United States Patent

Blake et al.

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[54] NITROGEN-CONTAINING DMAX MAINTAINERS FOR USE IN PHOTOSOLUBLE EMULSIONS

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[52] **U.S. Cl.** **96/64**, 96/94

[51] **Int. Cl.** **G03c 5/24**

[58] **Field of Search** 96/64, 94

[56] **References Cited**

UNITED STATES PATENTS

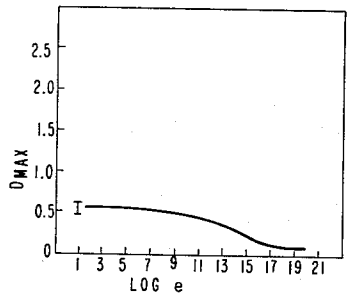
3,495,982	2/1970	Blake	96/64
3,493,373	2/1970	Blake	96/64
3,155,507	11/1964	Blake	96/64
2,497,917	2/1950	Stauffer	96/66

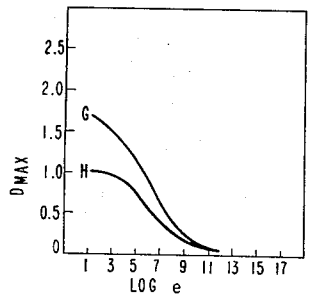
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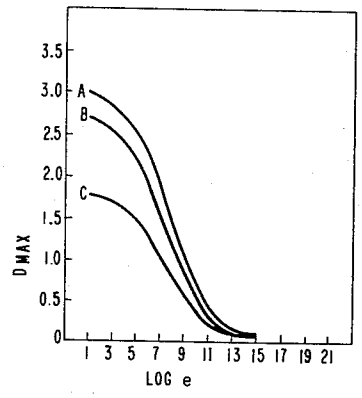
[57] **ABSTRACT**

An improved process for forming a silver halide image by selective exposure of a photosoluble silver halide layer and dissolution of the exposed photosoluble silver halide in a silver halide solvent characterized by the presence in either the layer, solvent, or both, of a heterocyclic nitrogen-containing compound which loses a proton to form anions at an elevated pH, e.g., benzotriazoles, naphthotriazoles, 5-nitroimidazoles, and 6-nitroindazole, which compounds enhance the action of mercaptan insolubilizers in photosoluble emulsions. New photosoluble elements for making direct positive images are provided by the invention.

