

[72] Inventor **Eugene Frederick Haugh**
Liftwood, Wilmington, Del.
 [21] Appl. No. **771,347**
 [22] Filed **Oct. 28, 1968**
 [45] Patented **Dec. 21, 1971**
 [73] Assignee **E. I. du Pont de Nemours and Company**
Wilmington, Del.
Continuation-in-part of application Ser. No.
688,996, Dec. 18, 1967, now abandoned.
This application Oct. 28, 1968, Ser. No.
771,347

[56] **References Cited**

UNITED STATES PATENTS			
3,155,507	11/1964	Blake	96/64
3,155,519	11/1964	Blake	96/64 X
3,495,982	2/1970	Blake	96/64

Primary Examiner—Norman G. Torchin
Assistant Examiner—John L. Goodrow
Attorney—Lynn Barratt Morris

[54] **PROCESS FOR PREPARING DIRECT POSITIVE**
IMAGES BY PHOTOSOLUBILIZATION
8 Claims, No Drawings

[52] U.S. Cl. **96/64**
 [51] Int. Cl. **G03c 5/24**
 [50] Field of Search **96/64**

ABSTRACT: Process for forming a positive silver halide image by treating an imagewise-exposed, light-sensitive silver halide layer with a photosolubilizing compound, e.g., 2-mercapto-4-phenylthiazole, and then removing the exposed silver halide with a silver halide solvent.

PROCESS FOR PREPARING DIRECT POSITIVE IMAGES BY PHOTOSOLUBILIZATION

This application is a continuation-in-part of Haugh Ser. No. 688,996, filed Dec. 8, 1967 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention concerns a process for forming a positive silver halide image by treating an imagewise exposed light-sensitive silver halide layer with a photosolubilizing compound and then removing the exposed silver halide by dissolution development (i.e., treating with a silver halide solvent solution).

2. Description of the Prior Art

Blake, U.S. Pat. No. 3,155,507 describes photosoluble elements wherein gelatin-silver halide emulsion layers have been treated with organic compounds, preferably mercaptans, which cause unexposed silver halide crystals to dissolve more slowly than exposed silver halide crystals when treated with a silver halide solvent. This process causes the formation of positive silver halide images from such photosoluble elements. This reference is entirely concerned with a process wherein the silver halide is treated with the insolubilizing organic compound prior to the imaging exposure to actinic radiation.

In assignee's copending applications of Blake, U.S. Ser. Nos. 648,229 and 648,250 and of Strange, U.S. Ser. No. 653,590, all filed June 23, 1967 patents Nos. 3,493,373, Feb. 3, 1970, 3,495,982 and 3,495,983, Feb. 17, 1970, respectively, there are disclosed several classes of "D_{max} maintaining" organic compounds which are useful in processing photosoluble films in that they further reduce the rate of dissolution of unexposed silver halide crystals while not interfering significantly in the dissolution (in a silver halide solvent solution) of the exposed silver halide crystals. Such D_{max} maintaining agents are useful in conjunction with the present invention in order to obtain satisfactory results. In assignee's application Blake, U.S. Ser. No. 684,924, filed Nov. 22, 1967, entitled "Photosoluble Layer Processing in Silver Halide Solvent in Presence of Reducing Agents," the processing of photosoluble layers is further improved by the presence of one or more reducing agents in small quantities during the dissolution development. Such reducing agents can be used during the dissolution development step in accordance with the invention.

Various photosoluble layers and elements are disclosed and claimed in U.S. Pat. Nos. 3,155,514 through 3,155,519, Nov. 3, 1967 and 3,284,206, Nov. 8, 1966 and in assignee's applications Blake & Fan, Ser. No. 403,660, Oct. 13, 1964 U.S. Pat. No. 3,368,899, Feb. 13, 1968, Fan Ser. Nos. 403,631 U.S. Pat. Nos. 3,407,068, Oct. 22, 1968 and Hunt Ser. No. 388,919, Aug. 11, 1964 3,418,124, Dec. 24, 1968, which are useful in accordance with this invention.

The invention is an improvement over the prior art in the sense that it enables one to obtain a positive image by reduction dissolution techniques in normal silver halide layers.

