

[54] **PROCESSING OF PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIALS**

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

[58] Field of Search .....**96/109, 66.5, 50 PT, 95**

[56]

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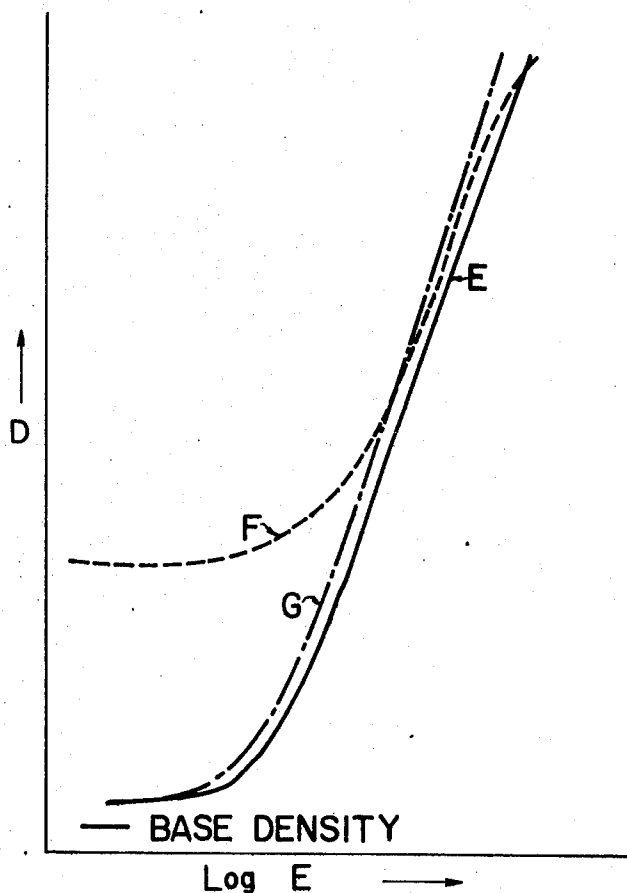
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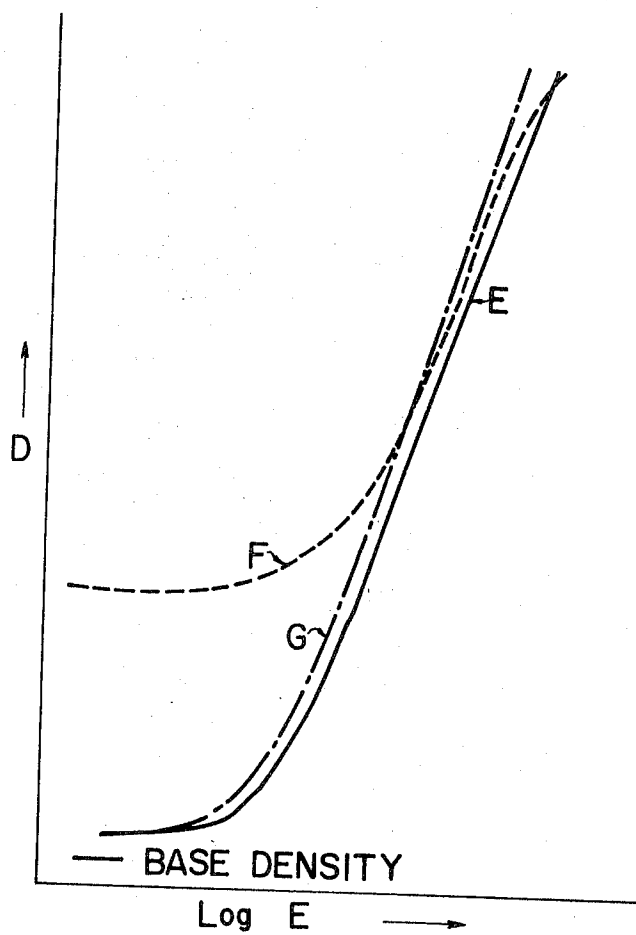
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**ABSTRACT**

Processing silver halide, light-sensitive photographic materials employing solutions containing aldehyde hardening agents and certain phenazine oxides or dioxides in order to maintain the mechanical strength of the emulsion layers thereof during processing without impairing the photographic characteristics of the processed materials.

