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(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650(US)

(72) Inventor: **Combu, Peter E., c/o EASTMAN KODAK COMPANY**
Patent Department, 343 State Street
Rochester, New York 14650-2201(US)
Inventor: **Brayer, Franklin C., c/o EASTMAN KODAK COMPANY**
Patent Department, 343 State Street
Rochester, New York 14650-2201(US)
Inventor: **Fitterman, Alan S., c/o EASTMAN KODAK COMPANY**
Patent Department, 343 State Street
Rochester, New York 14650-2201(US)

(74) Representative: **Parent, Yves et al**
Kodak-Pathé Département Brevets et Licences Centre de Recherches et de Technologie Zone Industrielle
F-71102 Chalon-sur-Saône Cédex(FR)

(54) Photographic developing solution for use with fore-hardened X-ray films.

(57) An aqueous alkaline photographic developing solution that is especially adapted for use in the development of fore-hardened X-ray films has a pH in the range of 9 to 12, is substantially free of both aldehydic hardening agents and silver halide solvents, and comprises (1) a dihydroxybenzene developing agent, such as hydroquinone, (2) at least 3.5 grams per liter of developing solution of a 4,4-disubstituted-1-aryl-3-pyrazolidinone, which functions as an auxiliary super-additive developing agent, such as 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone, (3) an alkaline agent, (4) an organic antifoggant, and (5) a preservative. The developing solution is capable of being packaged as a single part formulation and provides a very short process time and excellent sensitometric results.

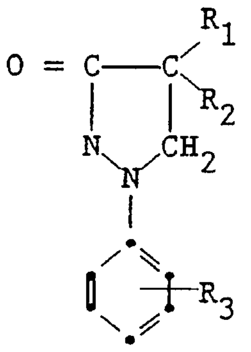
PHOTOGRAPHIC DEVELOPING SOLUTION FOR USE WITH FORE-HARDENED X-RAY FILMS

This invention relates in general to photography and in particular to the development of X-ray films. More specifically, this invention relates to an improved aqueous alkaline photographic developing solution that is especially adapted for use in the development of fore-hardened X-ray films.

Heretofore, developing solutions for use with X-ray film have typically been formulated using hydroquinone as the primary developing agent, 1-phenyl-3-pyrazolidinone as a super-additive auxiliary developing agent and glutaraldehyde as a hardening agent. These developing solutions have been packaged as three-part formulations. The need for the added cost and complexity of three-part packaging has been dictated by the fact that glutaraldehyde tends to react with 1-phenyl-3-pyrazolidinone, that 1-phenyl-3-pyrazolidinone tends to oxidize in alkaline solution, and that glutaraldehyde tends to polymerize in alkaline solution. To avoid these problems, the hydroquinone has been packaged in a first part which is alkaline, the 1-phenyl-3-pyrazolidinone has been packaged in a second part which is acidic, and the glutaraldehyde has been packaged in a third part which is acidic. Prior to use, the three parts are blended together and diluted with water to give the appropriate concentration and alkaline pH for use as working developing solution. Representative of the prior art relating to developing solutions for use with X-ray films are U. S. Patents 3,545,971, 4,046,571, 4,672,025 and 4,810,622, all of which describe developing solutions that contain aldehydic hardening agents, such as glutaraldehyde, and are packaged as three-part formulations. Aldehydic hardening agents are not needed in developing solutions intended for use in processing X-ray films which have been adequately fore-hardened, such as those described in U. S. Patent 4,414,304. The fore-hardened tabular grain emulsions of Patent '304 offer the advantage of exhibiting high levels of covering power that are relatively insensitive to increasing levels of fore-hardening. At the same time, by reason of being fore-hardened, the radiographic elements of Patent '304 ingest less water during processing and therefore lend themselves to accelerated processing, typically to total processing times of 45 seconds or less. It is essential, however, to be able to process such fore-hardened films in a process that provides a very short process time without sacrificing the equally important requirement of achieving proper sensitometry. A specific aim is to match the sensitometry of conventional radiographic products now processed in aldehydic developers, such as that of the standard 90 second Kodak RP X-Omat™ process. It is also highly advantageous to be able to avoid complex multi-part packaging and achieve the convenience of one-part packaging without compromising the performance of the developing solution.

It is an object of this invention to provide a developing solution that is especially adapted for processing fore-hardened X-ray films, that is capable of providing a very short process time, that is capable of producing sensitometric responses similar to those achieved with conventional aldehydic developers, and that exhibits the convenience and simplicity of one-part packaging while yielding excellent sensitometry.