SUMMARY OF THE INVENTION

The invention relates to a process which comprises in the order stated:

a. exposing, imagewise, to actinic radiation a gelatin-silver halide photographic emulsion layer,

b. treating said layer with an organic compound capable of forming a silver salt of lower solubility in water than silver chloride, preferably a mercaptan, the organic compound being present in at least such an amount that when admixed with an aqueous silver chlorobromide (70/30 mole percent) gelatin dispersion containing 10 g. of gelatin per mole of Ag and 0.57 mg. of Ag per ml., and said silver chlorobromide dispersion is treated with 10 percent, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver and 100 mg. of sodium thiosulfate), at least three times the amount of silver chlorobromide remains undissolved as compared with a similar dispersion successively treated

with 5 percent, by weight, aqueous sodium hypochlorite and 10 percent, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver, 25 mg. of sodium hypochlorite and 100 mg. of sodium thiosulfate), after vigorous agitation of both dispersions for 30 seconds at 25° C.,

c. treating said layer with an aqueous solution of a silver halide solvent containing at least one reducing agent for silver halide.

Preferably, there is present a D_{max} maintaining amount of an auxiliary organic compound devoid of ionizable iodine or oxidizing groups which are active at the working pH, which further reduces the rate of dissolution of unexposed silver halide in a silver halide solvent, thereby effecting the solubilization of the silver halide in the more exposed areas at a rate substantially greater than in the less exposed areas until a positive image comprised of silver halide is produced.

Preferably, the silver halide solvent is an aqueous solution of an alkali metal thiosulfate, e.g., sodium or potassium thiosulfate.

Suitable auxiliary compounds or D_{max} maintaining agents that can be used in accordance with the present invention include those defined and classified in aforesaid U.S. Pat. Nos. 3,493,373, 3,495,982 and 3,495,983.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In carrying out the invention, a colloid-silver halide photographic emulsion layer, coated on a suitable support, is exposed imagewise to actinic radiation. The exposed element is then treated with a solution containing an organic compound as described above, e.g., 2-mercapto-4-phenylthiazole, the silver salt of which is of lower solubility in water than silver chloride, so as to reduce the rate of dissolution of unexposed silver halide solvent, e.g., a solution of sodium thiosulfate. Thus, a positive modified silver halide image is formed in the silver halide emulsion layer.

As an optional step, the modified silver halide image may be intensified in various ways, as described in U.S. Pat. No. 3,155,507. The most useful means of intensification involves reducing the white to yellow silver halide image to a black, metallic silver image, preferably using a photographic silver halide developing agent. The silver halide image may be fogged prior to reduction by flashing to actinic radiation. Other methods of intensifying the silver halide image, e.g., by toning, color developing, etc., are disclosed in U.S. Pat. No. 3,155,507.

Although the preferred organic compounds used in step (b) in treating the exposed photographic element are mercaptans, various other organic compounds may be used such as those disclosed in the above U.S. patents and applications for the manufacture of photosoluble elements. The organic compounds disclosed in U.S. Pat. No. 3,155,519 are especially useful, e.g., 2-mercapto-4-phenylthiazole (MPT).

The silver halide solvent solution used in step (c) is an aqueous solution comprising two or three essential compounds: a silver halide solvent and a reducing agent, and, if desired, a D_{max} maintaining agent. The silver halide solvent may be any soluble thiosulfate, e.g., ammonium or alkali metal thiosulfate, but sodium thiosulfate is the preferred solvent. Suitable reducing agents and their useful concentrations are those disclosed in assignee's copending application, U.S. Ser. No. 684,924, filed Nov. 22, 1967. Reducing agents of the class recognized as conventional photographic developing agents for silver halide emulsions are preferred although other reducing agents are useful, including preferably N-methyl-p-aminophenol, 1-phenyl-4-methyl-3-pyrazolidone and 1-phenyl-3-pyrazolidone. Particularly useful D_{max} maintaining compounds are o-phenylphenol, 2-butoxyethanol, and 1-(1-naphthyl)-2-thiourea.

The silver halide layers or elements used in accordance with this invention may be silver chloride, silver bromide, silver chlorobromide, etc., and may contain gelatin or other macromolecular organic water-permeable colloid binding

agents including gelatin (preferred) and the specific colloids and the specific supports described in Blake U.S.P. 3,284,206 can be used in the layers and elements of this invention. Thus, the elements may be modified by variations in the silver halide, the binder (if present), and the adjuvants generally employed in silver halide systems, the supports, and in the relative concentrations of the various components in the layers. Various auxiliary layers, such as abrasion overcoatings, subbing layers, and antihalation undercoats or backing layers may be present in the photographic elements used in accordance with this invention. The elements may include multilayer as well as monolayer structures. The various layers, including the support, may include inert ingredients, e.g., pigments, organic polymer latices, and matting agents.

The invention will be further illustrated but is not intended to be limited by the following examples.

