

[54] **FOGGED, DIRECT-POSITIVE SILVER HALIDE EMULSION CONTAINING A COLOR COUPLER AND A HETEROCYCLIC MERCAPTAN DESENSITIZER**

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[22] Filed: **July 7, 1972**

[21] Appl. No.: **269,861**

[30] **Foreign Application Priority Data**

July 30, 1971 Great Britain..... 36017/71

[52] U.S. Cl..... **96/55, 96/100, 96/107, 96/108, 96/101**

[51] Int. Cl. **G03c 7/00, G03c 1/36, G03c 1/28, G03c 1/40**

[58] Field of Search..... **96/101, 100, 55, 96/107, 108**

[56] **References Cited**

UNITED STATES PATENTS

2,901,351 8/1959 Van Pee et al..... 96/101
3,501,305 3/1970 Illingsworth 96/108

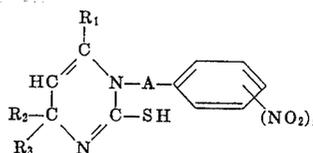
Primary Examiner—Norman G. Torchin

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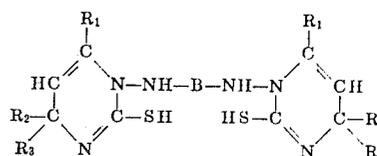
Attorney—Alfred W. Breiner

[57] **ABSTRACT**

A direct-positive photographic color element is described wherein the fogged silver halide emulsion comprises a color coupler and a desensitizing agent or precursor of such desensitizing agent wherein said desensitizing agent has one of the following general formulae, a tautomeric form thereof or is a corresponding disulphide :



and



wherein:

- R₁ is hydroxyl or C₁-C₅ alkyl,
- R₂ is hydrogen or C₁-C₅ alkyl,
- R₃ is C₁-C₅ alkyl or aryl,

A is a single bond or NH,

B is a phenyl or diphenyl sulphone group in which the or both phenyl group(s) is (are) substituted with one or more nitro groups, and

n is 1, 2, or 3.

The desensitizing agents are highly compatible with color couplers.

14 Claims, No Drawings

FOGGED, DIRECT-POSITIVE SILVER HALIDE EMULSION CONTAINING A COLOR COUPLER AND A HETEROCYCLIC MERCAPTAN DESENSITIZER

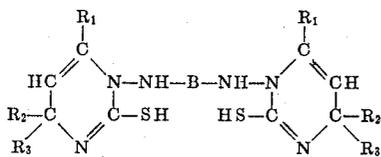
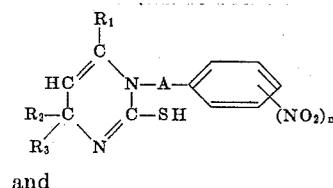
The present invention relates to direct-positive silver halide emulsions and elements comprising fogged silver halide grains and color forming couplers.

It is known that direct-positive images can be obtained with certain types of photographic silver halide reversal emulsions, which comprise uniformly fogged silver halide grains and photoelectron accepting or desensitizing compounds.

It has further been described to introduce color forming coupling compounds as used in conventional photographic silver halide emulsions, into such fogged silver halide emulsions comprising desensitizers.

However, most of the known desensitizers for use in direct-positive silver halide emulsions are unsuitable for use in the presence of color couplers in that they are easily desorbed from the silver halide grains by the color couplers, especially color couplers with water-solubilizing sulpho or carboxyl groups, which results in a reduction of the direct-positive image formation and thus is a reduced photographic speed or in a complete inhibition of the direct-positive image formation.

It has now been found that desensitizing agents corresponding to one of the following general formulae or a tautomeric form thereof :



wherein :

R₁ is a hydroxyl or C₁-C₅ alkyl,

R₂ is hydrogen or C₁-C₅ alkyl,

R₃ is C₁-C₅ alkyl or aryl,

A is a single bond or NH,

B is a phenyl or diphenyl sulphone group in which the or both phenyl group(s) is (are) substituted with one or more nitro groups, and

n is 1, 2, or 3,

are particularly suitable for use in direct-positive silver halide emulsions comprising color forming couplers.

The above desensitizing agents were found to be fully compatible with color couplers in that they favourably resist desorption from the silver halide grains by color forming couplers.