In one aspect this invention is directed to an aqueous alkaline photographic developing solution especially adapted for use in the development of fore-hardened X-ray films, said developing solution having a pH in the range of 9 to 12, being substantially free of both aldehydic hardening agents and silver halide solvents and comprising a dihydroxybenzene developing agent, an auxiliary super-additive developing agent, an alkaline agent, an organic anti-foggant and a preservative; characterized in that said super-additive auxiliary developing agent is present in a concentration of at least 3.5 grams per liter of said developing solution and is a 4,4-disubstituted-1-aryl-3-pyrazolidinone of the formula:



wherein R_1 and R_2 are the same or different and each is alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 1 to 6 carbon atoms, and R_3 is hydrogen, halogen, alkyl of 1 to 6 carbon atoms or alkoxy of 1 to 6 carbon atoms.

It has now been found, most unexpectedly, that by using a 4,4-disubstituted-1-aryl-3-pyrazolidinone in an amount of at least 3.5 grams per liter of developing solution as the auxiliary super-additive developing agent, it is feasible to formulate the developing solution in a single part and, at the same time, achieve a very short process time while meeting all sensitometric requirements that are important for X-ray film development.

In the present invention, no problem is encountered in packaging the 4,4-disubstituted-1-aryl-3-pyrazolidinone in an alkaline solution since such substituted pyrazolidinones are resistant to oxidation in alkaline solution. Use of this compound in the required amount of at least 3.5 grams per liter of developing solution provides the desired characteristics of very short process time with excellent sensitometry.

The developing solution of this invention is free, or at least substantially free, of aldehydic hardening agents such as glutaraldehyde. Since the developing solution is intended for use with X-ray films that have been adequately fore-hardened, the incorporation of hardening agents in the developing solution is unnecessary.

The developing solution of this invention is free, or at least substantially free, of silver halide solvents, such as thiosulfates or thiocyanates, as these solvents are detrimental to its performance in development of fore-hardened X-ray films and would provide unacceptable sensitometry.

The dihydroxybenzene developing agents employed in the aqueous alkaline developing solutions of this invention are well known and widely used in photographic processing. The preferred developing agent of this class is hydroquinone. Other useful dihydroxybenzene developing agents include:

chlorohydroquinone,
bromohydroquinone,
isopropylhydroquinone,
toluhydroquinone,
methylhydroquinone,
2,3-dichlorohydroquinone,
2,5-dimethylhydroquinone,
2,3-dibromohydroquinone,
1,4-dihydroxy-2-acetophenone-2,5-dimethylhydroquinone,
2,5-diethylhydroquinone,
2,5-di-p-phenethylhydroquinone,
2,5-dibenzoylaminohydroquinone,
2,5-diacetaminohydroquinone,
and the like.

In addition to the dihydroxybenzene developing agent, the developing solution must include a 4,4-disubstituted-1-aryl-3-pyrazolidinone, of the structure indicated hereinabove, which functions as an auxiliary super-additive developing agent. Specific examples of the 4,4-disubstituted-1-aryl-3-pyrazolidinone developing agents include:

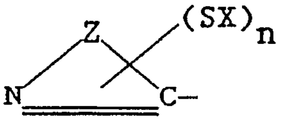
4,4-dimethyl-1-phenyl-3-pyrazolidinone,
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone (HMMP),
4,4-di-(hydroxymethyl)-1-phenyl-3-pyrazolidinone,
4,4-diethyl-1-phenyl-3-pyrazolidinone,
4-methyl-4-ethyl-1-phenyl-3-pyrazolidinone,
and the like.

Suitable alkaline agents which can be included in the developing solution to maintain the desired alkaline pH include hydroxides such as sodium hydroxide or potassium hydroxide, bicarbonates such as sodium bicarbonate or potassium bicarbonate, and borates such as sodium tetraborate.

To minimize problems of fog formation, an effective amount of an organic antifoggant is included in the developing solution of this invention. Particularly advantageous results are achieved with the use of benzotriazole antifoggants.

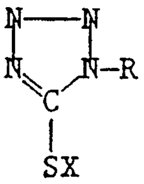
A further preferred class of organic antifoggants are the mercapto azole and mercapto azine antifoggants. Inorganic antifoggants or restrainers, such as alkali metal bromides, can be utilized in conjunction with the use of an organic antifoggant, if desired.