EXAMPLE I

A film strip of a gelatino-silver bromochloride emulsion (30% AgBr, 70% AgCl) on a polyethylene terephthalate support was exposed through a photographic $\sqrt{2}$ step wedge to a high-intensity, tungsten filament, incandescent lamp (General Electric Reflector Photoflood Lamp No. PH/RFL2) at a distance of 2 feet for 5 minutes. The exposed strip was bathed in hot water ($\approx 130^\circ$ F.) for 3 minutes to swell the gelatin and then in a 0.02 percent by weight solution of 2-mercapto-4-phenylthiazole (hereinafter designated as "MPT") in 50 percent by volume alcohol/water for 4 minutes at 68° F. The film was then washed in water for 2 minutes and treated for 8 minutes in the following solution containing a silver halide solvent:

H ₂ O	500 ml.
Na ₂ S ₂ O ₃	32 g.
3N NaOH	10 ml.
Na ₂ SO ₃ , anhyd.	10 g.
1-phenyl-3-pyrazolidone	0.5 g.
Ascorbic Acid	2.5 g.
CH ₃ COOK	19.6 g.
1N NaOH solution containing 5% by wt. o-phenylphenol plus	
10 g./liter Na ₂ SO ₃	10 ml.
Glacial acetic Acid	1.25 ml.
H ₂ O to	1 liter
pH adjusted with CH ₃ COOH to	8.8 at 68° F.

A direct positive silver halide image resulted which was intensified by developing for 1 minute in the following photographic developer solution to yield an image having as maximum density (D_{max}) of 3.2 and a minimum density (D_{min}) of 1.0:

p-Methylaminophenol sulfate	3 g.
Na ₂ SO ₃ , anhyd.	45 g.
Hydroquinone	12 g.
Na ₂ CO ₃ · H ₂ O	79 g.
KBr	1.9 g.
H ₂ O to	1 liter

EXAMPLE II

A strip of the film of example I was exposed for 2 minutes with other exposure conditions as described in example I. Processing was as in example I except that the strip was soaked for 8 minutes in a 0.02 percent by weight solution of MPT in 6×10^{-3} normal sodium hydroxide (instead of in an alcohol/water solution of MPT). Also the strip was treated for 4 minutes instead of 8 minutes in the dissolution developer of example I and then intensified as in example I. In this example the MPT was predominantly in its ionic form rather than in the molecular form as in the alcoholic solution of example I.

A direct positive image was obtained with $D_{max}=2.4$ and $D_{min}=0.4$.

EXAMPLE III

A strip of the exposed film described in example I (except that exposure was for 20 minutes) was soaked in hot water (about 130° F.) for 3 minutes, soaked in a 0.1 percent by wt. aqueous solution of 1-naphthyl-2-thiourea for 1 minute, washed for 2 minutes, treated for 1 minute in the dissolution developer of example I and intensified as in example I. A direct positive voltage was obtained with $D_{max}=2.8$ and $D_{min}=0.7$.

EXAMPLE IV

A sample of a pure silver chloride gelatin emulsion on the support of example I was exposed for 20 minutes as in example I, soaked for 4 minutes in a 0.02 percent solution of MPT in 6×10^{-3} normal sodium hydroxide washed for 2 minutes, treated for 5 minutes in the dissolution developer of example I, washed 2 minutes and intensified as in example I to yield a positive silver chloride image ($D_{max}=3.10$, $D_{min}=1.20$).

EXAMPLE V

A pure silver chloride emulsion having an average grain diameter of about 0.5 micron was chemically sensitized with gold and sulfur sensitizers, and spectrally sensitized with a merocyanine dye. A film strip of this emulsion coated on a polyethylene terephthalate support was exposed through a photographic $\sqrt{2}$ wedge for 1 sec. at a distance of 76 cm. to a 500-watt tungsten filament incandescent lamp operated at a color temperature of $2,890^\circ$ K., and fitted with a Wratten No. 79 filter. The exposed strip was soaked for 15 sec. in a solution prepared by dissolving 0.161 g. of 2-mercaptoquinoline in 50 ml. of ethanol, adding 350 ml. of distilled water, and adjusting the pH to 10. The strip was then rinsed in water and treated for 3 minutes in the reducing dissolution developer of example I, washed for 1 minute, intensified in the photographic developer of example I for 1 minute. All solutions were kept at 70° F. This strip had a D_{max} of 1.15 and a D_{min} of 0.09.

EXAMPLE VI

A sample of the emulsion of example V was coated, exposed and processed as in example V, except that the strip was soaked in the 2-mercaptoquinoline solution for 30 sec. and had a D_{max} of 3.70 and a D_{min} of 0.41.