The desensitizing agents corresponding to the above general formulae are not only suitable for use as such but it is also possible to use the corresponding disulphides thereof or such desensitizing agent precursor compounds e.g., compounds corresponding to the general formulae or a tautomeric form thereof wherein the tautomeric hydrogen atom is replaced by a —COX group in which X represents alkyl, aryl, aralkyl or a group identical to the diazine group linked to the carbonyl group of —COX, by a —SO₂Y group in which Y is alkyl, aryl or aralkyl or by a —COOZ group wherein Z is alkyl or aryl.

Therefore, in accordance with the present invention there is provided a direct-positive photographic emulsion comprising fogged silver halide grains, a color-forming coupler and a desensitizing agent corresponding to one of the above general formulae, a corresponding disulphide thereof or such desensitizing agent precursor compound.

The present invention further provides a method of producing direct-positive color images, which method comprises image-wise exposing a direct-positive element having prefogged silver halide grains and comprising a desensitizing agent according to one of the above general formulae, a corresponding disulphide thereof or such desensitizing agent precursor compound, and developing said element by means of an aromatic primary amino color developing agent in the presence of a color-forming coupler.

Representative examples of desensitizing agents for use according to the present invention can be found in British Pat. No. 796,873 filed Dec. 10, 1954 by Gevaert Photo-Producten N.V.

The amount of desensitizing compounds used according to the present invention may vary within very wide limits. They are preferably used in amounts ranging from about 100 mg to about 2 g per mole of silver halide.

Color forming coupling compounds are well known in the art of silver halide photography. These compounds couple whilst forming dyes with the oxidized aromatic primary amino color developing agent, e.g., p-phenylene diamine and derivatives thereof, such as N,N-dialkyl-p-phenylene diamines, e.g., N,N-diethyl-p-phenylene-diamine, 2-amino-5-diethylamino-toluene, 2-amino-[N-ethyl-N-(β-methylsulphonyl-amino)ethyl]amino-toluene, N-butyl-N-sulpho-butyl-p-phenylene diamine, etc.

These color-forming couplers include cyan-forming color couplers of the phenol or naphthol type, magenta forming color couplers of the pyrazolone or indazolone type and yellow forming open-chain reactive methylene compounds containing the —CO—CH₂—CO— group, e.g., benzoylacetanilide couplers. They include polymeric as well as non-polymeric color couplers.

The color-forming couplers can be incorporated into the direct-positive photographic silver halide emulsion any suitable technique, e.g., from aqueous alkaline solutions or by techniques of the type shown in U.S. Pat. Nos. 2,186,849 of Gustave Wilmanns, Kreis Bitterfield, Karl Kumetat, Alfred Fröhlich, Wilhelm Scheider and Richard Brodersen issued Jan. 9, 1940; 2,269,158 of Michele Martinez issued Jan. 6, 1942; 2,284,887 of Emil Vollenweider issued June 2, 1942; 2,304,939 of Emil Vollenweider issued Dec. 15, 1942; 2,304,940 of Leopold D.Mannes and Leopold Godowsky Jr. issued Dec. 15, 1942; 2,322,027 of Edwin E. Julley and Paul W. Vittum issued June 15, 1943 and 2,801,171 of Scheuring S. Fierke and Jonas John Chechak issued July 30, 1957, in British Pat. Nos. 719,219 filed Nov. 9, 1955 by Kodak Ltd.; 1,098,594, 1,099,414, 1,099,415, 1,099,416, 1,099,417 all filed Jan. 25, 1965 by Gevaert-Agfa N.V., in French Pat. No. 1,555,663, filed Oct. 20, 1967 by Gevaert-Agfa N.V. in Belgian Pat. No. 722,026 filed Oct. 9, 1968 by Gevaert-Agfa N.V., in German Pat. No. 1,127,714 filed Aug. 20, 1960 by Perutz Fotowerke G.m.b.H. and in French Pat. No. 2,039,738 filed March 19, 1970 by Gevaert-Agfa N.V.

The direct-positive emulsions can be prepared according to known methods. The silver halide composi-

tion is not critical and may consist of any of the known silver halides suitable for the formation of direct-positive silver halide emulsions, e.g., silver bromide, silver chloride, silver chlorobromide, silver bromoiodide and silver chlorobromoiodide.

Especially suitable for use according to the present invention are direct-positive silver halide emulsions, the silver halide grains of which have an average grain size of less than about 1 micron. The silver halide grains may be regular and have one of the commonly known shapes, e.g., cubic, octahedral or rhombohedral as described in British Pat. Application No. 14,224/71 filed May 11, 1971 by Gevaert-Agfa N.V. They preferably have a substantially uniform diameter.

