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(54) **Stable photographic developer and replenisher therefor.**

(57) An aqueous photographic silver halide developer/replenisher solution particularly useful in low throughput machine processing of exposed X-ray silver halide film contains 1-phenyl-3-pyrazolidone, hydroquinone, bromide ion, organic antifoggant and film speed restrainer and is buffered with an alkaline material to a pH of 10 ± 0.3, replenisher having a lower pH than developer.

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TITLE

STABLE PHOTOGRAPHIC DEVELOPER AND REPLENISHER THEREFOR

Technical Field:

This invention is in the field of photographic silver halide developer solutions and replenishers therefor, and is specifically directed to developer-replenisher solutions useful in low through-put machine processing (developing) of photographic film.

Background Art:

The use of so-called "automatic processors" is conventional for developing imagewise exposed silver halide elements such as X-ray films. The exposed films are fed into the processor from a safelight area, i.e. one in which the level of light is reduced below that which exposes the film further, and is transported through various chambers containing the developer, the fixer and the water washes. At the end of the processor, the film is dried and exits into normal light as a finished product ready for use. This is illustrated in U.S. Patent 3,545,971 "Rapid Processing of Photographic X-ray Film" (1966). This system is rapid and convenient and large numbers of films can be routinely handled in this manner over long periods of time without deleterious effects to the finished image. Of course, the processing solutions become exhausted by the passage of the exposed silver halide film and replenishment must be made to account for ingredient loss. Additionally, the processing fluids, especially the developer solution, are degraded aerobically by contact with air and anerobically when simply left for long periods of inaction.

When large amounts of film are being processed (high throughput), exhaustion of the developer is due almost entirely to development of the silver halide image. The development reaction as shown in Mason's "Photographic Processing Chemistry" Focal Press (1966) page 74, is:

$2AgBr + H_2Q + Na_2SO_3 \longrightarrow 2Ag + HBr + NaBr + HQSO_3Na$

Thus, some materials, i.e., hydroquinone and sulfite are lost while bromide, acid, and hydroquinone monosulfonate are formed. Also, not shown by this reaction, antifoggant may be lost. Current developer replenishers are formulated based on this reaction as follows: The replenisher is made higher in pH than developer and contains no bromide, so as to offset the acid and bromide released by the development reaction. The other ingredients are set at concentrations which allow for the expected losses, the hydroquinone being offset by the antifoggants, without substantially affecting the sensitometry. In this situation a replenishment rate can be conveniently calculated based on the approximate area of film fed into the processor.

The other situation presents a more difficult problem because when only small amounts of film are processed (low throughput), the developer deteriorates primarily from air oxidation and thermal reactions, and not from development reaction; Mason's "Photographic Processing Chemistry" supra at page 73:

$H_2Q + 2Na_2SO_3 + O_2 \longrightarrow HQSO_3Na + NaOH + Na_2SO_4$.

That is, hydroquinone and sulfite are lost but not bromide. Also, pH increases, not decreases as in the development reaction. Also, since film passage activates the replenishment, low throughput decreases replenishment.

Current practice is to compensate for low throughput by increasing replenishment rate significantly, e.g., as much as two-fold. This, however, can actually accelerate the problems caused by low throughput processing and cause sensitometric instability. It does so because the replenisher, which is being added, in excess, has higher pH than the developer and no bromide. The effect of this is to (1) maintain the increasing pH of the developer caused by oxidation, and (2) dilute the bromide content to levels so low as to cause sensitometric instability, reflected mainly in fog and speed. The present invention provides a replenisher formulation which is aimed at compensating for developer changes caused by nonuse, and not by the development reaction. Thus, the replenisher is characterized by a pH lower than that of the developer, and it contains the maximum amount of bromide consistent with acceptable sensitometry. Now when replenishment occurs, pH will remain constant or slightly decrease, the bromide will remain essentially constant, and the other changes will compensate as in state of the art formulations. Thus, by maintaining the developer composition more constant, the developer can maintain a useful lifetime equivalent to the high throughput processors.