8 Claims, 4 Drawing Figures







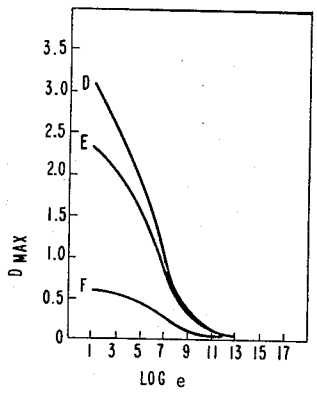


FIG. 1

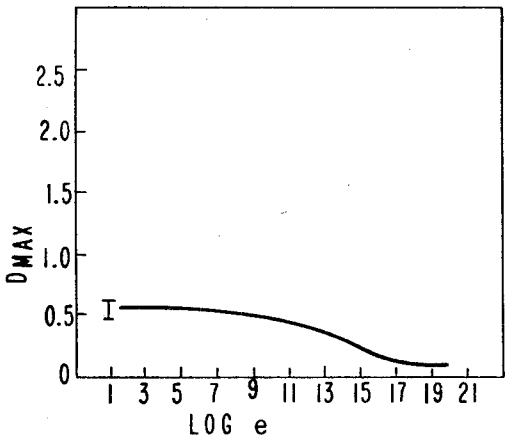


FIG. 2

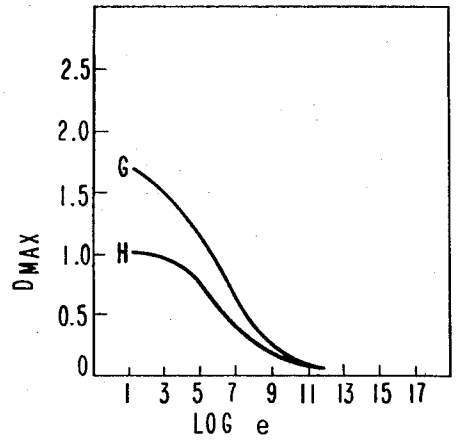


FIG. 3

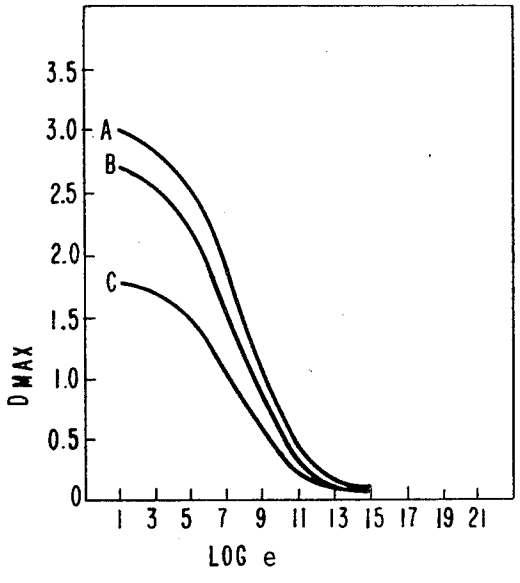
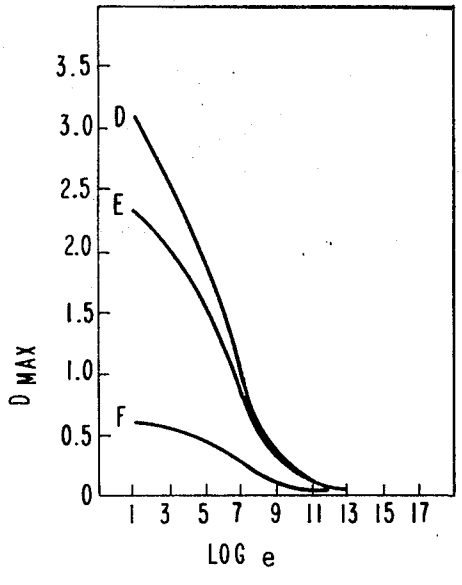


FIG. 4



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NITROGEN-CONTAINING DMAX MAINTAINERS FOR USE IN PHOTOSOLUBLE EMULSIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for forming images from photosoluble (photosolubilizable) silver halide layers. The present invention represents an improvement in a silver halide photosolubilization process by the use of a nitrogen-containing additive which aids in preventing dissolution of silver halide in unexposed areas while allowing dissolution to proceed in the exposed areas. Such an additive can be characterized as a maximum density maintainer, or Dmax maintainer.

2. Description of the Prior Art

Photosolubilization image-forming processes and photosoluble layers and elements useful in the basic process are described in assignees Blake, U.S. Pat. Nos. 3,155,507 and 3,155,514–9 Nov. 3, 1964; Blake application U.S. Ser. No. 629,426, filed Apr. 10, 1967 now U.S. Pat. 3,490,909; Haugh application U.S. Ser. No. 478,421 filed Aug. 9, 1965; now U.S. Pat. 3,451,819 and Strange Application U.S. Ser. 653,590 filed June 23, 1967 now U.S. Pat. 3,495,983. In these patents and applications there are described simple and useful layers and processes for obtaining a silver halide image in a single processing step. Intensification of the image, e.g., by reduction to a black metallic silver image, constitutes an optional additional step.

In the above mentioned patents various organic compounds are disclosed as insolubilizers. These compounds when included in the emulsion protect the silver halide crystals so that the unexposed silver halide is not dissolved by conventional fixing conditions. Of the group, the mercapto compounds have generally been found preferable as insolubilizers. The maximum density or Dmax obtainable with these insolubilizers is limited, especially when processing is carried out in high pH (8–13) reduction-dissolution developers. As the amount of mercaptan insolubilizer is raised, the speed of the element is lowered.

SUMMARY OF THE INVENTION

This invention has as its object an improvement in the photosolubilization process of forming a direct positive silver halide image, which process comprises

a. exposing, imagewise, a photosoluble layer containing silver halide made relatively less soluble in a silver halide solvent by treatment with an organic compound containing sulfur and nitrogen, and capable of forming a silver salt of lower solubility in water than silver chloride,

b. dissolving the exposed silver halide in a silver halide solvent comprising an aqueous bath of an alkali metal or ammonium thiosulfate, the improvement being characterized by the addition of small amounts of heterocyclic nitrogen-containing compounds having at least two intracyclic nitrogen atoms and being taken from the group consisting of benzotriazole, 1,2-naphtha-triazole, 5-nitrobenzimidazole, and 6-nitroindazole. These compounds lose a proton to form anions at an elevated pH.