Fogging of the silver halide emulsions may occur by exposure before or after coating of the emulsion, to actinic radiation but preferably fogging occurs by chemical means. Chemical fogging can be effected by chemical sensitization to fog and any of the usual chemical sensitizing methods may be used. Fogging can be effected successfully by means of reducing agents, e.g., hydrazine, hydroxylamine, tin(II) salts such as tin(II) chloride, ascorbic acid, formaldehyde, thiourea dioxide also called formamidine sulphinic acid, polyamines, phosphonium salts etc. The emulsions may also be sensitized chemically to fog by means of metal compounds, the metal of which is more electropositive than silver, e.g., compounds of gold, rhodium, platinum, palladium, iridium, and the like, e.g., gold (III) chloride, potassium chloroaurate, and ammonium chloropalladate. Fogging of the silver halide can be caused also by high pH and/or low pAg silver halide precipitating and digestion conditions.

The direct positive silver halide emulsions may further comprise all kinds of known emulsion ingredients, e.g., wetting agents, development accelerators, optical brightening agents, hardeners, such as formaldehyde and mucochloric acid, stabilizers, spectral sensitizing dyes, which include cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, and hemicyanines, etc.

Gelatin is preferably used as a vehicle for the silver halide but like in other silver halide emulsions the gelatin may be replaced wholly or partly by other hydrophilic colloids, e.g., colloidal albumin, zein, agar-agar, polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partly hydrolyzed cellulose esters, e.g., partly hydrolyzed cellulose acetate etc.

The emulsions may be coated on any of a wide variety of supports in accordance with usual practice to provide light-sensitive silver halide materials. The supports include glass, paper, baryta-coated paper, polyolefin-coated paper, e.g., coated with polyethylene and polypropylene, which in order to promote adhesion of the emulsion may be electron-radiated, film supports of cellulose acetate, cellulose acetate-butylate, polyesters, e.g., polyethylene terephthalate, etc.

The following examples illustrate the present invention.

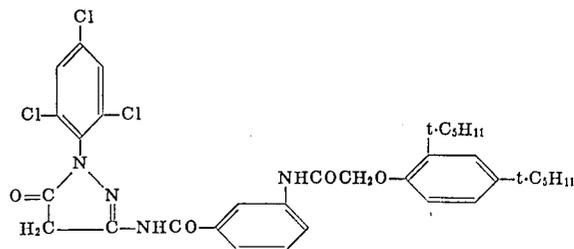
EXAMPLE 1

A monodisperse, cubic direct-positive photographic silver bromoiodide emulsion (2.5 mole percent of iodide) having an average grain size of about 0.2 micron, was prepared under controlled pH, pAg, and temperature conditions during precipitation of the silver halide. The pH was maintained at about 5.5, the pAg

at 8.2 and the temperature at 45°C. After adjustment of the pAg to 10, the emulsion was chill-set, shredded, and washed with cold water.

The emulsion was reduction- and gold-fogged by adjustment of the pAg to 5.3 and the pH to 7, by heating for 90 minutes at 60°C and by the addition of 30 mg of chloroaurate per mole of silver halide. Heating was continued for 80 minutes at 60°C whereupon the pAg was adjusted to 8.2 at 35°C.

The emulsion was divided into several samples and to each sample one of the desensitizing agents listed in the table below was added in an amount of 600 mg per mole of silver halide. To some samples a magenta-forming color coupler of the formula :

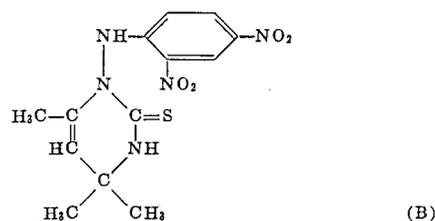


was added also in an amount of 40 g. per mole of silver halide.

The values of the speed obtained after exposure and conventional black-and-white or color processing are listed in the table below. The values given for the speed are relative log exposure values. An increase of these values by 0.30 means a doubling of the speed.