It is accordingly an object of this invention to provide an improved developer/-replenisher system for developing exposed silver halide photographic film. A further object is to provide a developer/replenisher system particularly useful for machine processing of X-ray film when low throughput of film is practised.

Summary of the Invention:

These and other objects are achieved in this invention by providing an aqueous processing solution useful as a photographic developer bath for automatic processing of silver halide photographic film, particularly X-ray film, and as a replenisher therefor, consisting essentially of, per liter:

1-phenyl-3-pyrazolidone photographic developing agent, or a derivative thereof	0.8 to 2.5 g
Hydroquinone developing agent or a derivative thereof	15 to 35 g
Bromide ion	1 to 7 g
Organic antifoggant and film speed restrainer	0.01 to 10.0 m mole
Alkaline material and buffer to provide a pH of 10.0 ± 0.3;	

with the proviso that the replenisher solution will not only contain bromide ion but also will have a lower pH than that of the developer solution.

Developers and replenishers made according to this invention can be used in processing machines for low throughput of X-ray film, for example, and will exhibit excellent stability over long periods of both use and nonuse. Hence, a further embodiment of the invention is a process for the automatic processing of exposed photographic silver halide X-ray film wherein the imagewise exposed X-ray film is developed in a photographic developer bath comprising a photographic developer, bromide ion, an alkaline material and buffer system to maintain the pH of the developer bath at a desired value, an organic antifoggant and film speed restrainer, and water; the developed X-ray film is fixed, washed and dried; and the developer bath is replenished by a

replenisher solution to maintain constant the photographic properties of the developer bath during processing of a large quantity of exposed X-ray film, characterized in that the processing solution described above serves as both the developer bath and the replenisher solution; with the proviso that the latter have a pH lower than that of the developer.

Detailed Disclosure of the Invention:

The processing solution of this invention can be used for both the developer and the replenisher therefor. In the latter embodiment, wherein the replenisher solution has a lower pH than that of the developer, it is only necessary to add a small amount of acid, acetic acid, for example, to adjust the pH. However, for a commercial put-up, a small amount of base (alkaline material) is added to the developer to raise the pH of the developer rather than adding acid to the replenisher to lower its pH. This will be illustrated in Example 1, wherein a small amount of base is added through the starter solution (Part D). The replenisher is added to the developer bath as needed, based on time and/or the amount of film processed, thus compensating for both forms of developer exhaustion. It is surprising that this particular formulation can be used so successfully for low throughput in automatic processors since the differences between it and the prior art are so slight. However, as will be seen in the Examples, the difference in performance between the formulation of this invention and the prior art is very large.

As the photographic developing agents in the processing solution, a combination of 1-phenyl-3-pyrazolidone (sold under the Ilford trademark Phenidone) or a derivative thereof such as

4-methyl or 4,4-dimethyl phenidone, and hydroquinone or a derivative thereof such as chlorohydroquinone or bromohydroquinone is used. This combination is particularly suited for automatic processing of X-ray films. These ordinarily comprise a gelatino-AgBr, AgBrI, or AgClBrI emulsion on a film support such as polyethylene terephthalate.

Any alkaline material may be used to provide the required pH, such as sodium or potassium hydroxide, sodium or potassium carbonate, etc. The buffer system may be any convenient system, e.g., the borate and carbonate buffers conventionally used in X-ray developer baths are both suitable.

The organic antifoggant may be any organic antifoggant and film speed restrainer. Such organic antifoggants are commonly employed in X-ray developer baths and include compounds of the benzimidazole, benzotriazole, benzothiazole, indazole, tetrazole, and thiazole group, as well as anthraquinone sulfonic acid salts. Two or more organic antifoggants may be used. It is preferred to use a mixture of two antifoggants such as 5-nitroindazole and benzotriazole.

