

[54] **PROCESSING FOR PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE ELEMENT**

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[51] Int. Cl.G03c 5/26, G03c 5/30

[58] Field of Search96/50, 50 PT, 66.5, 109, 111, 96/102, 140

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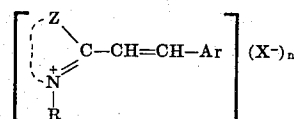
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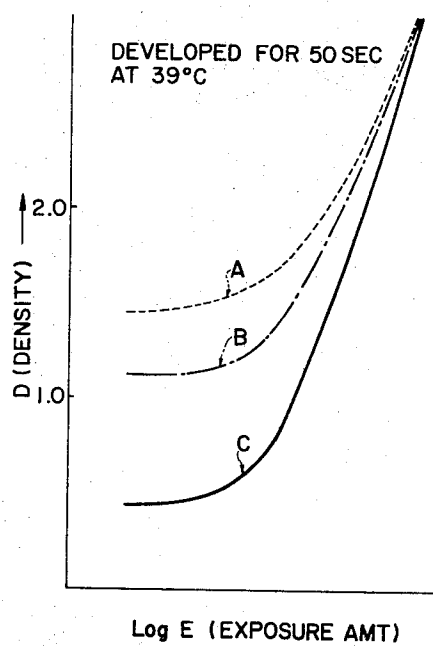
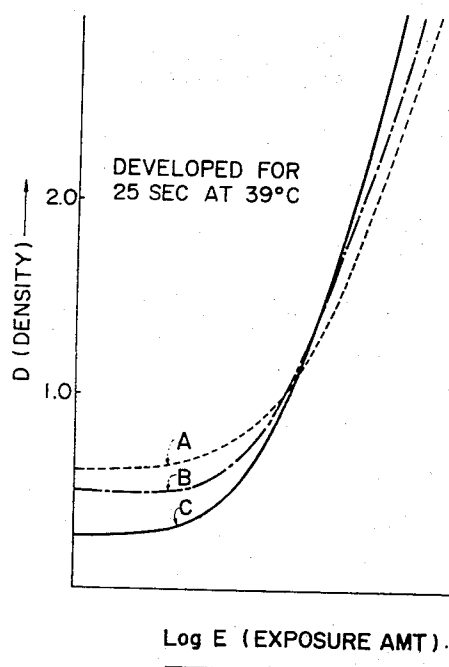
[57] **ABSTRACT**

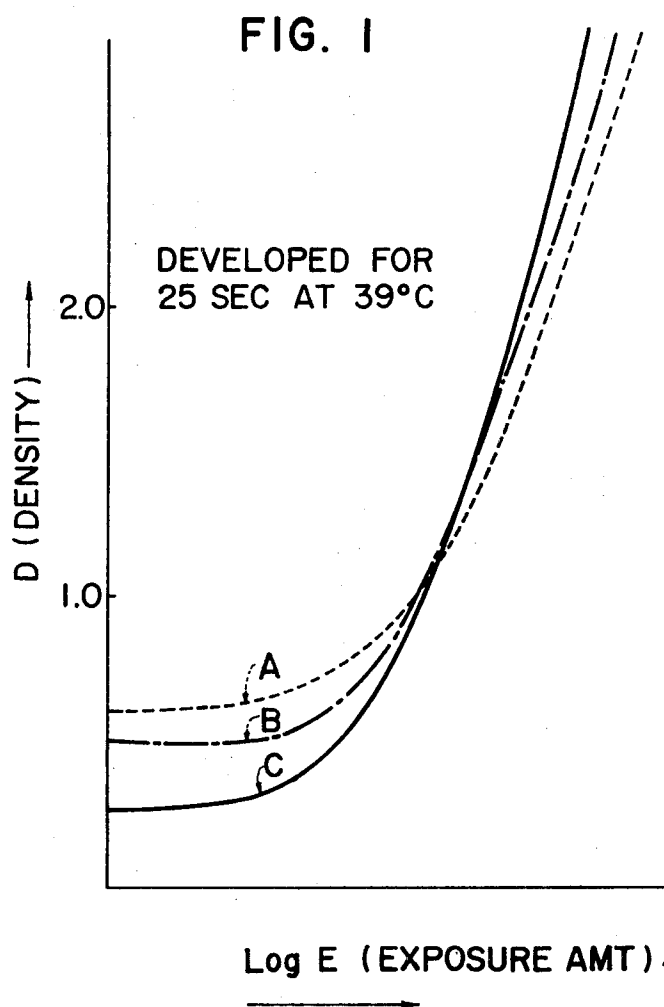
In a method of processing a photographic silver halide light-sensitive element wherein in the development processing steps of said photographic silver halide light-sensitive element, the improvement comprising processing the exposed photographic silver halide light-sensitive element in the presence of an aldehyde-type hardening agent and a compound represented by the formula



wherein Z represents an atom necessary to complete a heterocyclic ring, R represents a lower alkyl group or a substituted alkyl group, Ar represents a phenyl group or a substituted phenyl group, X represents an acid residual group, and n is 0 or 1, the n being 0 when the compound forms an internal salt.

14 Claims, 2 Drawing Figures

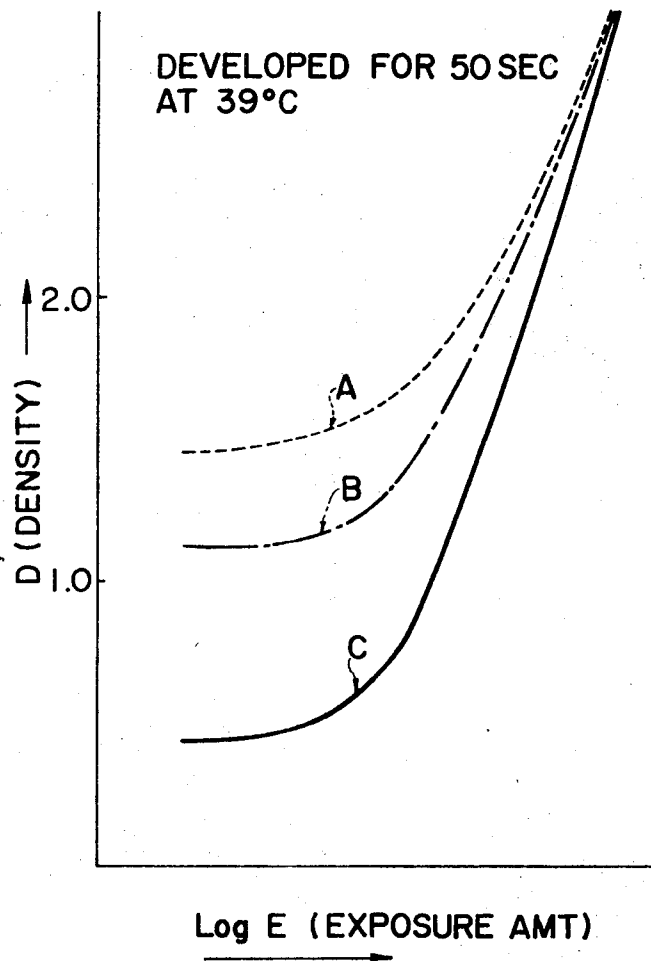




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FIG. 2



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PROCESSING FOR PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE ELEMENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method for processing photographic silver halide light-sensitive elements and more particularly to a method for processing photographic silver halide light-sensitive elements using an aldehyde-containing gelatin hardening agent and an antifoggant.

2. Description of Prior Art

As a method of efficiently conducting the development of photographic silver halide light-sensitive elements, there is known a so-called high temperature, high speed developing process by using a high temperature developer or other high temperature processing solutions and such a process is effectively applied to various photographic silver halide light-sensitive elements.

However, as light-sensitive elements are processed at a high temperature in such a conventional process, the mechanical strength of the emulsion layers of the light-sensitive elements in the high temperature developer or other processing solution must be prevented from being degraded. Therefore, it is necessary to increase the mechanical strength of the emulsion layer before development or during development and maintain the mechanical strength thereof throughout the development.

For this purpose, there has been proposed a method in which a photographic silver halide light-sensitive element is, before development, subjected to a prehardening processing in a prehardening solution containing an aldehyde type hardening agent. The aldehyde compound remaining unreacted in the emulsion layer is removed by water washing or is made harmless by processing it in a solution before development.

Such a method has the advantages that the processing time is shortened by the high temperature development and the efficiency of the processing is improved but has the disadvantage that the number of the processing steps is greater than those in the usual method.

The disadvantage is caused by the use of an aldehyde compound as the hardening agent, for example; when an aldehyde, particularly a dialdehyde, is added to a developer, the formation of fog of a black and white photographic film or a photographic color film processed in the developer is remarkably increased. The formation of the fog caused by the addition of such an aldehyde can be prevented by using a strong antifoggant such as benzotriazole or mercatobenzotetrazole. However, as the use of such an antifoggant strongly suppresses the progress of development at the same time, the sensitivity of the emulsion is greatly decreased.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 show the amount of fog occurring in various films after being processed in various developer solutions.

SUMMARY OF THE INVENTION

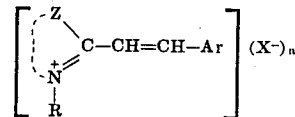
Thus, an object of the present invention is to provide a process for processing a light-exposed photographic silver halide light-sensitive element without forming fog.

Another object of this invention is to provide a process for preventing the formation of fog caused by processing a photographic silver halide light-sensitive element in a processing solution containing an aldehyde-type hardening agent.

A further object of this invention is to provide a process for developing a photographic silver halide light-sensitive element without reducing the developing speed and the sensitivity of emulsion.

The present inventors have investigated the methods of achieving the above-mentioned objects and, as a result thereof, have found that the aforesaid objects can be achieved by utilizing the present invention. More specifically, the above objects of this invention can be achieved by incorporating, in a

developing step for photographic silver halide light-sensitive elements, in the processing solution an aldehyde-type hardening agent and a compound represented by the general formula,



wherein Z represents an atom necessary to complete a heterocyclic ring, R represents a lower alkyl group or a substituted alkyl group, Ar represents a phenyl group or a substituted phenyl group, X⁻ represents an acid residual group, and n is 0 or 1, said n being 0 when the compound is an internal salt.

DETAILED DESCRIPTION OF THE INVENTION

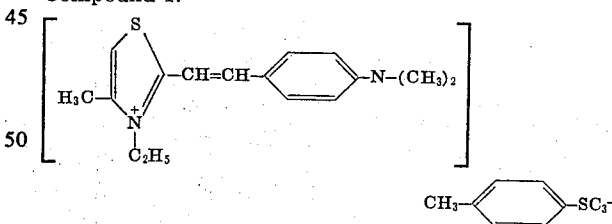
In the above-mentioned general formula, as the lower alkyl group R, the following may be used: a methyl group, an ethyl group, a propyl group and a butyl group and as the substituted alkyl group, a carboxymethyl group, a β-carboxyethyl group, a γ-carboxypropyl group, a β-hydroxyethyl group, a β-acetoxyethyl group, a β-sulfoethyl group, a γ-sulfobutyl group, a δ-sulfobutyl group, a methoxyethyl group and the like. Also, as the substituted phenyl group Ar the following are examples: phenyl groups substituted by a lower alkyl group; a hydroxyl group, an alkoxy group, a nitro group, a halogen atom, a carboxyl group, —NHCOR (wherein R represents a lower alkyl group), or



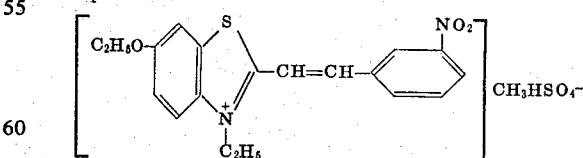
(wherein R' and R'' each represents a lower alkyl group, an aralkyl group or an aryl group, R' and R'' being the same or different). Also, as the acid residual group X⁻, there may be illustrated the following: halogen ions, such as a chlorine ion or a bromine ion, a methyl sulfate ion, a p-toluene sulfonate ion, and the like.

Typical examples of the compound represented by the aforesaid general formula are shown below:

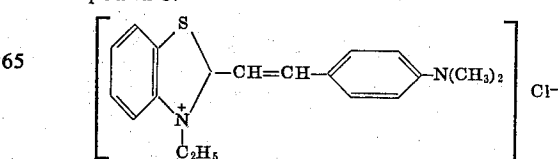
Compound 1.



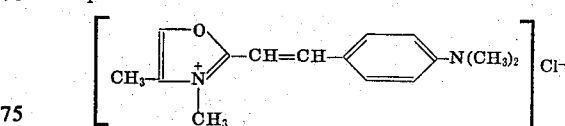
Compound 2.



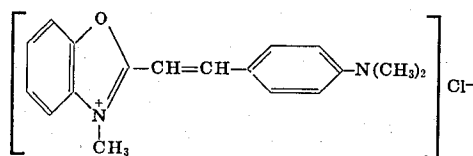
Compound 3.



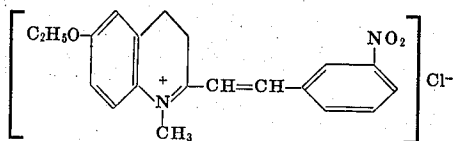
Compound 4.



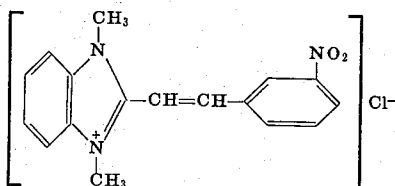
Compound 5.



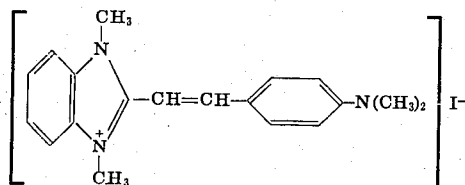
Compound 6.



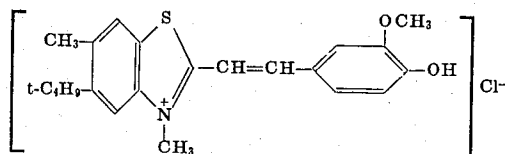
Compound 7.



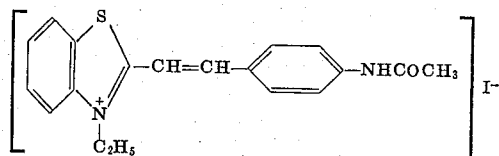
Compound 8.



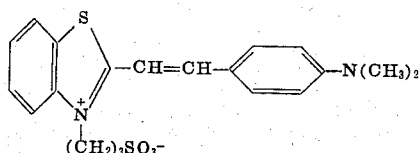
Compound 9.



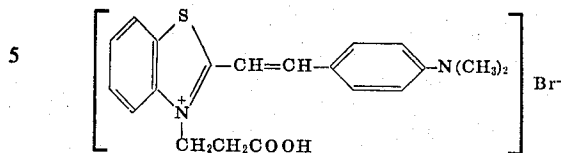
Compound 10.



Compound 11.



Compound 12.



10 The development processing steps in the specification of this invention mean a prehardening process and a development process.

It is most preferable that the light-exposed photographic silver halide element be processed in a developer containing the compound represented by the above-mentioned general formula and an aldehyde-type hardening agent but the light-exposed photographic element may be processed in a prehardening solution containing an aldehyde-type hardening agent and the aforesaid compound or may be processed in a prehardening agent and thereafter in a developer containing the aforesaid compound.

Furthermore, there is proposed another method wherein the compound represented by the aforesaid general formula is incorporated in a silver halide emulsion layer or a layer adjacent a silver halide emulsion layer and the light-sensitive element having said layer is processed in a processing solution containing the aldehyde-type hardening agent, which may be a hardening solution or a developer.

The amount of the compound represented by the aforesaid general formula giving an effective antifogging effect in the case of incorporating the compound in a developer containing the aldehyde-type hardening agent is usually 20-400 mg. particularly 100-300 mg. per 1 liter of developer. Thus, when the proportion is higher than 400 mg., the development is excessively suppressed with the result that the sensitivity is reduced. On the other hand, when the amount is lower than 20 mg., the antifogging effect is very small.

As the developer in the present invention, there may be employed an alkaline aqueous solution containing a developing agent such as N-methyl-p-aminophenol, dihydroxybenzene, 1-phenyl-3-pyrazolidine, phenylenediamine or derivatives thereof.

The aldehyde-test hardening agent used in this invention is a compound having at least one aldehyde group, such as formaldehyde, dimethylol urea, glyoxal, glutaraldehyde or the like, a sulfite thereof or a bisulfite thereof.

As the formation of fog is effectively prevented by incorporating the aldehyde-type hardening agent and the compound represented by the aforesaid general formula in a processing solution simultaneously or in processing solutions separately according to the present invention, high temperature development can be applied. Accordingly, since the water-washing process, or the process for making the remaining unreacted aldehyde harmless, required in the conventional method, becomes unnecessary, the processing time is reduced, which is profitable for high speed processing.

The process of this invention may be applied to the developing process for all photographic silver halide light-sensitive elements but may be particularly applied to a high temperature and high speed processing for black and white or color photographic elements.

The invention will further be explained by referring to the following preferable examples:

EXAMPLE 1

X-ray films exposed by using a standard sensitometer but not subjected to hardening processing were subjected to the following high temperature, high speed, processings in the following order using the following developers A, B, or C:

Development steps

Development (39° C.)	25 seconds	50 seconds
Fixing (39° C.)	5 min.	5 min.
Water washing (20° C.)	10 min.	10 min.

Developer A

1-phenyl-3-pyrazolidone	1.5 g.
Hydroquinone	20 g.
Anhydrous sodium sulfite	50 g.
Sodium hydroxide	20 g.
EDTA (2Na)	3 g.
Glutaldehyde (25%)	15 ml.
5-Methylbenztriazole	0.2 g.
Water to make 1 liter.	

Developer B

40 mg. of Compound 1 (described above) was added to 1 liter of developer A.

Developer C

170 mg. of Compound 1 was added to 1 liter of developer A.

The results are shown in FIGS. 1 and 2 of the accompanying drawings, which shows that the sample processed in developer B or developer C showed less fog than the sample processed in developer A (control). Also, the gamma and the effective sensitivity in the former (B or C) were higher than in the latter (A).

EXAMPLE 2

Commercially available high speed black and white negative photographic light-sensitive films were exposed by using a standard sensitometer and each of them was developed for 8 minutes at 20° C. in a developer shown in the following table prepared by adding only glutaldehyde (control) or glutaldehyde and Compound 7 (described above) to conventional developer D containing 1-phenyl-3-pyrazolidone, hydroquinone, anhydrous sodium sulfite, sodium carbonate, and potassium bromide and having a pH of 10.3. The results are shown in the following table:

	(A)* (ml./l.)	(B)* (mg.)	Photographic property relative intensity	gamma	fog
Developer E*	10		100	0.50	2.10
Developer F	10	50	400	0.78	1.75
Developer G	10	200	500	1.0	0.30

(A)* amount of 25% glutaldehyde;

(B)* amount of compound 7; Developer E* control case.

As shown in the above table, the photographic properties are similar to the results obtained in Example 1.

EXAMPLE 3

The photographic films as in Example 2 were exposed by using a sensitometer. One sample was then processed for 2 minutes in prehardening solution A (an aqueous solution having a pH of 10.3 and containing 10 ml. of 25 percent glutaldehyde per 1 liter of the solution) and another sample was processed for 2 minutes in prehardening solution B (an aqueous solution having a pH of 10.3 and containing 10 ml. of 25 percent glutaldehyde and 100 ml. of Compound 10 per 1 liter of the solution). Thereafter, the samples were processed for 8 minutes at 20° C. in developer D as in example 2. The results showed that the formation of fog in the sample processed in prehardening solution B was much less than that of the sample processed in prehardening solution A as in Examples 1 and 2.

EXAMPLE 4

Since a color development called "coupler-in-developer type color development", i.e., a development using a color developer containing a coupler, requires a long period of time for the processing, it is important that the emulsion layers of the color photographic film to be processed maintain their strong mechanical properties during the processing. For this purpose, a method has usually been employed in which the mechanical strength of the emulsion layers is increased by subjecting the layers to a prehardening treatment prior to the

color development procedure. That is, the color development is usually conducted as follows:

	Process I	Temp. (°C)	Time (min.)
5	1. Prehardening	27	1
	2. Washing	27	1
	3. First development	27	5
	4. Washing	27	2
	5. Reversal red exposure	-	-
	6. Cyan developer	27	5
10	7. Washing	27	1
	8. Reversal purple exposure	-	-
	9. Yellow development	27	5
	10. Washing	27	1
	11. Auxiliary development	27	1
	12. Washing	27	1
15	13. Magenta development	27	5
	14. Washing	27	1
	15. Bleaching	27	2
	16. Fixing	27	2
	17. Washing	27	2
	18. Drying	-	-

When the prehardening agent used in the above prehardening step was added to the first developing solution and the prehardening step and the washing step after the prehardening were omitted in order to shorten the processing time, the strong mechanical strength of the emulsion layers was maintained during the processing, but the coupling density was bitterly reduced and the quality of the image was lowered, which made the development process unpracticable. However, it has been found that when an aldehyde-type hardening agent and the compound of this invention shown by the above general formula were added to the first development solution, the formation of fog could be effectively suppressed, and hence the developing process could be simplified without reducing the coupling density and the mechanical strength of the emulsions while providing a better image quality.

In other words, according to the process of the present invention, the prehardening step and the water washing step before the first development in the so-called coupler-in-developer type color developing system can be omitted, as well as reducing the period of time required for finishing the first development by conducting the development at a high temperature without being accompanied with the aforesaid drawbacks, which make the process of this invention very profitable. An example of the improved steps for this development is shown below:

	Process II	Temp. (°C)	Time (sec.)
50	1. First development (hardening development)	40	90
	2. Water washing	40	30

Commercially available coupler-in-developer type reversal color photographic light-sensitive films to be processed according to Process I shown above, were exposed by using a sensitometer. One of them was processed by Process I above and another sample was processed by improved Process II (the procedures after the water washing step were the same as those in Process I).

The compositions for the processing solutions used in the above color developments are as follows:

First developer A	
N-methyl-p-aminophenol (1/2 sulfate)	20 g.
Anhydrous sodium sulfite	90 g.
Hydroquinone	8 g.
Sodium carbonate (mono-hydrate)	52.5 g.
Potassium thiocyanate	1 g.
Water to make 1 liter	

First developer B

20 ml. of 37% aqueous solution of formaldehyde was added to 1 liter of first developer A.

Improved first developer

236 mg. of Compound 11 of this invention was added to 1 liter of First developer B.

Cyan color developer

Anhydrous sodium sulfite	5.0 g.
4-amino-3-methyl-N,N-diethylaniline hydrochloride	0.6 g.
Sodium carbonate (mono-hydrate)	15.0 g.
Potassium bromide	0.25 g.
Potassium iodide (0.1% aq. soln.)	2 ml.
1,5-Dihydroxy-2,6-dibromonaphthalene	1.2 g.
Sodium hydroxide	2.0 g.
Water to make 1 liter	

Yellow color developer	
Anhydrous sodium sulfite	5.0 g.
4-amino-N,N-diethylaniline sulfate	2.5 g.
Potassium bromide	1.0 g.
Potassium iodide (0.1% aq. soln.)	5 ml.
ω -Benzoyl-4-(p-toluenesulfonamido)-acetanilide	1.2 g.
Sodium hydroxide	2.5 g.
Water to make 1 liter.	

Magenta color developer	
Anhydrous sodium sulfite	5.0 g.
4-amino-3-methyl-N,N-diethylaniline hydrochloride	2.0 g.
Potassium bromide	0.2 g.
1-phenyl-3-(m-nitrobenzylamino)-5-pyrazolone	1.4 g.
Sodium hydroxide	2.5 g.
n-butylamide	5 ml.
Water to make 1 liter	

Bleaching solution	
Ferricyanide	100 g.
Potassium bromide	10 g.
Borax	2 g.
Boric acid	1 g.
Water to make 1 liter	

Fixing solution	
Sodium thiosulfate	150 g.
Anhydrous sodium sulfite	10 g.
Water to make 1 liter	

The results are shown in the following table.

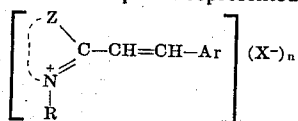
Process	Relative sensitivity			Maximum density		
	Cyan	Magenta	Yellow	Cyan	Magenta	Yellow
I*-----	100	101	107	3.50	3.80	3.20
II*-----	96	135	148	3.50	2.35	2.70
III*-----	104	96	111	3.50	4.00	3.30

(NOTE): I* (control) employing first developer A, II* (control) employing first developer B, III* employing improved developer of this invention.

The results showed that by using Process II, described above, better photographic properties could be obtained than those achieved when process I is employed.

What is claimed is:

1. A method of developing a photographic silver halide light-sensitive element, which comprises developing an exposed photographic silver halide light-sensitive element with a conventional developer containing therein, an aldehyde-type hardening agent and a compound represented by the formula:



wherein Z represents an atom necessary to complete a heterocyclic ring, R represents a member selected from the group consisting of a lower alkyl group and a substituted lower alkyl group of from one to four carbon atoms, Ar represents a member selected from the group consisting of a phenyl group and a substituted phenyl group, X represents an acid residual group, and n is 0 or 1, said n being 0 when the compound forms an internal salt.

2. The method of claim 1, wherein the amount of said compound present ranges from about 20 to about 400 mg. per 1 liter of said developer.

3. The method of claim 2, wherein the amount of said compound present ranges from about 100 to about 300 mg. per 1 liter of said developer.

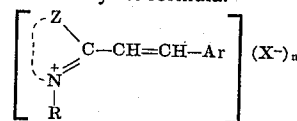
4. The method of claim 1, wherein said aldehyde-type hardening agent is a member selected from the group consisting of formaldehyde, dimethylol urea, glyoxal and glutalaldehyde.

5. The method of claim 4, wherein said hardening agent is a member selected from the group consisting of the sulfite and bisulfite adduct of formaldehyde, dimethylol urea, glyoxal and glutalaldehyde.

6. The method of claim 1, wherein said developing agent is a member selected from the group consisting of N-methyl-p-amino phenol, dihydroxy benzene, 1-phenyl-3-pyrazolidone, phenylene diamine and derivatives thereof.

7. The method of claim 1, wherein the substituted lower alkyl group is a member selected from the group consisting of a carboxymethyl group, a β -carboxyethyl group, a γ -carboxypropyl group, a β -hydroxyethyl group, a β -acetoxyethyl group, a β -sulfoethyl group, δ -sulfobutyl group, a γ -sulfobutyl group and a methoxyethyl group.

8. A method of developing a photographic silver halide light-sensitive element, which comprises prehardening and developing an exposed photographic silver halide light-sensitive element, wherein the element is pre-hardened in a solution containing an aldehyde-type hardening agent and subsequently processing in a conventional developer containing a compound represented by the formula:

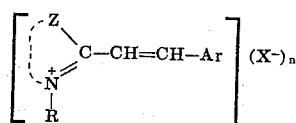


wherein Z represents an atom necessary to complete a heterocyclic ring, R represents a member selected from the group consisting of a lower alkyl group and a substituted lower alkyl group of from one to four carbon atoms, Ar represents a member selected from the group consisting of a phenyl group and a substituted phenyl group, X represents an acid residual group, and n is 0 or 1, said n being 0 when the compound forms an internal salt.

9. The method of claim 8, wherein the amount of said compound present ranges from about 20 to about 400 mg. per 1 liter of said developer.

10. The method of claim 9, wherein the amount of said compound present ranges from about 100 to 300 mg. per 1 liter of said developer.

11. A method of developing a photographic silver halide light-sensitive element, said element containing in the silver halide emulsion layer or in a photographic layer adjacent to said silver halide emulsion layer a compound represented by the formula:

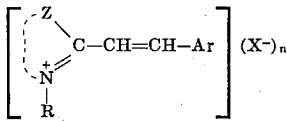


wherein Z represents an atom necessary to complete a heterocyclic ring, R represents a member selected from the group consisting of a lower alkyl group and a substituted lower alkyl group of from one to four carbon atoms, Ar represents a member selected from the group consisting of a phenyl group and a substituted phenyl group, X represents an acid residual group, and n is 0 or 1, said n being 0 when the compound forms an internal salt, which comprises processing said exposed photographic silver halide light-sensitive element with a processing solution containing an aldehyde-type hardening agent.

12. The method of claim 11, wherein the processing solution is a pre-hardener bath.

13. The method of claim 11, wherein the processing solution is a conventional developer bath.

14. A method of developing a photographic silver halide light-sensitive element, which comprises pre-hardening an exposed photographic silver halide light sensitive element in a pre-hardening solution containing an aldehyde-type hardening agent and a compound represented by the formula:



wherein Z represents an atom necessary to complete a heterocyclic ring, R represents a member selected from the group consisting of a lower alkyl group and a substituted lower alkyl group and a substituted lower alkyl group of from one to four carbon atoms, Ar represents a member selected from the group consisting of a phenyl group and a substituted phenyl group, X represents an acid residual group, and *n* is 0 or 1, said *n* being 0 when the compound forms an internal salt, and subsequently processing in a conventional developer.

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