The nitrogen-containing compounds have been found to be Dmax maintainers and enhance the action of the organic insolubilizing compound in preferentially retarding the dissolution of silver halide in the unexposed, as compared to the exposed areas of the photosoluble element. These Dmax maintaining compounds also exert this action when they are present in high pH reduction—dissolution developers.

The presence of the nitrogen-containing heterocyclic Dmax maintainers of this invention yield a higher speed direct positive than can be obtained by using only the insolubilizing mercaptains set out in the prior art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In practicing this invention, a photosoluble silver halide layer as defined in Blake, U.S. Pat. No. 3,155,519, preferably a layer of silver chloride emulsion insolubilized with 2-mercapto-4-phenylthiazole or a related mercaptan as disclosed in said patent is prepared. The element may have a photographic optical sensitizing dye associated with its silver halide crystals as disclosed in Blake U.S. Pat. No. 3,384,485, May 21, 1968. The nitrogen-containing Dmax maintainers of this invention are incorporated in the silver halide emulsion layer while the emulsion is in the liquid state, or the emulsion may first be coated on a support and dried, and the resulting element bathed or impregnated with a solution, e.g., an aqueous alcoholic solution of the organic compound. The amount of Dmax maintaining compound will vary depending on the desired application of the film, the particular organic compound, the size and nature of the silver halide crystals, and the presence of other materials which may partially cover the surface of the silver halide crystal, (e.g., the principal insolubilizer) but generally varies between 0.2 and 1.33 grams/mole of silver halide.

The nitrogen-containing heterocyclic compounds which are useful in this invention contain at least two nitrogen atoms on the heterocyclic ring, have a *pKa* between 6 and 11, and preferably contain no solubilizing groups, e.g., benzotriazoles, naphthotriazoles, 5-nitrobenzimidazoles and 6-nitroindazole.

Any of the various photosoluble silver halide elements described in the U.S. Patents and Blake and Haugh applications set forth above can be used in operating this invention. These may be modified as described in the U.S. patents and Blake and Haugh applications listed herein, by variations in the silver halide, the binder (if present), the additives generally employed in silver halide systems, the supports, and in the relative concentrations of the various components. The preferred organic compounds used as primary insolubilizers for the silver halide crystals are mercaptans, as set forth in the Blake, U.S. Pats. described above, since these function best in the high pH systems of this invention.

Various auxiliary layers may be present, such as antiabrasion layers, subbing layers, and antihalation under coats or backing layers. The elements may include multilayer as well as monolayer structures. Inert ingredients such as pigments, organic polymer latices and matting agents may be included in the various layers of this photosoluble element. As disclosed in U.S. Pat. No. 3,155,507, the silver halide may be insolubilized by treatment with an appropriate organic compound either during emulsion manufacture or by treating the coated element with a solution of the organic compound.

The photosoluble layer is exposed imagewise to actinic radiation and then treated in a solution of a silver halide solvent (e.g., sodium thiosulfate) to remove soluble silver halide in the exposed image ares, thus forming a positive silver halide image. The silver halide solvent bath may contain a phenolic Dmax maintainer as disclosed in U.S. Pat. 3,495,983. As illustrated by the Examples set out below, these phenolic Dmax maintainers are complementary to the heterocyclic nitrogen containing Dmax maintainers of this invention, and cannot by themselves provide similar results. The time and temperature of treatment will vary from 30 seconds to 5 minutes dependent on the concentration of the solution, exposure of the photosoluble element or other similar factors. This treatment removes silver halide from the exposed areas at a much faster rate than from the unexposed areas, leaving a positive silver halide image. The presence of the nitrogen containing heterocyclic Dmax maintainers of this invention, in the emulsion further lowers the rate of dissolution of the unexposed silver halide, relative to that of the unexposed silver halide, thus providing superior image formation and higher densities in unexposed areas. The film speed at equal Dmax levels is greater in films treated with the heterocyclic nitrogen containing Dmax maintainers of this invention.

A useful positive image, particularly for viewing by projection, is obtained by this single treatment, however, a washing step is generally employed. For most purposes, it is desirable to intensify the silver halide image, usually by treating with a photographic silver halide developer solution to reduce the image to one of black metallic silver. Prior to reduction, the

silver halide image may be fogged by flashing momentarily to white light or, by use of a prefogged element such as described in U.S. Pat. Nos. 3,490,909 and 3,451,819 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.

The presence of solubilizing groups (—COOH, —SO_3H) in the heterocyclic nitrogen containing Dmax maintainers of this invention should be avoided.

An alternative embodiment of this invention has the heterocyclic nitrogen-containing Dmax maintainer in the reduction-dissolution developer. In such event, the emulsion may or may not contain the Dmax maintaining compound.

The Dmax maintaining compounds of this invention effect an improvement by raising the speed of a photosoluble emulsion while maintaining a higher Dmax than is possible with o-phenylphenol or other prior art Dmax maintainers. An added advantage of the presence of these compounds is the fact that less precise control of processing conditions is allowable, e.g., concentration of silver halide solvent, temperature of the solution, and period of time required for treatment. A further advantage is that adequate Dmax can be maintained while using a smaller amount of he primary mercapto insolubilizer.

The invention will be further illustrated by the following examples, however, the scope of the invention is not intended to be limited thereby.

EXAMPLE I

A photosoluble element was prepared by coating a gelating silver chloride emulsion (average grain diameter about 0.18μ) containing 0.74 grams/mole of 2-mercapto-4-phenyl-thiazole (hereinafter referred to as MPT), 2.50×10^{-2} grams/mole of 3-ethyl-(3,7-dimethyl-2-thiazolinylidene) rhodanine on a vinylidene chloride copolymer subbed polyester base prepared as described in Example IV of Alles, U.S. Pat. No. 2,779,684 (and to which a gelatin sub layer has been subsequently applied). The emulsion contains the conventional gold and sulfur sensitizers. Normal emulsion adjuvants were added including gel hardening agents. A second photosoluble element, identical with the first was prepared, except that it contained 1.0 gram of 1,2-naphtho-triazole/mole of silver halide.

The following compositions were prepared.

Solution A (pH 8.85) Reduction - Dissolution developer	
Water	500 ml.
Sodium Thiosulfate	32 g.
3N Sodium Hydroxide	10 ml.
1-phenyl-3-pyrazolidone	0.5 g.
Sodium Sulfite (anhydrous)	10 g.
Ascorbic Acid	2.5 g.
Distilled Water to make	1 liter

Solution B Photographic silver halide developer	
Water	750 ml.
Metol	1.5 g.
Sodium Sulfite (anhydrous)	22.5 g.
Hydroquinone	6.0 g.
Sodium Carbonate	40.0 g.
Potassium Bromide	1.0 g.
Water to make	1 liter

Samples of the dried photosoluble film elements were exposed through a 2 step wedge for 15 seconds at 24 inches distance from a tungsten filament incandescent lamp (General Electric Reflector Photoflood Lamp No. PH/RFL/2). Each sample was processed in the reduction dissolution developer (A) described above for 5 minutes at 68° F. A second identical sample of each film was exposed in the same manner, but processed for only 1 minute in the developer. Positive silver chloride images of good quality were obtained in both films.

Both samples were washed for 50 seconds in water, and then given an overall exposure to white light for 3 seconds. The images were then intensified by treatment for 1 minute in a photographic silver halide developer solution (B) at 68° F. The films were then washed in water for 5 minutes and dried in air.

Of the films processed for one minute, the sample containing the heterocyclic Dmax maintainer of this invention had a maximum transmission optical density of 2.6, while the sample which did not contain the heterocyclic Dmax maintainer has a maximum transmission optical density (hereafter referred to as Dmax) of 0.07.

The samples processed for 5 minutes showed Dmax of 0.0, and 0.50 for the film not treated with heterocyclic Dmax maintainer, and that which was so treated, respectively.

These data indicate that incorporation of the heterocyclic Dmax maintainers of this invention in the emulsion make it possible to hold Dmax on processing in a reduction dissolution developer not containing a Dmax maintainer such as the orthophenylphenol of U.S. Pat. 3,495,983.

EXAMPLE II

Two photosoluble elements were prepared as in Example I except that 0.90 grams/mole of silver halide of MPT was incorporated into the emulsion. Exposure and processing yielded direct positive images and were identical to Example I with the following results:

No Dmax Maintainer	1,2-naphthotriazole
1 min. Processing = Dmax 1.20	1 min. Processing = Dmax 4.0+
5 min. Processing = Dmax 0.04	5 min. Processing = Dmax 1.25

EXAMPLE III

Photosoluble elements were prepared as in Example I and II, and exposed in the identical manner. Processing was for 5 minutes at 68° F. in a reduction-dissolution developer of the same composition as A in Example I except that it contained 10 ml. of a 5 percent o-phenylphenol solution prepared as follows:

o-Phenylphenol	5 g.
3N NaOH	33 ml.
Na_2SO_3 (anhyd.)	1 g.
H_2O to	100 ml.

Following this, the samples were intensified as in Example I.

mpt level	no heterocyclic Dmax maintainer	1.0 g./mole 1,2-naphthotriazole
0.79 g. per mole	Dmax = 0.07	Dmax = 4.0+
0.90 g. per mole	Dmax = 4.0	Dmax =4.0+

Good quality direct positive images were obtained.

This indicates that adequate Dmax may be maintained with a low quantity of MPT through use of 1,2-napthotriazole in the emulsion. A lower quantity of MPT is desirable in a photosoluble emulsion since film speed is inversely proportional to the amount of MPT in the emulsion.

EXAMPLE IV

A photosoluble element was prepared as in Example I with the modification that 0.02 g./mole of silver halide of 3-ethyle-(3,7-dimethyl-2-thiazolinylidene) rhodanine was used; the silver halide had an average grain diameter about 0.35μ; and 0.6 grams per mole of silver halide of 2-mercaptoquinoline was added to the emulsion as the primary insolubilizer. This sample was used as a control. Further identical samples were prepared except that one of the following heterocyclic Dmax maintainers was added to each emulsion in the specified amounts. A conventional gold sensitizer was used in this emulsion.

A — 5-nitrobenzimidazole — 0.34 g./mole of silver halide
B — 6-nitroindazole — 0.34 g./mole

C — 1,2naphthotriazole — 0.34 g./mole

After exposure as in Example I, I, the three samples, and control were processed for 5 minutes in the developing solution of Example III at 68° F. to form direct positive images.

The following Dmax measurements were obtained from these processed elements:

	Dmax
Control	2.95
A	3.39
B	3.65
C	3.85

Insolubilization was enhanced and hence Dmax when the primary insolubilizer was supplemented by a heterocyclic nitrogen containing Dmax maintainer.

EXAMPLE V

Ortho-phenylphenol and 1,2-naphthotriazole were compared as Dmax maintainers when incorporated in photosoluble emulsions.

A photosoluble element was prepared as in Example IV with the following modifications. This emulsion contained the usual amounts of the conventional gold and sulfur sensitizers, and 0.45 g./mole of silver halide of MPT was used as the primary insolubilizer (MPT level is low and only partially insolubilizes). This sample was used as a control. Two more samples were prepared containing 0.53 g./mole of silver halide of 1,2-naphthotriazole, and 0.53 g./mole of o-phenylphenol, respectively, as Dmax maintainers.

The element was exposed as in Example I and processed for 5 minutes at 68° F. in the developing solution of Example III to form direct positive images. The following results were obtained:

Emulsion	Dmax
Control	1.25
1,2-naphthotriazole	2.40
o-phenylphenol	1.17

In this emulsion presence of O-phenylphenol has little or no action in increasing Dmax, while 1,2-naphthotriazole almost doubles Dmax.

EXAMPLE VI

A photosoluble element was prepared as in Example I with the following specifications. The average grain diameter ca. 0.35μ. **The emulsion was gold and sulfur sensitized as in Example I, however,** 2×10^{-2} g./mole of silver halide of 3-ethyl-(3,7-dimethyl-2-thiazolinylidene) rhodanine was added, 0.34 g. of 2-mercapto-4-phenyl thiazole/mole of silver halide was added as the primary insolubilizer, and 0.54 g. of 1,2-naphthotriazole/mole of silver halide was then added.

A second emulsion was prepared, identical to the first except only 0.50 g. of MPT/mole of silver halide was added to the emulsion, and no Dmax maintainer was employed.

Both emulsions were coated, dried and exposed as in Example I, and processed with the same solution and technique as in Example III to yield direct positive images.

