSNH}_2$	2

The concentration of the sulfur donor compound in the invention in the photoreactive layer can vary widely. Normally the effective concentration is found to be quite dependent on the type of donor used with the more labile sulfur compounds, being more effective at lower levels than other compounds with less labile sulfur. A suitable range for the sulfide donors of the invention is found to be from about 0.005 gram to about 0.5 gram per liter of the coating composition. A preferred

range is found to be from 0.1 gram to about 0.2 gram per liter. When fuming, a stream of gas is directed at the surface having thereon photoconductive particles to provide an atmosphere rich in sulfide donor gas for from about 0.5 second to about 2 minutes.

Spectral sensitizing dyes may also be incorporated in the light sensitive layer in which case the coating becomes more sensitive to a particular wave length of the spectrum. For ex-

ample, certain dyes such as eosin and erythrosin spectrally sensitize coatings of zinc oxide, zinc hydroxide or the like. Dyes which can be used include those described in Kendall et al. U.S. Pat. No. 3,241,959. Other spectral sensitizing dyes which may be used include those which are found useful for silver halide systems and the like.

In one method of practicing the invention, a print is formed in a light sensitive layer of the invention by (1) exposing the light sensitive layer to an actinic light source from behind an imagewise transparency having opaque areas, and (2) developing the sensitive layer after exposure by contacting with an unexposed silver halide emulsion layer in the presence of a silver halide solvent and silver halide developing agent. After a brief contacting period of, say about 30 seconds, the layers can be separated showing a silver image in the exposed light sensitive layer corresponding to the exposed portions thereof and showing a reversed image in the contacting emulsion layer.

Another manner in which the latent image in exposed light sensitive layers of the invention can be developed comprises swabbing with an aqueous silver solution, such as dilute silver nitrate solution, and then immersing the swabbed layer in a photographic developing solution, followed by washing the developed print with water to stabilize it. Other methods for development of exposed layers of the invention comprise incorporating in said layers a silver complexing compound, such as a silver-thiosulfate complex or the silver salt of 4,5-(2,3-D-fructopyrano)-2-oxazolinolidenethione, and the like. In the processes where a silver complexing agent is incorporated in the photographic element, such element is normally developed by treatment with a conventional silver halide developing solution.

Actinic light exposing sources can be any suitable tungsten source, such as Kodak No. 2 Photoflood lamp, electrically heated incandescent filaments and the like.

In preparing the light sensitive elements, the inorganic materials and the sulfur donor are typically dispersed in a suitable binder and then the mixture is coated on a support using 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.

Suitable binders for incorporating the inorganic material and the sulfur donor can include any of the water permeable materials such as gelatin or other hydrophilic materials, such as collodion, albumin, cellulose derivatives, synthetic resins such as polyvinyl alcohol and the like.

For example, zinc nitrate in water can be mixed with sodium hydroxide and after the precipitation of zinc hydroxide and suitable washing of the slurry to remove unwanted components of the reaction, a water slurry of the precipitate is mixed with a suitable binder and coated on a support. The sulfur containing compound can be added to the final binder precipitate mixture and after adequate stirring, the mixture is ready for coating on a support.

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

Although the various components of light sensitive compositions of the invention can vary over a wide range, it has been found that quite useful compositions are prepared where the binder is present in the range of from about 2 percent to about 20 percent by weight of the total coating melt; where the inorganic compounds are present in the range from about 2 percent to about 20 percent by weight of the total coating melt. Particularly useful elements are prepared having about 20 mg./ft.² to about 2 g./ft.² or inorganic particles and about 0.1 mg./ft.² to about 10 mg./ft.² of sulfur donor. Of course, amounts outside of these ranges may also be used.

In developing the exposed layers of the invention, any of the usual developing agents can be used such as N-monomethyl-p-aminophenol sulfate; dihydroxybenzene; hydroquinone; dichlorohydroquinone, bromohydroquinone, etc.) 1-phenyl-3-pyrazolidone and its derivatives; triaminophenols and the like.

Silver halide solvents for use in the developing process of the invention include alkali metal thiosulfates, ammonium thiosulfates, alkali metal thiocyanate, ammonium thiocyanate, sodium sulfite, etc.

Silver halide emulsions useful in developing the exposed sensitive layers of the invention can comprise any of the conventional gelatin silver halide developing-out emulsions, e.g., gelatin silver chloride, -chlorobromide, -chloroiodide, -chlorobromoiodide, -bromide and -bromoiodide developing-out emulsions. Emulsions for use in the invention include emulsions having a silver halide carrier other than gelatin, for example, collodion, albumin, synthetic resins, and the like.

