

[54] **PHOTOGRAPHIC SILVER HALIDE RECORDING MATERIAL**
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[73] Assignee: **AGFA-Gevaert N.V., Mortsel, Belgium**

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 Dec. 21, 1970 Great Britain..... 60633/70

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[51] **Int. Cl.** G03c 5/30, G03c 1/06, G03c 1/02

[58] **Field of Search** 96/95, 114.1, 66 T, 48 HD, 96/61

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[57] **ABSTRACT**

A photosensitive heat-developable element comprising a silver halide emulsion, a developing agent and a post-exposure stabilizing agent. The post-exposure stabilizing agent can be for example, 3-allylimidazolin-2-thione. After exposure, an image can be developed and stabilized in one step by heating to a temperature within the range of about 80°-200°C.

14 Claims, No Drawings

PHOTOGRAPHIC SILVER HALIDE RECORDING MATERIAL

This invention relates to an improved process for the production of photographic images by means of a "dry" processing.

In the United Kingdom Patent Specification 930,572 filed Apr. 8, 1960 by Kodak Co. a process for the production of silver images has been described wherein a photographic silver halide emulsion layer containing an alkaline substance and a pyrazolidin-3-one silver halide developing agent is image-wise exposed to electromagnetic radiation in order to form a latent image whereupon said image is developed by subjecting the exposed material to heat.

As described in the United Kingdom Patent Specification 1,001,702 filed Oct. 12, 1961 by Gevaert Photo-Producten N.V. the heat-development of silver halide materials containing pyrazolidin-3-one can proceed in the absence of alkaline substances and in the presence of a substance or substances liberating water while the pH of the recording layer is kept at 7 or less.

The main problem associated with the application of said processes lies in the dry post-exposure stabilization of the visible image, since without effective stabilization an overall illumination of the developed material will bring about an undesirable background colouration.

For the post-exposure stabilization of heat-developable alkali-containing silver halide materials mercaptans such as thiosalicylic acid and 1-phenyl-5-mercaptotetrazole have been proposed. These mercaptans appear to react with the residual silver halide and form a much less light-sensitive silver salt than the original silver halide.

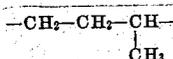
In practice, however, said mercaptans proved to having a desensitizing action on the silver halide and to react therewith already in the coating stage to such a considerable extent, that in fact little stabilizing agent was left for effecting the post-exposure stabilization.

According to the present invention photosensitive silver halide recording materials are used in a dry processing comprising a heat-development of a latent silver image by means of a reducing agent suited for the heat development of photoexposed silver halide whereupon the produced silver images are stabilized by means of a heterocyclic sulphur compound corresponding to the following general formula or the tautomeric thiol structure thereof:



wherein:

X represents sulphur or a -NR- group, wherein R represents hydrogen, a saturated or unsaturated aliphatic group, e.g. an alkyl group, preferably a C₁-C₅ alkyl group, a hydroxyalkyl group e.g. β-hydroxyethyl, an allyl group or an aromatic group such as a phenyl group, and Z represents the necessary carbon atoms to close a 5- or 6-membered nucleus, e.g. -(CH₂)₂-, -(CH₂)₃-, -CH=CH- or



Particularly suited stabilizing agents are those having the structural formulae mentioned in the following Table.

TABLE

1...		Can be prepared, e.g. according to Ber. 5 (1872), 240.
2...		Can be prepared, e.g. according to Ber. 22 (1889), 1354.
3...		Can be prepared, e.g. according to the French patent specification 1,094,167 filed March 2, 1954 by Ruhrchemie A.G.
4...		Prepared as described hereinafter.
5...		Prepared according to Am. J. Chem. 32 (1954) 59.
6...		Prepared according to Ber. 24 (1891) 2191.
7...		Prepared according to Ann. 607 (1957) 73-91.

PREPARATION OF 3-ALLYLIMIDAZOLIN-2-THIONE (COMPOUND 4)

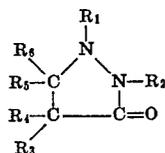
To 40 g (0.4 mole) of N-allylethylenediamine, prepared as described in J. Am. Chem. Soc. 67 (1945)

1581, and 80 ml of methylcellosolve 36.5 g (0.48 mole) of carbon disulphide were added dropwise with stirring at 50°C. A white precipitate formed. On boiling the reaction mixture is dissolved while hydrogensulphide evolved. The solution was cooled at 5°C and the precipitate filtered with suction. Yield : 50.9 g. Melting point : 87°-88°C.