A range of bromide ion can be used successfully in this invention and provides excellent stability. 1 to 10 g/liter of KBr, for example, will provide sufficient bromide ion. NaBr may also be employed. Optimum amounts depend on replenishment rate and specific formula.

These essential ingredients, when dissolved in water at the concentrations set forth above, enable the photographic solution of the invention to function as a developer bath and a shelf-stable replenisher.

Other materials may be included in the processing solution, such as gelatin hardening agents, aerial oxidation restrainers, sequestering agents, surfactants, dyes, etc., as well known in the art. See, e.g., U.S. Patent 3,545,971 and "Photographic Processing Chemistry", supra, page 149 et seq.

Conventionally, all of the ingredients of the developer are prepared in concentrated form in water. Separate portions of the concentrates are furnished users so that interaction between ingredients is lessened while in this concentrated state. Then, the user makes up the developer solution by measuring various amounts from each part and diluting with water to achieve the desired solution. The pH is then adjusted, e.g., to 10.0 $\pm$ 0.3, and the solution charged to the processing tank, e.g., of the type described in U.S. Patent No. 3,545,971, such as an "X-Omat Processor", in the amount required by the system. Development time is determined empirically or by the processor. Replenishment will be carried out at a rate per unit area of exposed film to provide processing of a large quantity of exposed film without change in sensitometric properties of the film, and will be determined empirically, as is known. As a guide, when using an X-Omat Processor to process X-ray film, a suitable replenishment rate will be about 55 ml per 240 square inches of exposed film for development to normal radiographic density, using the processing solution of the invention.

Some processors have a standby replenishment mode. This works as follows: if no film is passed in a given time, the processor goes into a standby mode which deactivates the drive train and dryer and

reduces water supply. After a given time, it comes back on for several minutes and then shuts off again. After a specified number of cycles, it replenishes a predetermined amount. This replenishment is not effective with current developer/replenisher formulations but very effective with this invention since more of the correct replenisher is used.

After development in the processing solution of the invention, the silver halide film is fixed, preferably in an acid fixer, and washed and dried in the usual manner. If a processing machine is used, these steps will be determined by the machine.

The following examples are illustrative of the invention, with Example 1 being the best mode contemplated by the inventor of carrying out the invention.

EXAMPLE 1

The following solutions were prepared in order to formulate a developer/replenisher (I) according to the present invention, and to compare it with a conventional developer/replenisher (II):

Ingredients	Amt.(g)
Part A	
Dist. Water	250
Ethylenediaminetetraacetic Acid (EDTA)	8
Sodium Bisulfite (43% aq.)	383
Hydroquinone	100
KBr	13
KOH (45% aq.)	323
K_2CO_3 (47% aq.)	116
Distilled Water to	1 liter

Part B

Acetic Acid	560	
Triethylene Glycol	240	
Phenidone	60	
5-nitroindazole	6.4	2.66 m moles
Benzotriazole	8.0	
Sodium Bisulfite (anhydr.)	5	

Part C

Dist. Water	500	
Glutaraldehyde (50% aq.)	300	
Sodium Bisulfite (anhydr.)	106	
Water to	1 liter	

Part D

Dist. Water	500	
KOH (45% aq.)	200	
KBr	171	-
Water to	1 liter	

To make developer I: 250cc A
25cc B pH 10.2
25cc C
Water to 1 liter
23.4cc D

To make replenisher 250cc A pH 10.0
25cc B
25cc C
Water to 1 liter

For comparison, a conventional high throughput medical X-ray developer II was prepared. The most significant difference was that Part A' (of developer II) contained no KBr, and Part D' contained 130 g

acetic acid/liter instead of 200 g KOH/liter. Developer II had a pH of 10.15, and replenisher II a pH of 10.35 (compared to pH 10.0 for replenisher I).

In an actual hospital situation, samples of exposed, high speed medical X-ray film were processed (ca. 15-20 sheets of 8" x 10" film/day) using developers I and II, which were charged to a CRONEX® QC-1 Medical X-ray Automatic Processor (E. I. du Pont de Nemours and Company, Wilmington, DE). The respective replenisher solutions were supplied to the replenisher tank thereof. The activities of the systems were checked by processing control strips of X-ray film exposed through a $\sqrt{2}$ 21-step wedge on a Cronex® Electroluminescent (ELS) Sensitometer (E. I. du Pont de Nemours and Company, Wilmington, DE). Two strips per day (one in the morning and one in the afternoon) were processed and the sensitometry checked to see whether the processor and its solutions were performing well. Processing time (dry-to-dry) was about 2-1/2 minutes at 92°F. The processor was equipped with a conventional ammonium thiosulfate fixer solution.

In the case of developer/replenisher II, above, high fog and lower speed was noted after about 2 weeks of use and the machine was shut-down and the solutions drained therefrom. In the case of developer/replenisher I, above, the fog and speed remained constant after more than 4 weeks of continued, low throughput use, demonstrating good long life performance.

EXAMPLE 2

Developer/replenisher I of Example 1 was operated for more than thirteen weeks at low throughput at St. Joseph's Hospital in Phoenix, Arizona in a Cronex QC-1 processor under essentially

the same conditions as Example 1. The same formula was also run over four weeks at high throughput, thus demonstrating that developer/replenishers of this invention exhibit excellent stability over long periods of time in both high and low throughput.

EXAMPLE 3

In order to differentiate this invention over another prior art developer/replenisher formulation, the example given in Mertz, U.S. Patent No. 4,046,571 "Processing Solution For Use As Photographic Developer Bath and Replenisher Therefor" (1977), Cols. 3, 4 and 5 was repeated. In this reference, the organic antifoggant and film speed restrainer is defined as being between 7-26 m mole/liter of solution, which compares to 2.66 m mole/liter in Part B of Example 1. Corresponding Part B of the Mertz example containing 3.6 g/liter of 5-chlorobenzotriazole and 5 g/liter of 5-nitrobenzimidazole was difficult to prepare and required heating to ca. 120°F. Preparation of the working strength developer/replenisher as described was also difficult and required constant heating to keep all the solids dissolved. For this reason the solutions could not be tested in a commercial, automatic processor. Instead, control strips of X-ray film were tray processed in this developer and took about 3 times as long to process as those processed in developer solution I of Example 1, above.

EXAMPLE 4

The following solutions were prepared:

Ingredients	Amt. (g)
Part A	
Dist. Water	ca. 3785 (1 gal)
EDTA	75
Sodium Bisulfite	1428
Hydroquinone	946
KOH (45% aq.)	3075
KOH (solid)	1383
Sodium Bicarbonate	315
KBr	113
Dist. Water	to 9.46 liters (2.5 gals)
Part B	
Triethylene Glycol	402
Acetic Acid	270
Phenidone	60
5-nitroinidazole	6
Benzotriazole	8
Dist. Water to	1 liter
Part C	
Water	500
Glutaraldehyde (50% Aq.)	267
Sodium Bisulfite (anhydr.)	106
Dist. Water to	1 liter

A developer solution was made up as follows:

Dist. Water	26.5 l. (7 gal.)
NaBr	120 g
Sodium Bisulfite (anhydr.)	270 g
Potassium Carbonate (anhydr.)	312 g
Sodium Carbonate	200 g
Part A, above	4.75 l. (5 quarts)
Part B, above	.95 l. (1 quart)
Part C, above	.95 l. (1 quart)
Dist. Water	to 37.85 l. (10 gallons) pH 10.17 ± 0.05