These emulsions can be coated in the usual manner on a suitable support, e.g., glass, cellulose nitrate film, cellulose ester film, paper or metal, etc. The emulsions of the invention can contain sensitizers or other addenda for improving the character of the emulsion as is well known in the art. The silver halide emulsions useful in the process of the invention can be prepared according to known methods such as those described in Hewitson and McClintock, U.S. Pat. No. 2,618,556 issued Nov. 18, 1952 for example.

As mentioned previously, the most preferred embodiments of the invention include nonsilver halide inorganic materials such as zinc oxide, zinc hydroxide, etc. However, we have also discovered that certain nonsilver halide inorganic materials which form printout images such as lead iodide and the like are useful. The metal sulfides formed upon exposure to light provide suitable sites for physical development and can be used to obtain an acceptable metallic image by physical development.

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

EXAMPLE I

A light-sensitive layer of the invention is prepared as follows:

150 g. of zinc nitrate is dissolved in 1500 ml. of methanol at 40° C. 40 g. of sodium hydroxide dissolved in 400 ml. of distilled water is added to the zinc nitrate solution over a 15-second interval to form a precipitate of zinc hydroxide which settles to the bottom of the container. Clear supernatant liquid is poured off and the precipitate is redispersed in distilled water, and after allowing the zinc hydroxide precipitate to settle again, the distilled liquid is poured off. The layer is then prepared by mixing 2.5 g. of zinc hydroxide precipitate dispersed in 25 ml. of distilled water with 100 ml. of a 5 percent gelatin solution. The solution is then pumped through a hand homogenizer and 4 ml. of a 7½ percent aqueous saponin solution and 3 ml. of a 10 percent formaldehyde solution are then added to the homogenized solution with suitable agitation. The mixture is then coated on a titanium dioxide pigmented cellulose acetate support.

The coating is then dried and fumed with a stream of gaseous H₂S for 10 seconds under low light illumination such as under red safelight conditions. After fuming, the coating is then exposed to a Kodak No. 2 Photoflood lamp at a distance of 20 inches for 4 seconds from behind a negative image transparency. The exposed layer is then physically developed by using it as a receiver for the diffusion transfer of silver from an unexposed fine-grain, negative-speed bromoiodide emulsion. The emulsion layer is soaked in a solution of the composition of table 2 for about 5 seconds prior to contacting with the receiving layer. After a 30-second contacting interval, the two layers are separated to show an imagewise deposit of silver in the areas of the zinc hydroxide incorporating layer which have received the exposure.

TABLE 2

Sodium sulfite	23 g.
Potassium sulfite	23 g.
N-methyl-p-aminophenol sulfate	6 g.
Sodium thiosulfate · 5 H ₂ O	7.7 g.
Sodium metaborate (H ₂ O)	46 g.
Hydroquinone	16 g.
15 M Ammonium hydroxide	10 ml.
Methylnaphthalene sodium sulfonate (23.2% solution)	3.5 ml.
Water to	1 liter

Zinc hydroxide of improved photographic characteristics for use in the zinc hydroxide sensitive coatings is obtained where the zinc hydroxide is precipitated in a portion of alcohol or where at least two or three washings of the precipitate is carried out before dispersing the coating melt.

EXAMPLE 2

To 50 g. of a 5 percent gelatin solution are added 5 g. zinc oxide and the mixture is pumped through a hand operated homogenizer. To the mixture is added 2 ml. of a 7½ percent saponin solution and 1½ ml. of a 10 percent formaldehyde solution. The preparation is then coated at 0.003 inch wet thickness on a titanium dioxide pigmented cellulose acetate support. After drying, the above coating is fumed with gaseous H₂S for 5 seconds, exposed to line negative for 4 seconds using the illumination of a Kodak No. 2 Photoflood lamp at a distance of 20 inches. The exposed coating is then developed by contacting said coating with a layer of fine-grain, negative-speed bromoiodide emulsion after immersing in a developer of the composition of table 2 for 2 seconds. After the emulsion layer is suitably soaked with the developer composition, it is rolled in contact with the exposed zinc oxide layer. After a 30-second contacting interval, the two elements are separated showing a good silver image produced by physical development in the exposed zinc oxide layer. The silver image is obtained in the areas corresponding to the exposed areas of the layer.

Exposure of similar print-forming layers using other imaged materials, such as positive continuous-tone prints, show similar results using zinc oxide incorporating layers, for example.