These stabilizing agents may be used as separate compounds or in admixture. They may be used in the photosensitive layer containing the silver halide or in an adjacent layer from which they can come in effective contact with the silver halide during the coating or heat-development step.

Preferred developing agents for reducing exposed silver halide with the aid of heat are pyrazolidin-3-one derivatives that have reducing properties. Other developing agents suited for the purpose are, e.g., aromatic polyhydroxy compounds and their reducing derivatives such as hydroquinone, pyrogallol, resorcinol, 2,3-dihydroxy-naphthalene and pyrocatechol, aromatic hydroxy-amino compounds and their reducing derivatives such as *p*-aminophenol hydrochloride, *p*-methylaminophenol sulphate, *p*-hydroxyphenylglycin and 8-hydroxy-1,2,3,4-tetrahydroquinoline; aromatic poly-amino compounds and their reducing derivatives such as *p*-phenylene-diamine and 4,4-diaminodiphenylamine; 3-aminopyrazoline derivatives that have reducing properties such as 1-phenyl-3-aminopyrazoline.

Pyrazolidin-3-one developing agents that are particularly suited for use according to the present invention correspond to the following general formula:



wherein:

R₁ represents an aryl group including a substituted aryl group e.g. phenyl, α -naphthyl or β -naphthyl including substituted aryl e.g. substituted by alkyl such as methyl, aralkyl such as benzyl, alkoxy such as methoxy, amino, dialkylamino, halogen such as bromine and chlorine, hydroxyalkyl, hydroxy or acetamido, or a heterocyclic group, R₂ represents hydrogen or an acyl group e.g. an acetyl group, each of R₃, R₄ and R₅ (equal or different) represents hydrogen, an alkyl group including a substituted alkyl group, or an aryl group including a substituted aryl group, and

R₆ represents hydrogen, an alkyl group preferably comprising at most 4 C-atoms, an alkoxy group preferably comprising at most 4 C-atoms, an aralkoxy group, an aryloxy group, or an aryl group including a substituted aryl group.

For example R₁ can be benzothiazolyl or an aryl group of the benzene or the naphthalene series, either substituted or not. The R₃, R₄, R₅ and R₆ are preferably hydrogen atoms or alkyl groups comprising from 1 to 4 carbon atoms or aryl groups such as phenyl or naphthyl, either substituted or not.

Together with the pyrazolidin-3-one developing agent, which is the primary developing agent, an auxiliary developing agent may be used. In that connection reference is made to ascorbic acid, hydroquinone, py-

rogallol, 2,3-dihydroxy-naphthalene, *p*-phenylenediamine, *p*-aminophenol, monomethyl-*p*-aminophenol, H₂SO₄, 8-hydroxy-1,2,3,4-tetrahydroquinoline and a 2-hydrazino-benzthiazole e.g. 2-hydrazino-6-sulpho-benzthiazole.

Examples of pyrazolidin-3-one developing agents useful for the purpose of the present invention are the following:

1. 1-phenyl-pyrazolidin-3-one
2. 1-(*p*-tolyl)-pyrazolidin-3-one
3. 1-(*p*-tolyl)-pyrazolidin-3-one
4. 1-phenyl-2-acetyl-pyrazolidin-3-one
5. 1-phenyl-4-methyl-3-pyrazolidin-3-one
6. 1-phenyl-5-methyl-3-pyrazolidin-3-one
7. 1-phenyl-4,4-dimethyl-pyrazolidin-3-one
8. 1-phenyl-5,5-dimethyl-pyrazolidin-3-one
9. 1,5-diphenyl-pyrazolidin-3-one
10. 1-(*m*-tolyl)-5-phenyl-pyrazolidin-3-one
11. 1-(*p*-tolyl)-5-phenyl-pyrazolidin-3-one
12. 1-*p*-chlorophenyl-pyrazolidin-3-one
13. 1-phenyl-5-phenyl-pyrazolidin-3-one
14. 1-*p*-methoxyphenyl-pyrazolidin-3-one
15. 1-phenyl-2-acetyl-4,4-dimethyl-pyrazolidin-3-one
16. 1-phenyl-4,4-dimethyl-pyrazolidin-3-one
17. 1-*m*-aminophenol-4-methyl-4-*n*-propyl-pyrazolidin-3-one
18. 1-*o*-chlorophenyl-4-methyl-4-ethyl-pyrazolidin-3-one
19. 1-*m*-acetamidophenyl-4,4-diethyl-pyrazolidin-3-one
20. 1-*p*-chlorophenyl-4-methyl-4-ethyl-pyrazolidin-3-one
21. 1-*p*-acetamidophenyl-4,4-diethyl-pyrazolidin-3-one
22. 1-(*p*- β -hydroxyethylphenyl)-4,4-dimethyl-pyrazolidin-3-one
23. 1-*p*-hydroxyphenyl-4,4-dimethyl-pyrazolidin-3-one
24. 1-*p*-methoxyphenyl-4,4-diethyl-pyrazolidin-3-one
25. 1-*p*-tolyl-4,4-diethylpyrazolidin-3-one
26. 1-(7-hydroxy-2-naphthyl)-4-methyl-4-*n*-propylpyrazolidin-3-one
27. 1-*p*-diphenyl-4,4-dimethylpyrazolidin-3-one
28. 1-(*p*- β -hydroxyethylphenyl)-pyrazolidin-3-one
29. 1-*o*-tolyl-pyrazolidin-3-one
30. 1-*o*-tolyl-4,4-dimethyl-pyrazolidin-3-one
31. 1-(2'-benzothiazolyl)-pyrazolidin-3-one
32. 1-phenyl-4,4-dihydroxymethyl-pyrazolidin-3-one
33. 1-phenyl-4,4-dimethyl-5-methoxy-pyrazolidin-3-one
34. 1-phenyl-4,4-dimethyl-5-ethoxy-pyrazolidin-3-one
35. 1-phenyl-4,4-dimethyl-5-*n*-propoxy-pyrazolidin-3-one
36. 1-phenyl-4,4-dimethyl-5-isopropoxy-pyrazolidin-3-one
37. 1-phenyl-4,4-dimethyl-5-benzyloxy-pyrazolidin-3-one
38. 1-phenyl-4,4-dimethyl-5-phenoxy-pyrazolidin-3-one
39. 1-phenyl-4-methyl-4-hydroxymethyl-pyrazolidin-3-one
40. 1-phenyl-4-ethyl-4-hydroxymethyl-pyrazolidin-3-one
41. 1-(*p*-tolyl)-4,4-dimethyl-5-methoxy-pyrazolidin-3-one

42. 1-(*p*-tolyl)-4,4-dimethyl-5-ethoxy-pyrazolidin-3-one
 43. 1-(*p*-tolyl)-4,4-dimethyl-5-*n*-propoxy-pyrazolidin-3-one
 44. 1-(*p*-tolyl)-4,4-dimethyl-5-isopropoxy-pyrazolidin-3-one
 45. 1-(*p*-tolyl)-4,4-dimethyl-5-*n*-butoxy-pyrazolidin-3-one
 46. 1-(*p*-tolyl)-4,4-dimethyl-5-benzyloxy-pyrazolidin-3-one.

The 1-aryl-pyrazolidin-3-one compounds of use according to the present invention can be prepared according to techniques known in the art, e.g. as described in the United States Patent Specifications 3,330,839 of Jozef Frans Willems, Albert Lucien Poot and Raymond Albert Roosen, issued July 11, 1967 and U.S. Pat. No. 2,772,982 of Vincent C. Vesce, issued Dec. 4, 1956.

The silver halide emulsion layers suited for heat development by means of a pyrazolidin-3-one developing agent may contain an alkaline substance as described in the United Kingdom Patent Specification 930,572 mentioned above, but have not to contain such substance to yield a photographic silver image as described in the United Kingdom Patent Specification 1,001,702 mentioned above.