EXAMPLE VII

A strip of the coated emulsion of example V was exposed as in example V, except that the exposure was for 2 sec. The exposed strip was soaked for 1 minute in a solution made by dissolving 0.193 g. of 2-mercapto-4-phenylthiazole in 50 ml. of ethanol, adding 350 ml. of distilled water and adjusting the pH to 9. This solution was kept at 115° F. The soaked strip was then treated as in example V, except that the treatment with the reducing dissolution developer was for 6 minutes. The strip had a D_{max} of 2.99 and a D_{min} of 0.25.

EXAMPLE VIII

A sample of the coated emulsion of example V was exposed as in example VII. The exposed sample was processed as in example VII, except that the dissolution developer contained no o-phenylphenol. After intensification as in example I, D_{max} was 3.36 and D_{min} 0.80.

EXAMPLE IX

A strip of the coated emulsion of example V was exposed as in example V. The exposed strip was soaked in a solution containing 0.34 g. of 1,2-naphthatriazole per 100 ml. of distilled water with pH adjusted to 9, for 1 minute at 120° F. The treated strip was then developed for 1 minute at 70° F. in the reducing dissolution developer of example I, washed for 30 sec., and intensified in the photographic developer of example I for 1 minute at 70° F. A direct positive image was obtained having a D_{max} of 0.89 and a D_{min} of 0.20.

The present invention has the advantages of the basic process of photosolubilization of Blake U.S. Pat. No. 3,155,507 and embodies simple processing to obtain a positive image. Conventional emulsions may be used by this process to yield the same results as obtained with specially prepared photosoluble emulsion layers described in said patent.

The embodiments of the invention which an exclusive property or privilege is claimed are defined as follows:

1. The process which comprises, in the order stated:

- a. exposing, imagewise, to actinic radiation a gelatino-silver halide photographic emulsion layer,
- b. treating said layer with an organic compound capable of forming a silver salt of lower solubility in water than silver chloride to form a photosoluble emulsion layer, and
- c. treating said layer with an aqueous solution of a silver halide solvent containing at least one reducing agent for silver halide.

2. A process according to claim 1, wherein said silver halide solvent of step (c) also contains a D_{max} maintaining amount of an auxiliary organic compound devoid of ionizable iodine or oxidizing groups which are active at the working pH, which further reduces the rate of dissolution of unexposed silver halide in a silver halide solvent, thereby effecting the solubilization of the silver halide in the more exposed areas at a rate substantially greater than in the less exposed areas until a positive image comprised of silver halide is produced.

3. A process according to claim 1, wherein said organic compound is 2-mercaptoquinoline.

4. A process according to claim 1, wherein said organic compound is 2-mercapto-4-phenylthiazole.

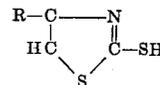
5. The process which comprises, in the order stated:

- a. exposing, imagewise, to actinic radiation a gelatino-silver halide photographic emulsion layer,
- b. treating said layer with an organic compound capable of forming a silver salt of lower solubility in water than silver chloride, the just-recited organic compound being one which if present in at least such an amount that when admixed with an aqueous silver chlorobromide (70/30 mole percent) gelatine dispersion containing 10 g. of gelatin

per mole of Ag and 0.57 mg. of Ag per ml., and said silver chlorobromide dispersion is treated with 10 percent, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver and 100 mg. of sodium thiosulfate), at least three times the amount of silver chlorobromide remains undissolved as compared with a similar dispersion successively treated with 5 percent, by weight, aqueous sodium hypochlorite and 10 percent, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver, 25 mg. of sodium hypochlorite and 100 mg. of sodium thiosulfate), after vigorous agitation of both dispersions for 30 seconds at 25° C., and

c. treating said layer with an aqueous solution of a silver halide solvent containing at least one reducing agent for silver halide and at least one D_{max} maintaining amount of an auxiliary organic compound devoid of ionizable iodine or oxidizing groups which are active at the working pH, which further reduces the rate of dissolution of unexposed silver halide in a silver halide solvent, thereby effecting the solubilization of the silver halide in the more exposed areas at a rate substantially greater than in the less exposed areas until a positive image comprised of silver halide is produced.

6. A process according to claim 5, wherein said organic compound is a mercapto compound of the formula:



where R is a hydrocarbon nucleus of 4-12 carbon atoms.

7. A process according to claim 6, wherein said compound is 2-mercapto-4-phenylthiazole.

8. A process according to claim 5, wherein the exposed element is treated with an aqueous solution containing 1,2-naphthatriazole before step (c).

* * * * *

40

45

50

55

60

65

70

75