EXAMPLE 3

To separate containers having 100 ml. of a 5 percent gelatin solution containing 6 g. of zinc hydroxide precipitates, prepared according to example 1, is added the following:

Container No. 1—no additions

Container No. 2—0.1 g./l. of thioacetamide

Container No. 3—0.1 g./l. of dithiooxamide

The contents of each container are then coated at 0.003 inch wet thickness on a white pigmented cellulose acetate support.

When the three coatings above are exposed for 5 seconds to the photoflood lamp at 36 inches (320 foot-candles) then physically developed as in example 2, a faint image is obtained with coating No. 1 and good dense images are obtained with coatings No. 2 and No. 3.

It is within the scope of our invention to employ integral systems wherein a silver halide layer is coated on the same support with the light sensitive layer of our invention. For instance, the silver halide can be coated on the support followed by a superimposed black layer, next a white layer, and then a layer of our invention. Exposure of the light sensitive material of our invention, followed by development employing a silver halide solvent, would result in diffusion of silver halide to the light sensitive material of our invention and physical development of the image. In a similar system, the light sensitive nuclei can be coated directly on the transparent support with a superimposed black stripping layer and a silver halide layer over the stripping layer. Exposure through the transparent

support, followed by development employing a silver halide solvent would result in physical development of the light sensitive material of our invention after which the silver halide layer could be removed along with the black stripping layer.

The light sensitive material of this invention, when normally exposed to image, results in a negative image upon physical development. However, a reversal system can be employed wherein a positive image will be obtained. After exposure to light of the light sensitive material, followed by mild physical development, a mild bleach is used to remove the silver. By flashing to light or by similar fogging action, followed by physical development, a positive image is obtained. As an alternative, the fogging action might take place during the bleaching step or during the second physical development stage.

In the above applications, our examples have been specific to images formed by physical development in which silver is used to form an image. However, other metals are known for use in physical development and can be used for the same purpose 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, arsenic, antimony, platinum, gold, mercury and the like. The use of these metals to form images is within the scope of this invention. It has not been practical to show an example for each and every one of these metals, but silver images are believed to be those most preferred and to be typical of physical development within the scope of this invention to obtain a metallic image.

By "photoconductive" as used herein is intended a light sensitive nucleating agent whose electrical resistance will decrease upon exposure to light.

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 set forth in the appended claims.

We claim:

1. A photographic element comprising a support having thereon photoreactive, substantially metal halide free, inorganic particles and a sulfur compound which will react with said particles upon exposure to light to form sulfur containing sites for physical development.

2. A photographic element of claim 1 in which said compound is a sulfur compound selected from the class consisting of dithiooxamide, 1,4-diphospha-2,3-dithia-1,1,4,4-tetramethoxy-1,4-butane dithione, 0,0-diethyl-8-methylphosphorothiolothionate, thioacetamide, 1,2-dihydroxy-3-mercaptopropyl, S-oligoethylenesulfide-4-oligohydroxymethylene-oxide-8, L-cystine, 7,13-dithia-1,19-nonadecanediol, tetramethylene-bis-methylsulfone, isopropylsulfonate, di-n-hexyl sulfide, 5-bromo-1-pentane thioacetate, 2-acetyl-chloropropyl mercaptan, Evan acid 3CS, thioglycerolaldehyde, bis(2-isothiuronium-methyl)aminodichloride HC1, 3,8-dithiadecane 1,10-bis(n-methylpiperidinium) p-toluene sulfonate, L-cysteine (free base), glutathione, 2-mercaptoethyl amine HC1, cysteine HC1, thiodipropionic acid, calcium thioglycolate, 2-hydroxyethyl isothiuronium trichloroacetate, 8-methyl tetrahydro thiapyran perchlorate, dithioammelide, sulfamic acid, mercapto acetic acid, ethyl xantic acid potassium salt, sodium dithionate, 3-mercaptopropane diol, sodium sulfide, β-dithio-carbamyl propionic acid, β-mercaptopropionic acid, 4,4'-dithio-dimorpholine, thioformanilide, β-morpholino ethyl-thioacetate, ethylene dithiocyanate, ammonium sulfamate, 5,5'-thiodisalicic acid, hydrogen sulfide and 2,5-dithiobiurea.

3. A photographic element of claim 1 in which said particles are selected from the class consisting of zinc oxide and zinc hydroxide.

4. A photographic element of claim 1 in which said particles are zinc oxide.

5. A photographic element of claim 1 in which said particles are zinc hydroxide.

6. A photographic element comprising a support having thereon about 20 mg./ft.² to about 2 g./ft.² inorganic light sensitive particles, substantially free of silver halide, and about 0.1 mg./ft.² to about 10 mg./ft.² sulfur compound which reacts with said particles upon exposure to light to form sulfur containing sites for physical development.