When a pyrazolidin-3-one is used in alkaline medium in combination with, e.g. hydroquinone as an auxiliary developing agent, less of the pyrazolidin-3-one is necessary to maintain high development activity and thus silver images can be produced with a minimum of heat energy.

An alkaline substance may be advantageous for accelerating the development of the latent image and such substance is therefore either present in the silver halide emulsion layer or in an adjacent layer from which on heating it can penetrate into the silver halide emulsion layer containing the pyrazolidin-3-one developing agent.

The alkaline substances, which may be employed in the sensitive materials together with the developing agents, include inorganic substances that when dissolved in water can yield a pH above 7 such as sodium hydroxide, sodium carbonate, sodium metaborate, sodium sulphite and organic alkaline substances such as aliphatic amines, e.g. ethanalamine and ethylenediamine or heterocyclic amines, e.g. morpholine and quaternary ammonium bases.

Since alkaline substances yield images with a fairly strong optical density but are disadvantageous with regard to the keepability of the recording material a compromise has to be found in the use of substances liberating alkali on heating. In that respect are particularly mentioned sodium formate, sodium acetate, ammonium acetate, sodium benzoate, tetramethylguanidine, aminoquinidine hydrogen carbonate, trichloroacetic acid guanidine salt (see the French patent of Addition 93,748 filed Jan. 24, 1968 by Kodak-Pathé), 4-amino-2,6-dimethyl-pyrimidine and an addition complex compound of diethylamine and 2,2'-bis(4-hydroxy-2,3,5,6-tetrachlorophenyl)-propane.

Additional ingredients, which may be present in the light-sensitive silver halide emulsion layer or in a layer wherefrom they can come in effective contact with the silver halide, are substances having a plurality of aliphatic ether and/or hydroxyl groups such as are present in polymers containing oxyalkylene e.g. oxyethylene

groups, and aliphatic polyols of which glycerol and the non-reducing oligosaccharides, e.g. sucrose and raffinose, are particularly useful for enhancing the development activity.

5 In order to improve the developability of the light-sensitive material it may contain likewise a compound or compounds liberating water on heating, e.g. salts that contain a high amount of crystal water and can easily set free a certain amount thereof as e.g. sodium carbonate-10-water or that contain a high amount of water in adsorbed or absorbed state as present, e.g., in a clathrate structure, or simply contain water associated with a hygroscopic compound, e.g. glycerol or polyethylene glycols.

15 In the presence of an alkaline substance effecting in the recording layer a pH of at least 8, 15 to 60 of pyrazolidin-3-one developing agent per mole of silver halide yield upon heating of the information-wise exposed recording material a high density silver image. 20 When in the alkaline medium an auxiliary developing agent such as an ascorbic acid developing agent or hydroquinone is present together with a saccharide, as little as 5 g of pyrazolidin-3-one per mole of silver halide are sufficient.

25 In the absence of a pH-increasing compound but in the presence of (a) compound(s) liberating water on heating the recording layer having a pH of 7 or less preferably contains from 0.1 mole to 2 moles of pyrazolidin-3-one developing agent per mole of silver 30 halide.

The auxiliary developing agents such as those containing ascorbic acid may be used in amounts of 30-100 g per mole of silver halide and the aromatic polyhydroxy developing agents such as hydroquinone 35 in the range of 15 to 75 g per mole of silver halide.

The saccharides and polymeric oxyalkylene compounds may be used in amounts ranging from 30 to 600 g per mole of silver halide.

40 The post-exposure stabilizing agent of the above general formulae (I) or (II) is preferably used in a range of molar ratios of 1:2 to 2:1 with respect to the silver halide.

Any kind of photosensitive silver halide may be used 45 in a recording material according to the present invention, but for reason of light-sensitive and development speed preference is given to silver bromide and silver chlorobromide emulsions.

50 The photosensitive coating composition may be applied to a paper support or film support. It may be advantageous to use a paper base having a thin foil of aluminium laminated thereto in order to have a better heat conductance in the heat-development step.

55 The heat-development of the silver halide recording materials may proceed in the range of 80° to 200°C. Application of heat may be carried out in different ways, e.g. by contact with a hot substance or body such as a hot plate or rollers, by high-frequency electric field heating, Joule effect heating, or by means of a hot gas stream.