Five gallons (approx. 19 liters) of this developer were charged to the processor described in Example 1. About 60 grams of acetic acid were added to the remaining 19 liters to give a pH of 10.0 ± 0.05 and this was used as the replenisher. The processor was also charged with standard ammonium thiosulfate fixer and set at 92°F. Two samples of exposed X-ray film (high speed CRONEX®4, E. I. du Pont de Nemours and Company), 14 x 17 inch size, were processed (developed) and the sensitometry of the system checked with control strips as described in Example 1. The processor was then allowed to stand by for the remainder of the day. About 2,000cc of replenisher was added by the machine during this time. At the end of the 8 hour day, the machine was shutdown. The processor was run for 10 days in this manner. No substantial change was noted in the sensitometry of the control strips used to check developer activity, indicating that this formula was

very stable to low throughput of silver halide film and resistant to anerobic and aerobic degradation.

EXAMPLE 5

The formula of Example 2 (pH about 10.2) was used in this example, as both developer and replenisher, in the processor of Example 1. Under low throughput conditions (7 to 10 sheets of X-ray film/day) it served for more than five weeks. At the end of this period of time, control strips processed in this machine showed that the activity of the developer was well within limits and produced excellent results. A conventional developer of the prior art deteriorates badly in less than two weeks under these conditions and requires shut-down and cleaning of the automatic processor followed by re-charging with fresh solution.

CLAIMS

1. An aqueous photographic processing solution useful as a photographic developer bath for automatic processing of X-ray film and as a replenisher therefor, consisting essentially of, per liter:

1-phenyl-3-pyrazolidone (photographic developing agent)	0.8 to 2.5 g
Hydroquinone (developing agent)	15 to 35 g
Bromide ion	1 to 7 g
Organic antifoggant and film speed restrainer	0.01 to 10.0 m mole
Alkaline material and buffer to provide a pH of 10.0 ± 0.3,	

and with the proviso that the replenisher has a pH lower than that of the developer.

2. A processing solution according to claim 1, wherein the organic antifoggant is at least one benzimidazole, benzotriazole, tetrazole, thiazole or anthraquinone sulfonic acid salt.

3. A processing solution according to claim 1, wherein the organic antifoggant and film speed restrainer is a mixture of 5-nitroindazole and benzotriazole.

4. A processing solution according to claim 1, 2 or 3 which contains at least one adjuvant selected from gelatin hardening agents, aerial oxidation restrainers, sequestering agents, surfactants and dyes.

5. Use of a processing solution as claimed in any one of the preceding claims as a developer/replenisher in an automatic processing system for exposed photographic silver halide X-ray film operating at low throughput.

6. A process for the automatic processing of exposed photographic silver halide X-ray film wherein an imagewise exposed X-ray film is developed in a

photographic developer bath comprising a photographic developer, bromide ion, an alkaline material and buffer to maintain the pH of the developer bath at a desired value, an organic antifoggant and film speed restrainer, and water; the developed X-ray film is fixed, washed and dried; and the developer bath is replenished by a replenisher solution to maintain substantially constant the photographic properties of the developer bath during processing of a large quantity of exposed X-ray film, characterised by using a processing solution as claimed in any one of claims 1 to 4 as both the developer bath and the replenisher solution, with the proviso that the replenisher solution has a pH lower than that of the developer.

European Patent Office

EUROPEAN SEARCH REPORT

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Application number

EP 82303347.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D,A	US - A - 3 545 971 (BARNES) * Column 2, line 72 - column 3, line 48; example 1 * --	1-6
A	GB - A - 1 429 919 (FUJI) * Page 4, line 6 - page 5, line 36; page 6, lines 4-18; page 8, lines 1-24 * --	1-6
A	US - A - 3 854 948 (VERSORESE) * Claims 1,5,6,9,10 * ----	1,5,6

CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

G 03 C 5/30
G 03 C 5/24
G 03 C 5/26

TECHNICAL FIELDS SEARCHED (Int.Cl. ³)

G 03 C

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	29-10-1982	SCHÄFER

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