**24 Claims, 1 Drawing Figure**





# PROCESSING OF PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIALS

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to a method of processing photographic silver halide light-sensitive materials. More particularly, it relates to a method of developing gelatino silver halide light-sensitive materials using a processing solution containing an aldehyde-type gelatin hardening agent and an antifoggant.

### 2. Discussion of the Prior Art

It is known to improve the efficiency of the development of various kinds of photographic light-sensitive materials by carrying out such development at high temperatures. When employing such processes, it is required that the mechanical strength of the emulsion layer of the photographic light-sensitive material be prevented from degradation from high temperatures. Therefore, it is necessary to improve the mechanical strength of the emulsion layer either prior to or during the development.

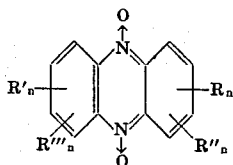
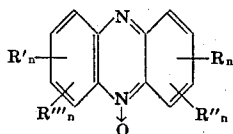
For this purpose, there has previously been practiced a method wherein the photographic emulsion layer is hardened in an aldehyde-type hardening solution during the development and the unreacted aldehyde remaining in the emulsion layer is thereafter removed by water washing or by processing with an intermediate processing solution. By means of such method, the total processing time may be shortened, since high-temperature processing can thereby be employed. However, although quick processing can be accomplished in this manner, it is accompanied by the disadvantage that the method requires an additional processing step. This disadvantage results from the use of an aldehyde compound as a hardening agent. For example, when a black and white or color photographic light-sensitive film is processed in a developer containing aldehyde, in particular, an aliphatic dialdehyde as a hardening agent, severe fog formation results. Furthermore, this tendency toward fog formation increases as the development temperature increases.

Fog formation resulting from the use of aldehydes may be prevented by the use of a powerful antifoggant such as benzotriazole or mercaptobenzotriazole, but as development is strongly suppressed by the use of such antifoggants, the sensitivity of the photographic emulsion is greatly reduced. Moreover, the characteristic curve is altered by the fog formation and linearity is adversely affected.

## SUMMARY OF THE INVENTION

The object of the present invention, therefore, is the reduction of fog formation when employing a developer containing an aldehyde hardening agent without the accompanying lowering of development speed and emulsion sensitivity.

We have found that the above object can be achieved by processing a photographic light-sensitive emulsion, prior to development, in a hardening solution containing a compound represented by the following general formula, or by developing the photographic emulsion in a developer containing said compound.



wherein R, R', R'', and R''' each represents hydrogen, alkyl, having one to four carbon atoms, aryl, halo, alkoxy, hydroxy, acylamino, carboxy or nitro and n is an integer of from 0 to 3.

## DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, combination hardening and developing processing is called the "development step."

Typical examples of the above compounds of this invention are as follows:

Compound 1.	Phenazine-5-oxide (m. p. 222° C.)
Compound 2.	1-Methylphenazine-5-oxide (m. p. 142° C.)
Compound 3.	1-Bromo-3-tert-butylphenazine -5-oxide (m. p. 128° C.)
Compound 4.	1-Phenylphenazine-5-oxide (m. p. 198° C.)
Compound 5.	2-Chlorophenazine-5-oxide (m. p. 177° C.)
Compound 6.	3-Bromophenazine-5-oxide (m. p. 161° C.)
Compound 7.	1-Methoxyphenazine-5-oxide (m. p. 188° C.)
Compound 8.	2-Ethoxyphenazine-5-oxide (m. p. 154° C.)
Compound 9.	3-Hydroxyphenazine-5-oxide (m. p. 258° C.)
Compound 10.	2-Chloro-3-hydroxyphenazine -5-oxide (m. p. 250° C.)
Compound 11.	1-Acetamidophenazine-5-oxide (m. p. 198° C.)
Compound 12.	1-Phenazinecarboxylic acid- 5-oxide (m. p. 223° C.)
Compound 13.	3-Nitrophenazine-5-oxide (m. p. 202° C.)
Compound 14.	Phenazine-5,10-dioxide (m. p. 204° C.)
Compound 15.	2-Chlorophenazine-5,10- dioxide (m. p. 190° C.)
Compound 16.	2-Methylphenazine-5,10- dioxide (m. p. 180° C.)
Compound 17.	2-Hydroxyphenazine-5,10- dioxide (m. p. 236° C.)

Compounds represented by the above formulas, including those compounds illustrated above, may be prepared by either of the following two known processes.

1. The Wohl-Aue reaction, in which an aniline derivative and a nitrobenzene derivative are reacted in a nonpolar solvent using potassium hydroxide as a condensing agent.

2. A method wherein the phenazine prepared by the condensation reaction of an o-quinone derivative and o-phenylenediamine is oxidized with hydrogen peroxide.

The compounds of this invention may be added to a developer together with an aldehyde-type hardening agent, or they may be added to a prehardening solution together with an aldehyde-type hardening agent.

In the case of adding the compound to a developer containing an aldehyde-type hardening agent, the amount of the compound added depends upon the amount of the aldehyde compound used, but is preferably 5-100 mg., more preferably 5-30 mg. per liter of developer. When amounts higher than 30 mg. are employed, although the fog formation can be effectively prevented without adversely affecting the photographic properties of the photographic light-sensitive materials processed in the developer, but, since the solubility of the compound is usually not very high, the use of a large amount of the compound tends to result in the formation of crystalline deposits in the developer. On the other hand, amounts of less than 5 mg. have no effect.

Developers which may be employed in the present invention are aqueous alkaline solutions containing, for example, N-methyl-p-aminophenol sulfate, dihydroxybenzene, 1-phenyl-3-pyrazolidone, phenylenediamine and the like, or derivatives thereof.

Hardening agents which may be employed in the present invention include compounds having at least one aldehyde group, for example formaldehyde, dimethylol urea, glyoxal,

glutaraldehyde or the like, as well as sulfite or bisulfite addition compounds thereof.

The process of the present invention can be applied to any development of silver halide light-sensitive materials, but is particularly suitable for high-temperature fast processing for black and white and color photographic light-sensitive materials.

The present invention will be further illustrated by the following examples.

### EXAMPLE 1

X-ray photographic films were exposed sensitometrically by means of a standard sensitometer and then subjected to the following fast, high-temperature processings using each of the four kinds of developers shown below:

Conditions of Treatment		
Development step	Temperature	Time
1. Development	39° C.	40 sec.
2. Fixing	35° C.	5 min.
3. Washing	20° C.	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.	
5-Methyl-benzotriazole	200 mg.	
Water to make	1 liter	

### Developer B

Ten ml. of 25 percent glutaraldehyde was added to 1 liter of developer A.

### Developer C

Ten ml. of 25 percent glutaraldehyde and 15 mg. of Compound 6, above, were added to 1 liter of developer A.

### Developer D

Ten ml. of 25 percent glutaraldehyde and 15 mg. of Compound 8, above, were added to 1 liter of developer A.

The fixing solution used in the above processings was a conventional one containing sodium thiosulfate as the solvent for removing silver halide.

The results are shown in the following table.

Developer	Relative Sensitivity (fog+1.0)	Gamma	Fog
A	100	1.95	0.11
B	100	1.43	0.68
C	103	1.95	0.12
D	103	1.90	0.14

The above results show that when the X-ray films were developed using developer C or developer D in accordance with the process of the present invention, the increase of fog caused by the presence of the aldehyde could be effectively prevented without lowering either the sensitivity or the gamma of the processed X-ray films. The mechanical strength of the emulsion layer of the X-ray films during processing was clearly higher in the presence of adding the glutaraldehyde and this hardening effect of the glutaraldehyde was not reduced by the addition of the antifoggant of this invention.

### EXAMPLE 2

X-ray photographic films as in Example 1 were exposed and developed in the following three kinds of developers, respectively (except as noted, the procedures were the same as those in Example 1).

#### 1. Developer E

Rendol, (trade name of a developer for X-ray films, made by Fuji Photo Film Co., Ltd.) Developed for 4 minutes at 20° C.

#### 2. Developer F

A developer prepared by adding 10 ml. of 25 percent glutaraldehyde to 1 liter of developer A of Example 1. Developed for 20 seconds at 40° C.

#### 3. Developer G

A developer prepared by adding 10 ml. of 25 percent glutaraldehyde and 15 mg. of compound 15, above, to 1 liter of developer A in Example 1. Developed for 25 seconds at 40° C.

The results obtained are shown in the accompanying figure, which shows that when the X-ray film was processed at a high temperature according to the process of this invention, the photographic properties obtained were equal to or superior to those obtained by developing at 20° C. and were obtained without reducing the mechanical strength of the emulsion layer of the film over a developing period of about one-tenth of the developing period required at 20° C.

### EXAMPLE 3

Commercially available high speed negative photographic light-sensitive films were exposed by means of a sensitometer and developed for 7 minutes at 20° C. by using the following four kinds of developers, respectively:

Developer H	
1-Phenyl-3-pyrazolidone	0.5 g.
Hydroquinone	15.0 g.
Anhydrous sodium sulfite	25.0 g.
Sodium carbonate (monohydrate)	25.0 g.
Potassium bromide	2.0 g.
Water to make	1 liter

### Developer I

A developer prepared by adding 10 ml. of 25 percent glutaraldehyde to 1 liter of Developer H.

### Developer J

A developer prepared by adding 10 ml. of 25 percent glutaraldehyde and 2 mg. of Compound 7, above, to 1 liter of Developer H.

### Developer K

A developer prepared by adding 10 ml. of 25 percent glutaraldehyde and 5 mg. of compound 7 to 1 liter of Developer H.

The results are as follows:

Developer	Fog
H	0.26
I	1.98
J	1.34
K	0.34

The results show that the formation of fog increased due to the addition of glutaraldehyde but that this tendency was prevented by the addition of the antifoggants of the present invention.

### EXAMPLE 4

In the so-called coupler-in-developer-type color development, that is, a developing process wherein a color photographic light-sensitive film is developed in a developer containing a coupler, a long processing period is usually required. Hence, it is important to maintain high-mechanical strength of the emulsion layers during processing. For this purpose, a method is usually employed in which the mechanical strength of the emulsion layers of the color photographic light-sensitive film or paper is maintained by subjecting the photographic material to a prehardening procedure prior to the development.

For example, the following procedures are usually employed: (processing temperature 27° C.).

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1.	Prehardening	1 minute
2.	Washing	1 minute
3.	First development	5 minutes
4.	Washing	2 minutes
5.	Reversal red exposure	
6.	Cyan development	5 minutes
7.	Washing	1 minute
8.	Reversal purple exposure	
9.	Yellow development	5 minutes
10.	Washing	1 minute
11.	Subsidiary development	1 minute
12.	Washing	1 minute
13.	Magenta development	5 minutes
14.	Washing	1 minute
15.	Bleaching	2 minutes
16.	Fixing	2 minutes
17.	Washing	2 minutes
18.	Drying	

When the prehardening and subsequent washing processes are omitted and a hardening agent is incorporated in the primary developer to shorten the period required, the mechanical strength of the emulsion layers may be maintained but coupling densities are severely reduced, which results in a reduction of image quality.

However, by incorporating an aldehyde-type hardening agent together with the antifoggant of the present invention in the primary developer, the formation of fog may be effectively prevented without reducing the coupling densities when the aforesaid two steps were omitted. Hence color developing procedures may be simplified without reducing the mechanical strength of the emulsion layers of color photographic light-sensitive material during processings while providing good image quality.

Thus, according to the process of the present invention, the prehardening step and the subsequent washing step prior to the primary development step in such coupler-in-developer-type color developing systems can be omitted, without being accompanied by increased fog formation or reduction in mechanical strength of emulsion layers. Further, the period of time required for finishing the primary development can be shortened by processing at a high temperature, which fact renders the process of this invention extremely economical.

An example of such processes, conducted in accordance with this invention is as follows:

Development Step	Temperature	Time
1. First development (hardening and development)	40° C.	90 sec.
2. Washing	40° C.	30 sec.

Those steps from reversal red exposure to drying were same as shown in the aforesaid usual color development procedures of this type.

Commercially available reversal color photographic light-sensitive films were exposed by means of a sensitometer and then each processed by the aforesaid usual color development procedures and by the improved color development procedures as shown below in detail. The results are shown in the following table:

Steps	First developer	Relative sensitivity			Maximum density		
		R	G	B	R	G	B
I*	T	100	100	100	3.83	3.00	3.20
II*	S	98	103	105	3.70	2.40	2.75
II**	S*	100	103	104	3.70	2.93	3.15

I\*: usual color development steps mentioned above.

II\*: control procedure wherein the prehardening step and the subsequent washing step in step I\* were omitted and a hardening agent was added to the first developer (composition S). II\*\*: procedure of the present invention wherein 15 mg./liter of compound 5 was added to composition S (to form composition S\*).

The compositions of the processing solutions employed in the above color processing steps were as follows:

Composition T (for first developer)  
N-methyl-paraaminophenol sulfate

2.0 g.

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Anhydrous sodium sulfite	90 g.
Hydroquinone	8.0 g.
Sodium carbonate (monohydrate)	52.5 g.
Potassium thiocyanate	1.0 g.
Water to make	1 liter

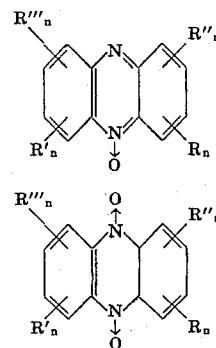
#### Composition S (for first developer)

A developer prepared by adding 15 ml. of an aqueous 37 percent formaldehyde solution to 1 liter of developer T.

Cyan color developer	
Anhydrous sodium sulfite	5.0 g.
4-Amino-3-methyl-N,N-diethyl-aniline hydrochloride	0.6 g.
Sodium carbonate (monohydrate)	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.
$\omega$ -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 sulfate	2.0 g.
Potassium bromide	0.2 g.
1-Phenyl-3-(m-nitrobenzoylamino)-5-pyrazolone	1.4 g.
Sodium hydroxide	2.5 g.
n-Butylamine	5 ml.
Water to make	1 liter
Bleaching solution	
Ferricyanide	100 g.
Potassium bromide	10 g.
Borax	2.0 g.
Boric acid	1.0 g.
Water to make	1 liter
Fixing solution	
Sodium thiosulfate	150 g.
Anhydrous sodium sulfite	10 g.
Water to make	1 liter

#### What is claimed is: Brevibacterium

1. In a process for the development of exposed silver halide photographic light-sensitive material by developing the photographic material with a developer, the improvement which comprises the developer containing an aldehyde hardening agent and at least one compound selected from the group consisting of compounds having the formula:



wherein R, R', R'', and R''' are each selected from the group consisting of hydrogen, alkyl having one to four carbon atoms, aryl, halogen, alkoxy, hydroxy, acylamino, carboxy, and nitro, and n is an integer of from 0 to 3.

2. The process of claim 1 wherein said compound is selected from the group consisting of phenazine-5-oxide, 1-methylphenazine-5-oxide, 1-bromo-3-tert-butylphenazine-5-oxide, 1-phenylphenazine-5-oxide, 2-chlorophenazine-5-ox-

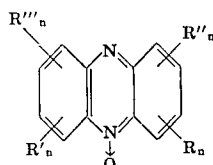
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ide, 3-bromo-phenazine-5-oxide, 1-methoxyphenazine-5-oxide, 2-ethoxyphenazine-5-oxide, 3-hydroxyphenazine-5-oxide, 2-chloro-3-hydroxyphenazine-5-oxide, 1-cetamidophenazine-5-oxide, 1-phenazinecarboxylic acid-5-oxide, 3-nitrophenazine-5-oxide, phenazine-5,10-dioxide, 2-chlorophenazine-5,10-dioxide, 2-methylphenazine-5,10-dioxide, and 2-hydroxyphenazine-5,10-dioxide.

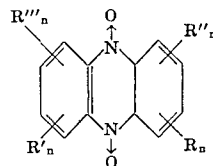
3. The process of claim 1 wherein said hardening agent is selected from the group consisting of formaldehyde, glutaraldehyde, dimethylol urea, glyoxal, sulfite addition products thereof and bisulfite addition products thereof.

4. The process of claim 1 wherein the amount of said compound is present in an amount of 5-100 mg. per liter of developer.

5. A developing bath for an exposed silver halide light-sensitive material containing a developer, an aldehyde hardening agent and at least one compound selected from the group consisting of compounds having the formula:

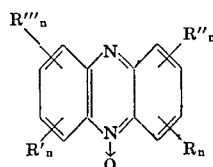


and

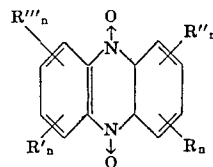


wherein R, R', R'', R''' are each selected from the group consisting of hydrogen, alkyl having one to four carbon atoms, aryl, halogen, alkoxy, hydroxy, acylamino, carboxy, and nitro, and n is an integer of from 0 to 3.

6. A prehardening solution for silver halide light-sensitive material containing an aldehyde hardening agent and at least one compound selected from the group consisting of compounds having the formula:



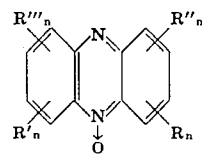
and



wherein R, R', R'', and R''' are each selected from the group consisting of hydrogen, alkyl having one to four carbon atoms, aryl, halogen, alkoxy, hydroxy, acylamino, carboxy, and nitro, and n is an integer of from 0 to 3.

7. In a process for the development of exposed silver halide photographic material by prehardening the photographic material with a prehardening solution and then developing it with a developer, the improvement which comprises the prehardening solution containing an aldehyde hardening agent and at least one compound selected from the group consisting of compounds having the formula:

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wherein R, R', R'' and R''' each is selected from the group consisting of hydrogen, alkyl having one to four carbon atoms, aryl, halogen, alkoxy, hydroxy, acylamino, carboxy and nitro, and n is an integer of 0 to 3.

8. The process of claim 7 wherein said compounds are selected from the group consisting of phenazine-5-oxide, 1-methylphenazine-5-oxide, 1-bromo-3-tert-butylphenazine-5-oxide, 1-phenylphenazine-5-oxide, 2-chlorophenazine-5-oxide, 3-bromo-phenazine-5-oxide, 1-methoxyphenazine-5-oxide, 2-ethoxyphenazine-5-oxide, 3-hydroxyphenazine-5-oxide, 2-chloro-3-hydroxyphenazine-5-oxide, 1-cetamidophenazine-5-oxide, 1-phenazinecarboxylic acid-5-oxide, 3-nitrophenazine-5-oxide, phenazine-5,10-dioxide, 2-chlorophenazine-5,10-dioxide, 2-methylphenazine-5,10-dioxide, and 2-hydroxyphenazine-5,10-dioxide.