60 The development may also proceed by infra-red radiation absorbed by suitable substances present in heat-conductive contact with the silver halide. In that case the silver halide emulsion layer is used, e.g., in combination with a carbon-black-containing layer from which it is separated by means of a heat-conductive white pigment layer containing, e.g., zinc oxide or titanium dioxide. The exposure to infrared radiation is

then carried out preferably through the rearside of the recording material.

The following examples illustrate the present invention. The amounts are expressed in parts by weight, unless otherwise indicated.

EXAMPLE 1

A photographic paper support of 90 g/sq.m was coated at a coverage of 75 g per sq.m with a following mixture for forming a heat-developable photosensitive silver

6 % aqueous gelatin solution	200 g
polyoxyethylene glycol (average molecular weight: 200)	30 g
imidazolidin-2-thione as a post-exposure stabilizing agent	16 g
ethanol	240 g
1-phenyl-pyrazolidin-3-one	10 g
4 % aqueous formaldehyde solution	10 ml
10 % aqueous saponine solution	3 ml
a gelatino-silver chlorobromide emulsion (50 mole percent bromide) containing 0.45 mole of silver halide per kg (average particle size of silver halide grains: 0.4 nm)	500 g

The pH of the coating mixture was 5.8

After drying the photosensitive layer was exposed through a microfilm halftone print in a commercial microfilm enlarging copying apparatus, and developed by heating it for 5 sec. at 140°C in contact with a hot plate.

The obtained image had a maximum optical density of 0.62 and a minimum optical density of 0.10. It showed no background colouration after a several days exposure to daylight.

EXAMPLE 2

A photographic paper support of 90 g/sq.m was coated at a coverage of 100 g per sq.m with a following mixture for forming a heat-developable photosensitive silver halide recording layer:

6 % aqueous gelatin solution	200 g
glycerol	20 g
1-methyl-2-mercapto-imidazole as a post-exposure stabilizing agent	17 g
ethanol	240 G
1-phenyl-pyrazolidin-3-one	10 g
4 % aqueous formaldehyde solution	10 ml
12 % aqueous saponine solution	3 ml
a gelatino-silver chloride emulsion containing 75 g of silver chloride per kg (average particle size of silver halide grains : 0.3 nm)	300 g

The pH of the coating mixture was 4.9.

After drying the photosensitive layer was exposed in contact with a transparent halftone original. The development proceeded by heating the image-wise exposed material for 7 sec. at 130°C by conveying it between a pair of hot rollers. The obtained image had a maximum density of 0.93 and a minimum density of 0.08 and proved to be stable under overall daylight exposure for several weeks.

EXAMPLES 3-6

Similar results were obtained after having replaced the 1-phenyl-pyrazolidin-3-one from the recording layer in example 2 by the same amount of:

- 1-phenyl-4-methyl-4-hydroxymethyl-pyrazolidin-3-one
- 1-phenyl-4-ethyl-4-hydroxymethyl-pyrazolidin-3-one

1-phenyl-4,4-dihydroxymethyl-pyrazolidin-3-one, or

1-phenyl-4-methyl-pyrazolidin-3-one.

EXAMPLE 7

A photographic paper support of 90 g/sq.m was coated at a coverage of 75 g per sq.m with a following mixture for forming a heat-developable photosensitive silver halide recording layer:

6 % aqueous gelatin solution	200 g
polyoxyethylene glycol (average molecular weight: 200)	30 g
imidazolidin-2-thione as a post-exposure stabilizing agent	16 g
ethanol	240 g
1-phenyl-pyrazolidin-3-one	10 g
4 % aqueous formaldehyde solution	10 ml
12 % aqueous saponine solution	3 ml
trichloroacetic acid guanidine salt	40 g
a gelatino-silver chlorobromide emulsion (50 mole percent bromide) containing 0.45 mole of silver halide per kg (average particle size of silver halide grains : 0.4 nm)	500 g

The pH of the coating mixture was 5.9.

The photosensitive layer dried at 30°C was exposed through a microfilm halftone print in a commercial microfilm enlarging copying apparatus and developed by heating it for 1-20 sec. at 100°-150°C in contact with a hot plate.