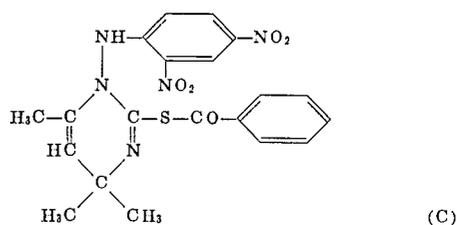
TABLE

Desensitizing agent	Black-and-white processing		Color processing in the presence of color coupler
	without color coupler	in the presence of color coupler	
pinacrytol yellow (A)	2.80	0	0
	2.80	2.40	2.00



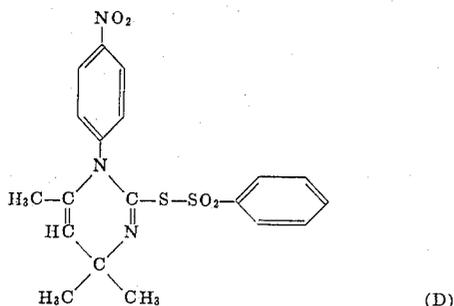
The above results show that pinacrytol yellow is completely desorbed by the color coupler used, so that no direct-positive image is formed whereas the desensitizing agent of the present invention resists desorption by the color coupler.

When the above desensitizing agent B was replaced by one of the following desensitizing agent precursors C and D



and

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prepared as described hereinafter, it was also found that no substantial desorption by the color coupler occurred.

The desensitizing agent precursor C was prepared as follows :

The desensitizing agent B was dissolved in pyridine, whereupon benzoyl chloride was added with cooling. The mixture was left standing for 12 hours, whereupon the precipitate of pyridinium chloride was filtered off by suction and the filtrate poured out into water. The precipitate formed was filtered off by suction and was washed till free of pyridine.

Melting point : 200°C (with decomposition).

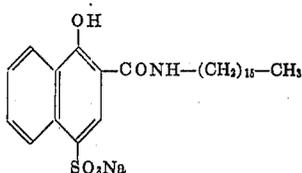
The desensitizing agent precursor D was prepared as follows :

The corresponding mercapto compound of compound D, which was prepared as described in British Pat. No. 796,873 filed Dec. 10, 1954 by Gevaert Photo-Producten N.V., was dissolved in pyridine, whereupon benzene sulphochloride was added at 50°C. The mixture was heated for 4 hours at 70°C and then poured into water. The precipitate formed was filtered off by suction and washed till free of pyridine.

Melting point : 170°C (with decomposition).

EXAMPLE 2

Example 1 was repeated with the difference that the magenta-forming color coupler was replaced by the cyan forming color coupler corresponding to the formula :



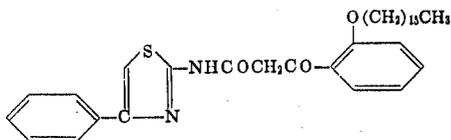
The values of the speed obtained are listed in the following table.

TABLE

Desensitizing agent	Black-and-white processing		Color processing in the presence of color coupler
	without color coupler	in the presence of color coupler	
A	2.80	0	0
B	2.80	1.60	1.20

EXAMPLE 3

Example 1 was repeated with the difference that the magenta-forming color coupler was replaced by a yellow-forming color coupler corresponding to the formula :



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The values of the speed obtained are listed in the following table.

TABLE

Desensitizing agent	Black-and-white processing		Color processing in the presence of color coupler
	without color coupler	in the presence of color coupler	
A	2.80	2.00	0
B	2.80	2.60	1.80

The above results show that even though by black-and white processing in the presence of a color coupler, pinacrytol yellow gives rise to the formation of a direct-positive image, no direct-positive image formation could be observed when the element was color processed.

EXAMPLE 4

Example 1 was repeated with the difference that 5-m-nitrobenzylidene rhodanine was used as comparative desensitizing agent instead of pinacrytol yellow.

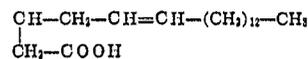
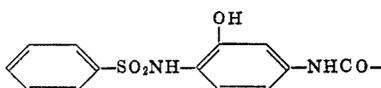
The values of the speed obtained are listed in the following table.

TABLE

Desensitizing agent	Black-and-white processing		Color processing in the presence of color coupler
	without color coupler	in the presence of color coupler	
5-m-nitrobenzylidene rhodanine	2.80	0	0
B	2.80	2.60	2.40

EXAMPLE 5

Example 4 was repeated with the difference that the magenta-forming color coupler was replaced by the color coupler of the formula :



The values of the speed obtained are listed in the following table.