Preferred mercapto azole or mercapto azine antifoggants are those represented by the formula:



wherein Z represents the atoms necessary to complete a 5 or 6 member heterocyclic ring, such as pyrimidine, triazine, tetrazole, triazole, imidazole, diazole, oxadiazole or thiadiazole ring; and SX represents a mercapto function, n being a whole number, typically a number from 1 to about 3, any free bonds being satisfied by hydrogen atoms. In the mercapto function or group, X is a cation which includes hydrogen, an alkali metal, e.g., sodium or potassium, ammonium or an organic amine residue of such amines as triethyl amine, triethanolamine, morpholine and the like.

Mercapto tetrazole antifoggants are especially suitable in the practice of this invention and include those of the formula:



wherein R is an aliphatic or aromatic radical containing up to about 30 carbon atoms and SX is a mercapto function.

Particularly preferred benzotriazole antifoggants for use in the developing solutions of this invention are benzotriazole, halo-substituted benzotriazoles such as 4-chlorobenzotriazole; 4-bromobenzotriazole and 5-chlorobenzotriazole, and alkyl-substituted benzotriazoles such as 5-methylbenzotriazole.

Specific examples of mercapto azole antifoggants include:
mercapto-substituted pyrimidines such as thiobarbituric acid and thiouracil,
mercapto-substituted oxadiazoles or thiadiazoles such as 5-phenyl-2-mercapto-1,3,4-oxadiazole and 5-o-tolyl-2-mercapto-1,3 ,4-thiadiazole,
mercapto triazines such as 2,4,6-trimercapto-1,3,5-triazine,
mercapto imidazoles such as 2-mercapto-5-phenyl-imidazole,
condensed imidazoles such as 2-mercaptobenzimidazole,
triazoles such as 3,4-diphenyl-5-mercapto-1,2,4-triazole and 3-mercapto-5-methyl-1,2,4-triazole,
mercapto tetrazoles such as 1-phenyl-5-mercaptotetrazole and 1-(3-capramido)phenyl-5-mercaptotetrazole.

The aqueous alkaline photographic developing solutions of this invention preferably contain a sulfite preservative at a level sufficient to protect the developing agents against aerial oxidation and thereby promote good stability characteristics. Useful sulfite preservatives include sulfites, bisulfites, metabisulfites, and carbonyl bisulfite adducts. Typical examples of sulfite preservatives include:
sodium sulfite,
potassium sulfite,
lithium sulfite,
ammonium sulfite,
sodium bisulfite,
potassium metabisulfite,
sodium formaldehyde bisulfite,
and the like.

Other preservatives such as hydroxylamine and ascorbic acid can be used instead of or in combination with the sulfites.

In addition to the primary developing agent, auxiliary developing agent, alkaline agent, organic antifoggant and preservative, the aqueous alkaline photographic developing solution of this invention can optionally contain other ingredients including sequestering agents, surfactants, and organic solvents such as diethylene glycol.

The aminopolycarboxylic acid sequestering agents are particularly useful in the developing solutions of this invention. Typical examples of the aminopolycarboxylic acid sequestering agents include:
nitrilotriacetic acid, (NTA),

ethylenediaminetetraacetic acid, (EDTA),
1,3-propylenediaminetetraacetic acid (PDTA),
1-3-diamino-2-propanol-N,N,N′,N′-tetraacetic acid (DPTA),
diethylenetriaminepentaacetic acid (DTPA),
N,N′-bis(2-hydroxybenzyl) ethylenediamine-N,N′-diacetic acid (HBED),
hydroxyethylenediaminetriacetic acid,
cyclohexanediaminotetraacetic acid,
aminomalonic acid,
and the like.

The aqueous alkaline developing solutions of this invention can vary widely in regard to the concentration of the various ingredients included therein. Typically, the dihydroxybenzene developing agent (e.g., hydroquinone) is used in an amount of from about 20 to about 60 grams per liter, the 4,4-disubstituted-1-aryl-3-pyrazolidinone (e.g., 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone) is used in an amount of greater than 3 grams per liter, more preferably in an amount of 3.5 to 10 grams per liter and most preferably in an amount of 4 to 8 grams per liter, the alkaline agent (e.g., potassium hydroxyde) is used in an amount of about 10 to about 50 grams per liter, the organic antifoggant (e.g., 5-méthyl-benzotriazole) is used in an amount of about 0.1 to about 0.5 grams per liter, and the preservative (e.g., potassium sulfite) is used in an amount of about 20 to about 100 grams per liter. The pH of the developing solution is in the range of from 9 to 12 and more preferably in the range of from 9.5 to 11.

The developing process is typically carried out at a temperature of about 25° C to about 50° C. With the developing solution of this invention, very short developing times, such as times of 10 seconds, or less, are feasible, with total processing times of 45 seconds or less being contemplated. For example, fore-hardened radiographic elements when processed in the following 45 second cycle using the developer of this invention can produce sensitometric characteristics matching those obtained with conventional radiographic products processed in a 90 second cycle using an aldehydic developer:

development	10.2 sec. 35° C
fixing	8.7 sec. 35° C
washing	7.2 sec. 35° C
drying	17.0 sec. 65° C

Time otherwise unaccounted for is used for film transport.

A particularly preferred aqueous alkaline photographic developing solution within the scope of this invention is a solution consisting essentially of 25 to 50 grams per liter of hydroquinone, 4 to 8 grams per liter of 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone, 5 to 10 grams per liter of sodium bicarbonate, 20 to 40 grams per liter of potassium hydroxide, 0.1 to 0.3 grams per liter of 5-methyl-benzotriazole, 50 to 80 grams per liter of potassium sulfite, 5 to 10 grams per liter of sodium metabisulfite, 1 to 4 grams per liter of sodium bromide, 10 to 30 grams per liter of diethylene glycol and 2 to 4 grams per liter of diethylenetriaminepentaacetic acid.

The invention is further illustrated by the following examples of its practice.

Examples 1-4

Aqueous alkaline photographic developing solutions were prepared in accordance with the following formulations:

Table I

	Amount (grams)			
Ingredient	EX 1	EX 2	Ex 3	Ex 4
Sodium metabisulfite	8.0	8.85	8.85	8.85
Potassium hydroxide (45% solution)	60.0	50.0	57.8	60.0
Diethylenetriamine-pentaacetic acid (40% solution)	7.1	7.1	7.1	7.1
Sodium bromide	2.25	2.25	2.25	2.25
Sodium bicarbonate	7.5	7.5	7.5	7.5
Potassium sulfite (45% solution)	119.3	159.0	159.0	159.0
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone	3.5	5.0	4.51	3.67
5-Methylbenzotriazole	0.12	0.12	0.151	0.119
Diethylene glycol	20.0	20.0	20.0	20.0
Hydroquinone	39.0	32.0	34.2	51.3
Water to one liter				
pH at 25° C	10.7	10.5	10.83	10.71

The above-described developing solutions were each employed at a temperature of 35° C to develop a fore-hardened X-ray film as described in U. S. patent 4,414,304. Development was completed in 10.2 seconds in each of Examples 1 and 2, in 9.2 seconds in Example 3 and in 7.8 seconds in Example 4. The total processing cycle time was 45 seconds for Examples 1 and 2, 40 seconds for Example 3, and 35 seconds for example 4. Measurements were made with respect to gross fog, film speed at a density of 1.0 above gross fog (1.0CR), mid scale contrast (MSC), lower scale contrast (LSC), upper scale contrast (USC), and upper density point (UDP) and were found, in each case, to be acceptably similar to those obtained in the standard KODAK RP X-OMAT™ process. Each of the developing solutions was capable of being formulated and packaged as a single-part composition which exhibited acceptable shelf life and stability.

Example 5

In this Example the sensitometric performance obtained using the processing of Example 2 and three controls 2-A, 2-B and 2-C, differing from the Example 2 solely by the level of HMMP present, were compared with the sensitometric performance of a radiographic product intended to be processed in an aldehydic developer, such as a Kodak RP X-Omat™ 90 second process. Specifically, in Table II below the RP X-Omat performance indicates the performance of a radiographic element of the type described in U.S. Patent 4,900,652 processed in the following cycle:

development	24 sec. 35° C
fixing	20 sec. 35° C
washing	10 sec. 35° C
drying	20 sec. 65° C

Total processing time being 90 seconds, with time not otherwise accounted for being used in film transport. The developer exhibited the following composition:

Hydroquinone	22 g
1-Phenyl-3-pyrazolidone	1.35 g
KOH	19.32 g
$NaHCO_3$	5.81 g
K_2SO_3	75 g
NaBr	3.5 g
5-Methylbenzotriazole	0.06 g
Glutaraldehyde	4.44 g
Water to 1 liter at pH 10.1	

In addition another developer having a still higher HMMP level than that of Example 2 was compared. This developer, referred to the Example 5 developer, had the following composition:

Hydroquinone	32 g
HMMP	6 g
KOH	24.4 g
$NaHCO_3$	7.5 g
K_2SO_3	75
NaBr	2.25 g
5-Methylbenzotriazole	0.12 g
Water to 1 liter at pH 10.35	

A radiographic element identical to that employed in Example 2 was processed in the Example 5 developer using the following 45 second process cycle:

development	10.2 sec. 35° C
fixing	8.7 sec. 35° C
washing	7.2 sec. 35° C
drying	17.0 sec. 65° C

Time not otherwise accounted for was consumed in film transport.

The results are compared below in Table II.

Table II

Test No.	Concentration of HMMP (grams/liter)	Gross Fog	Film Speed	MSC	LSC	USC	UDP
2-A (Comp.)	0.5	0.20	416	3.20	2.26	2.70	3.70
2-B (Comp.)	1.0	0.20	424	3.24	2.20	3.05	3.75
2-C (Comp.)	3.0	0.21	433	2.94	2.09	2.66	3.59
Ex. 2	5.0	0.21	437	2.81	2.02	2.60	3.57
RP X-Omat	1.5*	0.20	438	2.89	2.00	3.34	3.65
Ex. 5	6.0	0.22	439	2.91	2.05	3.07	3.70

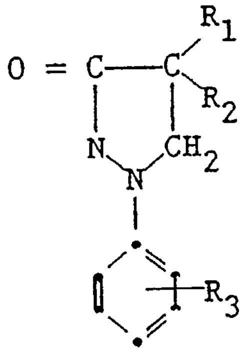
*1-Phenyl-3-pyrazolidinone

The data reported in Table II indicate that the developers of Examples 2 and 5 produced sensitometric results closely approximating those obtained with the RP X-Omat 90 second process in terms of speed, lower scale contrast (LSC) and middle scale contrast (MSC). These sensitometric parameters affect the lower density image regions to which the eye is particularly sensitive. While some divergence in upper scale contrast (USC) and upper density point (UDP) were observed, the eye is much less sensitive to variances in upper density image regions; therefore, these variances were deemed acceptable.

Comparing the performance of Controls 2-A, 2-B and 2-C, it can be seen that lower levels of HMMP in these developers resulted in relatively poor matches in speed, MSC and LSC. Specifically, speeds were lower than those produced by RP X-Omat 90 second process and lower and middle scale contrasts were both elevated, indicating the importance of employing higher levels of HMMP in the aldehydic hardener free developers of the invention.

Claims

1. An aqueous alkaline photographic developing solution especially adapted for use in the development of fore-hardened X-ray films, said developing solution having a pH in the range of 9 to 12, being substantially free of both aldehydic hardening agents and silver halide solvents and comprising a dihydroxybenzene developing agent, an auxiliary super-additive developing agent, an alkaline agent, an organic anti-foggant and a preservative; characterized in that said super-additive auxiliary developing agent is present in a concentration of at least 3.5 grams per liter of said developing solution and is a 4,4-disubstituted-1-aryl-3-pyrazolidinone of the formula:



wherein R_1 and R_2 are the same or different and each is alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 1 to 6 carbon atoms, and R_3 is hydrogen, halogen, alkyl of 1 to 6 carbon atoms or alkoxy of 1 to 6 carbon atoms.

2. The developing solution as claimed in claim 1 further characterized in that said dihydroxybenzene developing agent is hydroquinone.

3. The developing solution as claimed in claim 1 or 2 further characterized in that said 4,4-disubstituted-1-aryl-3-pyrazolidinone is 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone.

4. The developing solution as claimed in any one of claims 1 to 4 inclusive wherein said organic antifoggant is 5-methylbenzotriazole.

5. The developing solution as claimed in any one of claims 1 to 4 inclusive further characterized in that the amount of said 4,4-disubstituted-1-aryl-3-pyrazolidinone is from 3.5 to 10 grams per liter of said developing solution.

6. An aqueous alkaline photographic developing solution according to any one of claims 1 to 5 inclusive further characterized in that said hydroquinone is present in a concentration ranging from about 20 to about 60 grams per liter.

7. An aqueous alkaline photographic developing solution according to any one of claims 1 to 6 inclusive further characterized in that said developing solution consists essentially of 25 to 50 grams per liter of hydroquinone, 4 to 8 grams per liter of 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone, 5 to 10 grams per liter of sodium bicarbonate, 20 to 40 grams per liter of potassium hydroxide, 0.1 to 0.3 grams per liter of 5-methyl-benzotriazole, 50 to 80 grams per liter of potassium sulfite, 5 to 10 grams per liter of sodium metabisulfite, 1 to 4 grams per liter of sodium bromide, 10 to 30 grams per liter of diethylene glycol and 2 to 4 grams per liter of diethylenetriaminepentaacetic acid.

8. A method of processing a fore-hardened X-ray film, said method comprising the step of developing said film by contacting it with an aqueous alkaline photographic developing solution according to any one of claims 1 to 7 inclusive.