The obtained image had a maximum optical density of about 0.80 above fog and proved to remain stable under overall daylight exposure.

EXAMPLE 8

A photographic paper support of 90 g/sq.m was coated at a coverage of 132 g per sq.m with a following mixture for forming a heat-developable photosensitive silver halide recording layer:

6 % aqueous gelatin solution	220 ml
6-methyl-tetrahydro-1,3-thiazinc-2-thione	20 g
ethanol	240 ml
1-phenyl-pyrazolidin-3-one	10 g
4 % aqueous formaldehyde solution	10 ml
12 % aqueous saponine solution	3 ml
a gelatino-silver chloro-bromide emulsion (50 mole % bromide) containing 0.55 mole of silver halide per kg (average particle size of silver halide grains: 0.4 nm)	300 g
25 % aqueous ethanolamine solution	10 ml

The pH of the coating mixture was 8.0

After drying the photosensitive material was exposed through a transparent halftone original and developed by heating the image-wise exposed material for 5 sec at 135°C in contact with a hot plate.

The obtained image had a maximum density of 0.91 and a minimum density of 0.09. It proved to be stable under normal daylight conditions.

EXAMPLE 9

A photographic paper support of 90 g/sq.m was coated at a coverage of 105 g per sq.m with a following mixture for forming a heat-developable photosensitive silver halide recording layer:

6 % aqueous gelatin solution	204 g
polyoxyethylene glycol (average molecular weight : 200)	30 g
imidazolidin-2-thione	16 g
ethanol	240 g
P-methylaminophenol sulphate	12 g
sodium acetate-3-water	40 g

EXAMPLE 9—Continued

4 % aqueous formaldehyde solution
12 % aqueous saponine solution

10 ml
3 ml

The dispersion obtained was adjusted to a pH of 8 by addition of 1N sodium hydroxide whereupon 340 g of a mixed galatino-silver chlorobromiodide emulsion (approximately 55/42.5/2.5 percent) were added containing 0.49 mole of silver halide per kg (the silver halide grains sizing 0.4 nm on the average).

After drying, the photosensitive material was exposed through a transparent halftone original and developed by heating said material for 5 sec at 140°C in contact with a hot plate. A visible image was obtained with a maximum density of 0.54 and a minimum density of 0.10. It proved to be stable under normal daylight conditions.

EXAMPLES 10-14

Other heat-developable photosensitive silver halide recording layers were obtained by replacing the p-methylaminophenol sulphate in example 9 by the same amount of

hydroquinone
pyrogallol
resorcinol
2,3-dihydroxy-naphthalene, or
p-hydroxyphenylglycin.

After image-wise exposure and heat development for 2-20 sec at 120° to 150°C all these recording layers yielded images that were stable under normal daylight conditions.

EXAMPLE 15

A photographic paper support of 90 g/sq.m was coated at a coverage of 125 g per sq.m with the following mixture for forming a heat-developable photosensitive silver halide recording layer:

6 % aqueous gelatin solution	350 g
polyoxyethylene glycol (molecular weight: ca. 200)	18 g
imidazoline-2-thione	9.7 g
ethanol	80 g
1-phenyl-pyrazolidin-3-one	8 g
2-hydrazino-6-sulpho-benzothiazole	18 g
4 % aqueous formaldehyde solution	10 ml
12 % aqueous saponine solution	3 ml
a gelatino-silver chlorobromide emulsion (50 mole percent bromide) containing 0.52 mole of silver halide per kg (average particle size of silver halide grains : 0.4 nm)	210 g

The pH of the coating mixture was 5.5.

After drying, the photosensitive material was exposed through a transparent halftone original and developed by heating said material for 2 sec at 140°C in contact with a hot plate. The obtained greyish-blue image had a maximum density of 0.85 and a minimum density of 0.15. It proved to be stable under normal daylight conditions.

When the 2-hydrazino-6-sulpho-benzothiazole was omitted, the colour of the image was greyish-brown and the maximum density had a lower value.