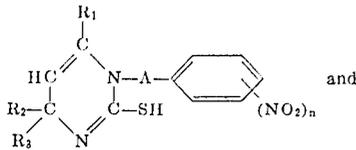
TABLE

Desensitizing agent	Black-and-white processing		color processing in the presence of color coupler
	without color coupler	in the presence of color coupler	
5-m-nitrobenzylidene rhodanine	2.80	0	0
B	2.80	3.00	2.60

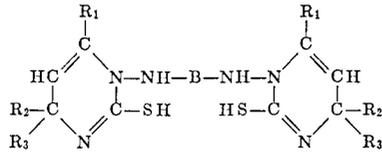
We claim :

1. A direct-positive photographic color element, which comprises uniformly fogged radiation-sensitive silver halide, a color forming coupling product capable of forming a dye on coupling with an oxidized aromatic primary amino color developing agent and a desensitizing agent or a desensitizing agent precursor wherein said desensitizing agent has one of the following gen-

eral formulae, a tautomeric form thereof, or is a corresponding disulphide :



and



wherein :

R₁ is hydroxyl or C₁-C₅ alkyl,

R₂ is hydrogen or C₁-C₅ alkyl,

R₃ is C₁-C₅ alkyl or aryl,

A is a single bond or NH,

B is phenyl or diphenyl sulphone group in which the or both phenyl group(s) is (are) substituted with one or more nitro groups, and

n is 1, 2, or 3.

2. A direct-positive photographic element according to claim 1, wherein the said desensitizing agent precursor is a compound corresponding to one of the general formulae of claim 1, or a tautomeric form thereof, wherein the tautomeric hydrogen atom is replaced by a -COX group in which X represents alkyl, aralkyl, aryl, or a group identical to the diazine group linked to the carbonyl group of -COX, by a -SO₂Y group in which Y is alkyl, aryl, or aralkyl, or by a -COOZ group wherein Z is alkyl or aryl.

3. A direct-positive photographic element according to claim 1, wherein the said desensitizing agent or desensitizing agent precursor is present in an amount comprised between 100 mg and 2 g per mole of silver halide.

4. A direct-positive photographic element according to claim 1, wherein the silver halide has been fogged uniformly by chemical means.

5. A direct-positive photographic element according to claim 4 wherein the silver halide has been fogged uniformly by means of reducing agents.

6. A direct-positive photographic element according to claim 5, wherein said reducing agent is thiourea dioxide.

7. A direct-positive photographic element according to claim 4, wherein the silver halide has been fogged uniformly by means of a gold compound.

8. A direct-positive photographic element according to claim 4, wherein the silver halide has been fogged uniformly by means of a reducing agent and a gold compound.

9. A direct-positive photographic element according to claim 8, wherein said reducing agent is thiourea dioxide.

10. A direct-positive photographic element according to claim 1, wherein the silver halide has been fogged uniformly by means of high pH and/or low pAg silver halide precipitating and digestion conditions.

11. A direct-positive element according to claim 1, wherein the silver halide has been fogged uniformly by means of a gold compound and by high pH and/or low pAg silver halide precipitating and digestion conditions.

12. A direct-positive photographic element according to claim 1, wherein the silver halides of the emulsion have a substantially uniform diameter.

13. A direct-positive photographic element according to claim 1, wherein the silver halide grains have an average grain size of less than 1 micron.

14. A method of producing a direct-positive image, which comprises exposing image-wise to radiation a direct-positive element according to claim 1, and developing the exposed material in a silver halide developer comprising an aromatic primary amino color developing agent.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,779,776 Dated December 18, 1973

Inventor(s) Willy Joseph VANASSCHE ET AL

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

Title page, in the heading, [73] Assignee, "AFGA-Gevaert, N. V., Mortsel, Belgium" should read -- Agfa-Gevaert, N. V., Mortsel, Belgium --. Column 1, lines 62 - 63, before "general" insert -- above --. Column 2, lines 34 - 35, "2-amino- [N-ethyl-N-(β -methylsulphonyl-amino)ethyl] amino-toluene" should read -- 2-amino-5-[N-ethyl-N-(β -methylsulphonyl-amino)ethyl] amino-toluene --. Column 3, line 13, "Gevaert-Agfa N. V." should read -- Agfa-Gevaert, N. V. --; Column 3, lines 67 - 68, "temperature" should read -- thermal --.

Signed and sealed this 29th day of october 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents