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PHOTOGRAPHIC DEVELOPER SOLUTION CONTAINING NON-SLUDGING SILVER HALIDE SOLVENT

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12 Claims. (Cl. 96—61)

Photographic processing solutions in which a silver halide solvent is added to a developer solution have been known for more than 60 years. These combined developing and fixing solutions, also known as a monobath, are generally prepared by combining a developer solution which contains all the conventional developer ingredients with water-soluble thiosulfate salts such as sodium thiosulfate or ammonium thiosulfate which acts as a silver halide solvent. Other silver halide solvents, which have been proposed for a monobath solution, include potassium thiocyanate and potassium cyanide, but the latter cannot be used in practice because it is a lethal poison.

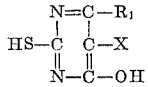
The two processes of development and fixing proceed separately and simultaneously. However, the sensitometric properties of the final results can be influenced within certain limits depending on the kinetic characteristics of the two processes.

All of the monobath solutions described so far have the undesirable property of causing the formation of a silver sludge after short use. This is not surprising from a thermodynamical point of view, because the dissociation constant of the dissolved silver halide present in the thiosulfate complex will favor reduction in such a solution. The precipitation of the silver sludge has, so far, been considered as a disadvantage of the monobath solutions because it requires for its removal the use of filtration equipment.

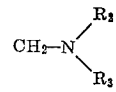
U.S. Patent 2,525,532 describes the use of 4-amino-6-hydroxy-2-pyridine, 4-amino-6-hydroxy-2-mercaptopyridine and 6-amino-4-hydroxy-2-mercaptopyrimidine as additives to sodium carbonate containing developers which can be described as stabilizing developers. This patent mentions specifically that its solutions differ from the customary combined fixing and devolping solutions because all or most of the silver remains in the emulsion after processing.

It is, therefore, an object of the instant invention to provide a monobath which, even after extended use, is substantially free from silver sludge. Other objects will be apparent from the following description.

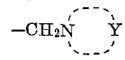
We have found that these objects can be accomplished by the use of a monobath solution by adding to a conventional black and white developer solution, a heterocyclic silver halide solvent of the following general formula:



wherein R_1 represents hydrogen, alkyl such as methyl, ethyl, propyl, isobutyl, butyl and the like; aryl, such as phenyl, tolyl and the like; aralkyl, such as benzyl, phenethyl and the like; carboxyalkyl such as carboxymethyl, carboxyethyl, carboxypropyl; X represents, in addition to hydrogen, the grouping



wherein R_2 and R_3 are lower alkyl groups having the value given above for R_1; and the group



wherein Y represents the atoms necessary to complete a heterocyclic nucleus, such as a piperidine and morpholine nucleus.

The combined fixing and developing solution prepared with the above 2-mercapto-6-hydroxypyrimidine derivatives are superior to the previously known monobath solutions because they remain free from silver sludge even after extended use and development of large quantities of film. Thus, the keeping qualities of the combined fixing developing solutions are noticeably improved on use.

Another defect that was common to the previously known fixing developers which contained a thiosulfate as the silver halide solvent was the separation of sulfur from the solution. This defect, which could be traced to the decomposition of the thiosulfate, caused a highly undesirable fog in the processed photographic materials. Both the decomposition and the fog were completely eliminated by the use of our fixing developers.

When compared with the so-called stabilizing developers, the combined fixing and developing solution of this invention offer the advantage of dissolving all of the undeveloped silver halide left in the emulsion layer. For this reason, our new monobaths are eminently suitable for the processing of photographic transparencies.

The fixing developers of our invention can be used for the processing of films and paper. The processing time required varies somewhat with the type of photographic material and with the extent of agitation but is generally within a time limit of from two to seven minutes.

In preparing the combined fixing developing solution, there can be used any of the known photographic developing agents such as hydroquinone, paramethylaminophenol sulfate (Methol), 1-phenyl-3-pyrazolidone (Phenidone), 1-(p-methylaminophenyl)-3-amino-Δ-2-pyrazoline, 4-aminopyrazolone and the like.

The combined developer fixer solutions may also contain the usual developer additives including sequestering agents, such as ethylenediamine, tetracetic acid and its alkali metal salts; an alkali, such as potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate; an antioxidant, such as an alkali metal sulfite or bisulfite; developer accelerators, such as cetyl pyridinium bromide or thallium nitrate; antifoggants, such as potassium bromide, sodium bromide, nitrobenzimidazole; and, substances which influence the image tone and act also as restrainers such as mercaptobenzimidazole and mercaptobenzothiazole, benzotriazole and phenylmercaptotetrazole.

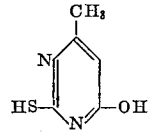
The addition of a thickening agent, such as sodium carboxymethylcellulose, tragacanth, the copolymer of an alkyl vinyl ether and a maleic acid derivative or similar materials makes it possible to obtain fixing developers having a paste-like consistency which can be used for

processing paper and film in certain developing equipment which requires the use of highly viscous processing solutions.

The preparation of suitable silver halide solvents which can be used in accordance with our invention is described in the following list of preparations.

PREPARATION I

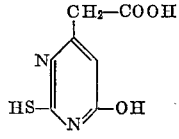
2-mercapto-6-hydroxy-4-methylpyrimidine



This compound was prepared in accordance with the method described in Beilstein, volume 24, page 351.

PREPARATION II

2-mercapto-6-hydroxy-4-carboxymethylpyrimidine

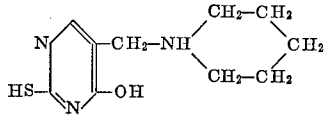


70 grams of thiourea and 202 grams of the diethyl ester of acetone dicarboxylic acid were added to a solution of 23 grams of sodium in 1 liter of absolute alcohol and the mixture heated for three hours under reflux. The alcohol was evaporated, the residue dissolved in water and weakly acidified with hydrochloric acid. An oil separated which solidified on stirring with a glass rod. The purification was carried out by recrystallizing the product from a mixture of one part of water and two parts of alcohol; M.P. 158° C.

20 grams of the ester thus obtained, 15 grams of potassium hydroxide and 150 milliliters of alcohol were heated for two hours under reflux. The potassium salt which separated was filtered off, dissolved in water and acidified with hydrochloric acid, thus yielding the free acid.

PREPARATION III

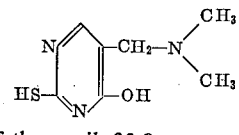
2 - mercapto - 6 - hydroxy - 5 - (N - piperidylmethylene)-pyrimidine



12.8 grams of thouracil, 9.5 grams of piperidine, 1 milliliter of glacial acetic acid, 10 grams of a 30% of formaldehyde solution and 250 milliliters of alcohol were refluxed on a steam bath. After 1½ hours, an additional 12.5 grams of piperidine, 8 milliliters of formaldehyde solution and 1 milliliter of glacial acetic acid were added and the mixture refluxed for an additional five hours. The product which separated was recrystallized from water; M.P. 225° C.

PREPARATION IV

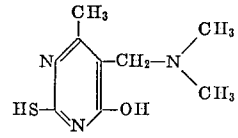
2 - mercapto - 6 - hydroxy - 5 - (dimethylaminomethylene)-pyrimidine



12.8 grams of thouracil, 33.8 grams of a 40% aqueous solution of dimethylamine, 20 grams of a 30% formaldehyde solution, 1 milliliter of glacial acetic acid and 250 milliliters of alcohol were heated for four hours under reflux. The alcohol was distilled off and the residue recrystallized from aqueous alcohol; M.P. 194° C.

PREPARATION V

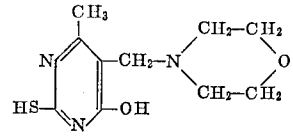
2-mercapto-6-hydroxy - 5 - (dimethylaminomethylene)-4-methylpyrimidine



14.2 grams of 6-hydroxy-4-methyl-2-mercaptopyrimidine prepared as described in Beilstein, volume 24, page 351, 20 grams of a 30% formaldehyde solution, 33.8 grams of a 40% aqueous dimethylamine solution, 1 gram of glacial acetic acid and 250 milliliters of ethanol were heated on a steam bath under reflux for three hours. The alcohol was slowly distilled off during a period of about 1½ hours and the residue recrystallized from one to one mixture of water and methanol. Yield: 16 grams; M.P. 185° C. (dec).

PREPARATION VI

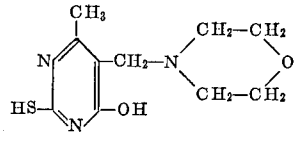
2 - mercapto-6-hydroxy-5-(N-morpholylmethylene)-4-methylpyrimidine



14.2 grams of 6-hydroxy-4-methyl-2-mercaptopyrimidine, 10.4 grams of morpholine, 16.6 grams of a 30% formaldehyde solution, 1 gram of glacial acetic acid and 250 milliliters of alcohol were heated under reflux. After five hours, 10.4 grams of morpholine, 16.6 grams of a 30% formaldehyde solution dissolved in 50 milliliters of alcohol were added and refluxing continued for another three hours. The solvent was distilled off and the residue was recrystallized from methanol. Yield: 11.5 grams; M.P. 224° C. (dec).

PREPARATION VII

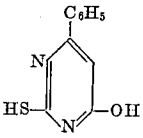
2 - mercapto-4-methyl-6-hydroxy-5-(N-morpholylmethylene)-pyrimidine



26.1 grams of morpholine, 20.0 grams of a 30% formaldehyde solution, 1 mol of glacial acetic acid and 12.8 grams of thiouracil and 250 milliliters of alcohol were heated under reflux for five hours. The alcohol was then distilled off and the residue recrystallized from aqeous ethanol; M.P. 223° C.

PREPARATION VIII

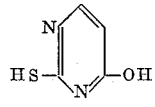
2 - mercapto-6-hydroxy-4-phenylpyrimidine (4-phenyl-2-thiouracil)



11.5 grams of sodium dissolved in 500 milliliters of absolute alcohol were mixed with 96 grams of ethyl benzoylacetate and 39 grams of thiourea. The mixture was heated under reflux for five hours. The reaction product which had separated was dissolved in hot water, treated with charcoal and precipitated with glacial acetic acid. The compound recrystallized from glacial acetic acid; M.P. 270 to 273° C.

PREPARATION IX

2-mercapto-6-hydroxypyrimidine



This compound was prepared in accordance with the method described in Beilstein, volume 24, page 323.

The use of the novel silver halide solvent in combined developing and fixing solutions is illustrated in the following examples.

Our invention will be further illustrated by reference to the following specific examples.

Example I

An exposed panchromatic black and white 35 mm. film having a sensitivity of 13° DIN, commercially available under the name of Agfa Isopan I FF film, was processed in a monobath having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1 - (p - methylaminophenyl)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2 - mercapto - 6 - hydroxy-5-(dimethylaminomethylene) - 4 - methylpyrimidine, grams	12
Water to make, liter	1
pH of the solution	13.4

After washing and drying, an image was obtained which had a gamma value of 0.5 and a fog level of 0.10. The solution remained clear without the formation of silver sludge after it had been used for the development of 14 meters of 35 mm. film and left standing for three days.

A comparison monobath, which contained in place of the pyrimidine derivative, the molecular equivalent of 16 grams of sodium thiosulfate was quite unstable. A heavy silver sludge started to precipitate as soon as the monobath had been used for the processing of a small quantity of film. The same silver sludge precipitation was obtained with a monobath which contained 140 grams of thiosulfate.

Example II

A blue-sensitive black and white film used for photomechanical reproduction and commercially available as Agfa Phototechnisch B was processed in a monobath of the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
p-Methylaminophenol sulfate, grams	4
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2 - mercapto - 6 - hydroxy-4-carboxymethylenepyrimidine, grams	10
Water to make, liter	1

After washing and drying, a gamma value of 1.4 and a fog of 0.075 was observed.

Example III

A graphic art film of the type used in Example II was processed in a combined fixing and developing solution having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
p-Methylaminophenol sulfate, grams	4
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2 - mercapto - 6 - hydroxy-5-(N-piperidylmethylene) pyrimidine, grams	20
Water to make, liter	1

After washing and drying, an image having a gamma value of 0.7 and a fog level of 0.06 was obtained.

Example IV

A graphic art type black and white film as described in Example II was processed in a monobath having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
p-Methylaminophenol sulfate, grams	4
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2 - mercapto-6-hydroxy-5-(dimethylaminomethylene) pyrimidine, grams	10
Water to make, liter	1

The washed and dried film had a gamma value of 1.6 and a fog level of 0.08.

Example V

A silver chloride contact printing paper was processed in a monobath having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1 - (p-methylaminophenol)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium carbonate (anhydrous), grams	30
Potassium bromide, grams	5
2 - mercapto - 6-hydroxy-5-(dimethylaminomethylene)-4-methyl pyrimidine, grams	10
Water to make, liter	1

Example VI

A black and white enlarging paper (Agfa Brovira) was developed in a fixing developer having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
Sodium carbonate (anhydrous), grams	30
Potassium bromide, grams	5
2 - mercapto-4-methyl-5-(1'-morpholylmethylene)-6-hydroxypyrimidine, grams	8
1-phenyl-3-pyrazolidone, gram	0.5
Water to make, liter	1

Example VII

A film as used in Example I was developed in a monobath of the following composition:

Sodium sulfite, grams	30
Hydroquinone, grams	14
p-Methylaminophenol sulfate, grams	4
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2-mercapto-4-methyl-6-hydroxypyrimidine, grams	10
Water to make, liter	1

The developed, washed and dried film had a gamma of 0.6 and a fog of 0.14.

Example VIII

A film as used in Example I was developed in a fixing developer of the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1 - (p - methylaminophenyl)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2-mercapto-4-methyl-6-hydroxypyrimidine, grams	10
Water to make, liter	1

The washed and dried film had a gamma of 0.6 and a fog of 0.19.

Example IX

A film as used in Example I was developed in a fixing developer of the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1 - (p - methylaminophenyl)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium hydroxide, grams	20
Potassium bromide, grams	10
6 - hydroxy-2-mercapto-4-carboxymethylene-pyrimidine, grams	10
Water to make, liter	1

The film obtained after washing and drying had a gamma of 0.7 and a fog of 0.09.

Example X

An orthochromatic microfilm (Agfa Agepe) was processed in a fixing developer having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1-phenyl-3-pyrazolidone, gram	0.5
Sodium carbonate, grams	30
Potassium bromide, grams	5
2 - mercapto-4-methyl-5-(1'-morpholylmethylene)-6-hydroxypyrimidine, grams	8
Water to make, liter	1

The washed and dried film had a gamma of 1.4 and a fog of 0.045.

Example XI

A film as used in Example I was developed in a fixing developer of the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1 - (p-methylaminophenyl)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2 - mercapto-5-(N-morpholylmethylene)-6-hydroxy-pyrimidine, grams	10
Water to make, liter	1

The washed and dried film had a gamma of 0.8 and a fog of 0.19.

Example XII

A film as used in Example I was developed in a fixing developer of the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1-(p-methylaminophenyl)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium hydroxide, grams	20
Potassium bromide, grams	10
4-phenyl-2-thiouarcyl, grams	20
Water to make, liter	1

The washed and dried film had a gamma of 0.4 and a fog of 0.12.

Example XIII

A silver chloride contact printing paper was processed with a combined fixing and developing paste having the following composition:

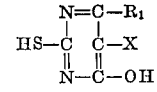
Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1-(p-methylaminophenyl)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium carbonate, grams	30
Potassium bromide, grams	10
2-mercapto-4-methyl-5-(dimethylaminomethylene)-6-hydroxypyrimidine, grams	10
Carboxymethylcellulose, grams	140
Water to make, liter	1

This paste was applied to the exposed paper and removed after three minutes developing time.

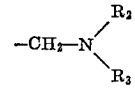
The examples and compounds set forth in the present specification are illustrative only and it is to be understood that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A combined photographic developing and fixing bath composition, comprising an alkaline photographic silver halide developer solution containing a silver halide solvent of the following general formula:



wherein R_1 is a member of the group consisting of a hydrogen atom, lower alkyl, phenyl, tolyl, benzyl, phenethyl and lower carboxy-alkyl groups, and X is a member of the group consisting of hydrogen, the grouping



wherein R_2 and R_3 each represents a lower alkyl group, and the grouping

wherein Y represents the atoms necessary to complete a mononuclear ring.

2. A combined photographic developing and fixing composition according to claim 1 which contains in addition to said developer and fixing agent a thickening agent so as to provide the combined fixing and developing composition with a paste-like consistency.

3. A combined developing and fixing bath solution according to claim 1 wherein said silver halide solvent is 2-mercapto-6 - hydroxy - 5 - (dimethylaminomethylene)-4-methylpyrimidine.

4. A combined developing and fixing bath solution according to claim 1 wherein said silver halide solvent is 2 - mercapto - 6 - hydroxy - 5 - (N - piperidylmethylene)-pyrimidine.

5. A combined developing and fixing bath solution according to claim 1 wherein said silver halide solvent is 2-mercapto-6-hydroxy-4-(carboxymethylene)-pyrimidine.

6. A combined developing and fixing bath solution according to claim 1 wherein said silver halide solvent is 2-mercapto - 6 - hydroxy - 5 - (N - morpholylmethylene)-pyrimidine.

7. A combined developing and fixing bath solution according to claim 1 wherein said silver halide solvent is 2 - mercapto - 6 - hydroxy - 5 - (1' - morpholymethylene)-4-methylpyrimidine.

8. A combined developing and fixing bath solution having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1-(p-methylaminophenol)-3-amino-Δ-2-pyrazoline-dihydrochloride, gram	0.25
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2-mercapto-6-hydroxy-5-(dimethylaminomethylene)-4-methylpyrimidine, grams	12
Water to make, liter	1

9. A combined developing and fixing bath solution having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
p-Methylaminophenol sulfate, grams	4
Sodium hydroxide, grams	20
Potassium bromide, grams	10

2 - mercapto - 6 - hydroxy - 4 - carboxymethylene-pyrimidine, grams	10
Water to make, liter	1

10. A combined developing and fixing bath solution having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
p-Methylaminophenol sulfate, grams	4
Sodium hydroxide, grams	20
Potassium bromide, grams	10
2 - mercapto - 6 - hydroxy - 5 - (N - piperidylmethyl-ene pyrimidine, grams	20
Water to make, liter	1

11. A combined developing and fixing bath solution having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
Sodium carbonate (anhydrous), grams	30
Potassium bromide, grams	5
2 - mercapto - 4 - methyl-5-(1'-morpholylmethylene)-6-hydroxyprimidine, grams	8

1-phenyl-3-pyrazolidone, gram	0.5
Water to make, liter	1

12. A combined developing and fixing bath solution having the following composition:

Sodium sulfite (anhydrous), grams	30
Hydroquinone, grams	14
1 - (p - methylaminophenyl)-3-amino-Δ-2-pyrazoline dihydrochloride, gram	0.25
Sodium carbonate, grams	30
Potassium bromide, grams	10
2 - mercapto-4-methyl-5-(dimethylaminomethylene)-6-hydroxy-pyrimidine, grams	10
Carboxymethylcellulose, grams	140
Water to make, liter	1

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