9. The process of claim 7 wherein said hardening agent is selected from the group consisting of formaldehyde, glutaraldehyde, dimethylol urea, glyoxal, sulfite addition products thereof and bisulfite addition products thereof.

10. The process of claim 1 wherein said developer contains at least 5 mg. per liter of developer of said compound.

11. The process of claim 10 wherein said developer is an aqueous alkaline developer.

12. The process of claim 11 wherein said developer contains a member selected from the group consisting of N-methyl-p-aminophenol sulfate, dihydroxybenzene, 1-phenyl-3-pyrazolidone and phenylenediamine.

13. The process of claim 2 wherein said developer contains from 5 to 30 mg. of said compound per liter of developer.

14. The developing bath of claim 5 which contains at least 5 mg. per liter of said compound per liter of developing bath.

15. The developing bath of claim 14 wherein said compound is selected from the group consisting of phenazine-5-oxide, 1-methylphenazine-5-oxide, 1-bromo-3-tert-butylphenazine-5-oxide, 1-phenylphenazine-5-oxide, 2-chlorophenazine-5-oxide, 3-bromophenazine-5-oxide, 1-methoxyphenazine-5-oxide, 2-ethoxyphenazine-5-oxide, 3-hydroxyphenazine-5-oxide, 2-chloro-3-hydroxyphenazine-5-oxide, 1-cetamidophenazine-5-oxide, 1-phenazinecarboxylic acid-5-oxide, 3-nitrophenazine-5-oxide, phenazine-5,10-dioxide, 2-chlorophenazine-5,10-dioxide, 2-methylphenazine-5,10-dioxide, and 2-hydroxyphenazine-5,10-dioxide.

16. The developing bath of claim 5 wherein said hardening agent is selected from the group consisting of formaldehyde, glutaraldehyde, dimethylol urea, glyoxal, sulfite addition products thereof and bisulfite addition products thereof.

17. The developing bath of claim 15 wherein said developing bath is an aqueous alkaline developing bath.

18. The developing bath of claim 17 which contains a member selected from the group consisting of N-methyl-p-aminophenol sulfate, dihydroxybenzene, 1-phenyl-3-pyrazolidone and phenylenediamine.

19. The developing bath of claim 15 wherein said compound is present in an amount of 5 to 100 mg. per liter of said developing bath.

20. The developing bath of claim 15 wherein said compound is present in an amount of 5 to 30 mg. per liter of said developing bath.

21. The prehardening solution of claim 6 wherein said compound is selected from the group consisting of phenazine-5-oxide, 1-methylphenazine-5-oxide, 1-bromo-3-tert-butylphenazine-5-oxide, 1-phenylphenazine-5-oxide, 2-chlorophenazine-5-oxide, 3-bromo-phenazine-5-oxide, 1-methoxyphenazine-5-oxide, 2-ethoxyphenazine-5-oxide, 3-hydroxyphenazine-5-oxide, 2-phenazinecarboxylic acid-5-oxide, 3-nitrophenazine-5-oxide, phenazine-5,10-dioxide, 2-chlorophenazine-5,10-dioxide, 2-methylphenazine-5,10-dioxide, and 2-hydroxyphenazine-5,10-dioxide.

22. The prehardening solution of claim 6 wherein said compound is selected from the group consisting of formaldehyde, glutaraldehyde, dimethylol urea, glyoxal, sulfite addition products thereof and bisulfite addition products thereof.

23. The process of claim 7 wherein said developer is an aqueous alkaline developer.

24. The process of claim 7 wherein said developer contains a member selected from the group consisting of N-methyl-p-aminophenol sulfate, dihydroxybenzene, 1-phenyl-3-pyrazolidone and phenylenediamine.

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