The sample containing MPT and 1,2-naphthotriazole provided a higher speed direct positive with a Dmax equivalent to the sample containing only MPT. More MPT was necessary in the absence of 1,2-naphthotriazole to give Dmax obtained with the combination of MPT and 1,2-naphthotriazole.

EXAMPLE VII

Photosoluble elements were prepared as in Example I, however, the amount of insolubilizer and heterocyclic Dmax maintainer was as set out in Table A below. Exposure and processing were similar to Example I and yielded direct positive images.

TABLE A

Sample No.	g/mole MPT (Insolubilizer)	g/mole Dmax Maintainer	Dmax
Y	0.34	0.00	0.0
H	0.34	0.27	1.0
G	0.34	0.53	2.1
F	0.42	0.00	0.7
E	0.42	0.27	2.5
D	0.42	0.53	3.6
C	0.50	0.00	2.1
B	0.50	0.27	2.9
A	0.50	0.53	3.1
X	0.00	0.83	0.0

The curves in the attached drawing, which forms part of this application, illustrate that higher Dmax at higher speed is possible with the combination of MPT and the heterocyclic nitrogen-containing compounds of this invention, e.g., a comparison of samples Y, H, G, and X indicates that a higher Dmax and higher film speeds are obtainable through use of a smaller amount of the primary insolubilizer in combination with the nitrogen-containing compounds of this invention, rather than through use of a larger amount of insolubilizer alone. Sample Y uses the same amount of primary insolubilizer as Samples H and G, yet it may be seen that no visible density is produced in Sample Y. Similarly, Sample X reveals that the effect of this invention depends on use of the nitrogen-containing compounds and the primary insolubilizers together, and is not due solely to the presence of the nitrogen-containing compounds. Samples H and G provide further documentation of the synergistic effects of this invention, as progressively higher Dmax are obtainable, while maintaining speed through addition of the nitrogen-containing compounds of this invention.

In assignee's copending application of Jack No. Freshwater Strange (filed June 23, 1967, Ser. No. 653,590 now U.S. Pat. No. 3,495,983) entitled "Photosolubilization Process Using Phenols as Dmax Maintainers," there is described and claimed a similar process using phenolic Dmax maintainers. The nitrogen-containing Dmax maintainers of this invention are, in general, equal or superior to the phenolic Dmax maintainers of said application.

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

1. An improved process for forming a direct positive silver halide image which comprises

a. exposing, imagewise, a photosoluble layer containing silver halide made relatively less soluble in a silver halide solvent by treatment with an organic compound containing sulfur and nitrogen, and capable of forming a silver salt of lower solubility in water than silver chloride, and

b. dissolving the exposed silver halide in said layer with a silver halide solvent comprising an aqueous bath of an alkali metal or ammonium thiosulfate, in the presence of a silver halide reducing agent;

the improvement being characterized in that a small amount of a heterocyclic nitrogen-containing compound having at least two intracyclic nitrogen atoms and being taken from the group consisting of benzotriazoles, 1,2-napthotriazoles, nitrobenzimidazoles, and nitroindazoles, is present during step (b).

2. A process according to claim **1**, wherein the amount is in the range 0.2 to 1.33 grams per mole of silver halide.

3. A process according to claim **1**, wherein the organic compound containing sulfur and oxygen is 2-mercapto-4-phenylthiazole.

4. A process according to claim **1**, wherein the heterocyclic nitrogen-containing compound is present in the aqueous silver halide solvent solution of having a pH of at least about 8.

5. A process according to claim **1**, wherein the heterocyclic nitrogen-containing compound is present initially in the silver halide emulsion.

6. In a photographic element comprising a support bearing a photosoluble silver halide layer containing an organic compound containing sulfur and nitrogen as the insolubilizing

compound the improvement comprising the presence in said layer of a heterocyclic nitrogen-containing compound containing at least 2intracyclic nitrogen atoms being taken from the group consisting of benzotriazoles, 1,2-naphthotriazoles, nitrobenzimidazoles, and nitroindalzoles.

7. An element according to claim 6, wherein said heterocyclic nitrogen-containing compound is taken from the group consisting of benzotriazole, 1,2-naphthotriazole, 5-nitrobenzimidazole, and 6-nitroindazole.

8. A process according to claim 1, wherein said heterocyclic nitrogen-containing compound is selected from the group consisting of benzotriazole, 1,2-naphtho-triazole, 5-nitrobenzimidazole, and 6-nitroindazole.

* * * * *