7. A photographic element of claim 6 in which said compound is a photoreactive sulfur compound selected from the class consisting of dithiooxamide, 1,4-diphospha-2,3-dithia-1,1,4,4-tetra-methoxy-1,4-butane dithione, 0,0-diethyl-8-methylphosphorothiolothionate, thioacetamide, 1,2-dihydroxy-3-mercaptopropyl, S-oligoethylene-sulfide-4-oligohydroxymethylene-oxide-8, L-cysteine, 7,13-dithia-1,19-nonadecanediol, tetramethylene-bismethylsulfone, isopropyl-sulfoxide, di-n-hexyl sulfide, 5-bromo-1-pentane thioacetate, 2-acetyl-chloropropyl mercaptan, Evan acid 3CS, thioglyceraldehyde, bis(2-isothiuronium-methyl)aminodichloride HC1, 3,8-dithiadecane 1,10-bis(n-methylpiperidinium) p-toluene sulfonate, L-cysteine (free base), glutathione, 2-mercaptoethyl amine HC1, cysteine HC1, thiodipropionic acid, calcium thioglycolate, 2-hydroxyethyl isothiuronium trichloroacetate, 8-methyl tetrahydro thiapyran perchlorate, dithioammelide, sulfamic acid, mercapto acetic acid, ethyl xanthic acid potassium salt, sodium dithionate, 3-mercapto-1,2-propane diol, sodium sulfide, β -dithiocarbamyl propionic acid, β -mercaptopropionic acid, 4,4'-dithiodimorpholine, thioformanilide, β -morpholino ethyl-thioacetate, ethylene dithiocyanate, ammonium sulfamate, 5,5'-thiodisalicic acid, and hydrogen sulfide and 2,5-dithiobiurea.

8. A photographic element of claim 6 in which said particles are selected from the class consisting of zinc oxide and zinc hydroxide.

9. A photographic element of claim 6 in which said particles are zinc oxide.

10. A photographic element of claim 6 in which said particles are zinc hydroxide.

11. A process for forming a metallic image in a light sensitive photographic element comprising a support having

thereon photoconductive, substantially silver halide free, inorganic particles and a sulfur compound which will react with said particles upon exposure to light to form sulfur containing sites for physical development, comprising (a) exposing said element to actinic radiation and (b) contacting said element with a solution of a reducible metallic compound and a silver halide developing agent.

12. A process of claim 11 in which said compound is a sulfur compound selected from the class consisting of dithiooxamide, 1,4-diphospha-2,3-dithia-1,1,4,4-tetra-methoxy-1,4-butane dithione, 0,0-diethyl-8-methyl-phosphorothiolothionate, thioacetamide, 1,2-dihydroxy-3-mercaptopropyl, S-oligoethylenesulfide-4-oligohydroxymethylene-oxide-8, L-cystine, 7,13-dithia-1,19-nonadecanediol, tetramethylene-bismethylsulfone, isopropylsulfoxide, di-n-hexyl sulfide, 5-bromo-1-pentane thioacetate, 2-acetyl-chloropropyl mercaptan, Evan acid 3CS thioglyceraldehyde, bis (2-isothiuronium-methyl)aminodichloride HC1, 3,8-dithiadecane 1,10 bis(n-methylpiperidinium) p-toluene sulfonate, L-cysteine (free base), glutathione, 2-mercaptoethyle amine HC1, cysteine HC1, thiodipropionic acid, calcium thioglycolate, 2-hydroxyethyl isothiuronium trichloroacetate, 8-methyl tetrahydro thiapyran perchlorate, dithioammelide, sulfamic acid, mercapto acetic acid, ethyl xanthic acid potassium salt, sodium dithionate, 3-mercapto-1,2-propane diol, sodium sulfide, β -dithiocarbamyl propionic acid, β -mercaptopropionic acid, 4,4'-dithiodimorpholine, thioformanilide, β -morpholino ethyl-thioacetate, ethylene dithiocyanate, ammonium sulfamate, 5,5'-thiodisalicic acid, hydrogen sulfide and 2,5-dithiobiurea.

13. A process of claim 11 in which said particles are selected from the class consisting of zinc oxide, zinc hydroxide and lead iodide.

14. A process of claim 11 in which said particles are zinc oxide.

15. A process of claim 11 in which said particles are zinc hydroxide.

16. A process of claim 11 in which said particles are lead iodide.

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