We claim:

1. In a photosensitive heat-developable recording material comprising a support bearing at least one recording layer containing photosensitive silver halide, a reducing agent for heat-developing exposed silver halide and including a post-exposure stabilizing agent which is in effective contact with the silver halide dur-

ing heat-development, the improvement wherein said stabilizing agent corresponds to the following general formula or the tautomeric thiol form thereof:



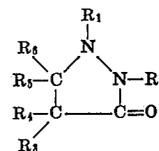
wherein:

- 10 X represents sulphur or a -NR- group, wherein R represents hydrogen or a C₁-C₃ alkyl, allyl, a β-hydroxyethyl, or phenyl group, and
Z represents -(CH₂)₂-, -(CH₂)₃-, -CH=CH- or

said recording layer having a pH not higher than 7 and said stabilizing agent is present in an amount having a molar ratio of 0.5-2:1 relative to said photosensitive silver halide.

2. A photosensitive material according to claim 1, wherein the silver halide is dispersed in gelatin as binding agent.

- 25 3. A photosensitive material according to claim 1, wherein as developing agent a pyrazolidin-3-one developing agent is used, which corresponds to the following general formula:



wherein:

R₁ represents an aryl group or a heterocyclic group,

R₂ represents hydrogen or an acyl group, each of R₃, R₄ and R₅ represents hydrogen, an alkyl group or an aryl group and may be similar or different, and

R₆ represents hydrogen, an alkyl group, an alkoxy group, an aralkoxy group, an aryloxy group or an aryl group.

4. A photosensitive material according to claim 1, wherein the silver halide is used in combination with a compound liberating water on heating.

5. A photosensitive material according to claim 1, wherein the silver halide is used in combination with a hygroscopic compound.

6. A photosensitive material according to claim 1, wherein the silver halide is used in combination with a polymer containing oxyalkylene groups.

7. A photosensitive material according to claim 1, wherein the silver halide is used in combination with a polyol.

8. A photosensitive material according to claim 1, wherein an alkaline compound is present in an adjacent layer to said recording layer from which it can penetrate into the recording layer so that during development the pH of the recording layer is raised above 7.

9. A photosensitive material according to claim 8, wherein said alkaline compound is sodium formate, sodium acetate, ammonium acetate, sodium benzoate, tetramethylguanidine, aminoguanidine hydrogen car-

11

bonate, trichloroacetic acid guanidine salt, 4-amino-2,6-dimethyl-pyrimidine, or an addition complex compound of diethylamine and 2,2-bis(4-hydroxy-2,3,5,6-tetrachlorophenyl)-propane.

10. A photosensitive material according to claim 3, wherein the pyrazolidin-3-one developing agent is used in conjunction with a minor amount of an auxiliary developing agent.

11. A photosensitive material according to claim 10, wherein 2-hydrazino-benzothiazole is said auxiliary developing agent.

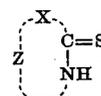
12. A photosensitive material according to claim 1, wherein the stabilizing agent is present in the layer containing the silver halide.

13. A photosensitive material according to claim 1, wherein the stabilizing agent is present in a layer adjacent to the silver halide containing layer.

14. A process for the production of silver images, which comprises information-wise exposing to electromagnetic radiation a photosensitive recording material comprising a support bearing at least one recording layer containing photosensitive silver halide, a reducing agent for heat-developing exposed silver halide and including in effective contact with the silver halide during heat-development, a post-exposure stabilizing agent corresponding to the following general formula or the

12

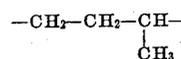
tautomeric thiol form thereof:



wherein:

X represents sulphur or a -NR- group, wherein R represents hydrogen or a C₁-C₅ alkyl, allyl, a β-hydroxyethyl, or phenyl group, and

Z represents -(CH₂)₂-, -(CH₂)₃-, -CH=CH- or



said recording layer having a pH not higher than 7 and said stabilizing agent is present in an amount having a molar ratio of 0.5-2:1 relative to said photosensitive silver halide, forming a latent image in accordance with the light-struck areas; and heating the exposed material to a temperature within the range of about 80°-200°C to develop a silver image in the exposed areas of the material and to form in the unexposed areas a silver compound that is more stable to light than silver halide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,801,330 Dated April 2, 1974

Inventor(s) Eric Maria BRINCKMAN 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 10, Claim 1, approximately line 15, after "or",

insert -- $-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-$ --.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents