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

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Description

This invention is in the field of photographic silver halide developer solutions and replenishers therefor, and is specifically directed to the use of developer-replenisher solutions in low throughput machine processing (developing) of photographic film, which solutions can also be used in high throughput processing.

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 US—A—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:

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

Thus, some materials, i.e., hydroquinone (H_2Q) 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:

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

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.

US—A—4046571 describes an aqueous photographic processing solution useful as a developer both for automatic processing of X-ray film and as a replenisher therefor, stated to consist essentially of, per liter:

A 1-phenyl-3-pyrazolidone photographic developer	0.8 to 1.8 g
Hydroquinone or a derivative thereof	15 to 35 g
Bromide ion	0 to 4 g
Organic anti-foggant and film speed restrainer	7 to 26 mmol
Alkaline material and buffer to provide a pH at	25°C of $10.0{+0.8 \atop -0.5}$

This processing solution is used without a starter solution and preferably contains no bromide ion. No mention is made of throughput, high or low, and hence there is no mention of the different problems encountered in high and low throughput operations.

According to the invention there is provided the use of an aqueous processing solution as a developer/replenisher in an automatic processing system for exposed photographic silver halide X-ray film, characterised in that said solution comprises, per liter:

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

with the proviso that a solution used as a replenisher has a pH lower than that of a solution used as a developer.

Developers and replenishers can be used according to this invention 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 characterized in that the processing solution described above serves as both the developer bath and the replenisher solution; with the proviso that the replenisher has a pH lower than that of the developer.

The processing solution 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 package, 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, or sodium or potassium carbonate. 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. 1.5 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 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 and dyes, as well known in the art. See, e.g. US—A—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±0.3, and the solution charged to the processing tank, e.g. of the type described in US—A—3,545,971, such as an "X-Omat Processor" (Registered Trade Mark of Eastman Kodak Company), 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 1550 cm^2 (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 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

Ingredients	Amt. (g)	
5-nitroindazole	6.4	corresponds to 2.66 m moles in developer I below
Benzotriazole	8.0	
Sodium Bisulfite (anhydr.)	5	
Water to	1 liter	
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:	250 cc A	
	25 cc B	pH *10.2*
	25 cc C	
	Water to 1 liter	
	23.4 cc D	
To make replenisher	250 cc A	pH *10.0*
	25 cc B	
	25 cc 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 (45% aq.)/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 20 cm×25 cm (8"×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 33°C (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, demonstrated 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 used in this invention exhibit excellent stability over long periods of time in both high and low throughput.

Example 3

The following solutions were prepared:

Ingredients	Amt. (g)
Part A	
Dist. Water	ca. 3785 (1 U.S. 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 U.S. 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 U.S. gal.)
NaBr	120 g

Ingredients	Amt. (g)
Sodium Bisulfite (anhydr.)	270 g
Potassium Carbonate (anhydr.)	312 g
Sodium Carbonate	200 g
Part A, above	4.75 l. (5 U.S. quarts)
Part B, above	0.95 l. (1 U.S. quart)
Part C, above	0.95 l. (1 U.S. quart)
Dist. Water	to 37.85 l. (10 U.S. gallons) pH 10.17±0.05

Five U.S. 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 33°C (92°F). Two samples of exposed X-ray film (high speed Cronex® 4, E. I. du Pont de Nemours and Company), 36×43 cm (14×17 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 2,000 cm^3 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 4

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. Use of an aqueous processing solution as a developer/replenisher in an automatic processing system for exposed photographic silver halide X-ray film, characterised in that said solution comprises per liter:

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

with the proviso that a solution used as a replenisher has a pH lower than that of a solution used as a developer.

2. 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, characterised

by using a processing solution as defined in claim 1 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.

3. Use or process according to claim 1 or 2 wherein the organic antifoggant is at least one benzimidazole, benzotriazole, benzothiazole, indazole, tetrazole, thiazole or anthraquinone sulfonic acid salt.

4. Use or process according to claim 1 or 2, wherein the organic antifoggant and film speed restrainer is a mixture of 5-nitroindazole and benzotriazole.

5. Use or process according to any one of the preceding claims wherein the solution contains at least one adjuvant selected from gelatin hardening agents, aerial oxidation restrainers, sequestering agents, surfactants and dyes.

Patentansprüche

1. Verwendung einer wäßrigen Verarbeitungslösung als Entwickler/Regenerator in einem automatischen Verarbeitungssystem für exponierte photographische Silberhalogenid-Röntgenfilme, dadurch gekennzeichnet, daß die Lösung pro Liter enthält:

1-Phenyl-3-pyrazolidon oder ein Derivat desselben als photographisches Entwicklungsmittel	0,8 bis 2,5 g,
Hydrochinon oder ein Derivat desselben als photographisches Entwicklungsmittel	15 bis 35 g,
Bromid-Ionen	1 bis 7 g,
organisches Antischleiermittel und Filmgeschwindigkeits-Verzögerungsmittel	0,01 bis weniger als 7 mmol und
alkalisches Material und Puffer zur Erzeugung eines pH von	10,0±0,3,

mit der Maßgabe, daß eine als Regenerator verwendete Lösung einen niedrigeren pH als eine als Entwickler verwendete Lösung aufweist.

2. Verfahren zur automatischen Verarbeitung von exponierten photographischen Silberhalogenid-Röntgenfilmen, wobei ein bildmäßig belichteter Röntgenfilm in einem photographischen Entwickler-Rad, das einen photographischen Entwickler, Bromid-Ionen, ein alkalisches Material und einen Puffer zur Einhaltung eines gewünschten pH-Wertes des Entwickler-Bades, ein organisches Antischleiermittel und Filmgeschwindigkeits-Verzögerungsmittel und Wasser enthält, entwickelt wird, der entwickelte Röntgenfilm fixiert, gewaschen und getrocknet wird und des Entwickler-Bad mit Hilfe einer Regenerator-Lösung regeneriert wird, um die photographischen Eigenschaften des Entwickler-Bades während der Verarbeitung im wesentlichen konstant zu halten, dadurch gekennzeichnet, daß eine Verarbeitungslösung nach Anspruch 1 sowohol als Entwickler-Bad als auch als Regenerator-Lösung verwendet wird, mit der Maßgabe, daß die Regenerator-Lösung einen niedrigeren pH als der Entwickler aufweist.

3. Verwendung oder Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß das organische Antischleiermittel wenigstens eine der Substanzen Benzimidazol, Benzotriazol, Benzothiazol, Indazol, Tetrazol, Thiazol oder Anthrachinon-sulfonsäure-salz ist.

4. Verwendung oder Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß das organische Antischleiermittel und Filmgeschwindigkeits-Verzögerungsmittel ein Gemisch aus 5-Nitroindazol und Benzotriazol ist.

5. Verwendung oder Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Lösung wenigstens ein Hilfsmittel (Adjuvans) ausgewählt aus Gelatine-Härtungsmitteln, Verzögerungsmitteln der Luft-Oxidation, Maskierungsmitteln, grenzflächenaktiven Mitteln und Farbstoffen enthält.

Revendications

1. Utilisation d'une solution de traitement aqueuse comme développateur/régénérateur dans un système de traitement automatique pour pellicule photographique radiologique à base d'halogénure d'argent exposée, caractérisée en ce que ladite solution comprend, par litre:

1-phényl-3-pyrazolidone ou un dérivé de celle-ci comme agent de développement photographique	0,8 à 2,5 g
Hydroquinone ou un dérivé de celle-ci comme agent de développement	15 à 35 g
Ion bromure	1 à 7 g
Antivoile et modérateur de rapidité d'émulsion organique	0,01 à moins de 7 mmoles
Matière alcaline et tampon pour donner un pH de	10±0,3,

avec la condition qu'une solution utilisée comme régénérateur ait un pH inférieur à celui d'une solution utilisée comme développateur.

2. Un procédé de traitement automatique de pellicule photographique radiologique à base d'halogénure d'argent exposée dans lequel une pellicule radiologique exposée selon une image est développée dans un bain de développement photographique comprenant un développateur photographique, de l'ion bromure, une matière alcaline et un tampon visant à maintenir le pH du bain de développement à une valeur désirée, un antivoile et modérateur de rapidité d'émulsion organique, et de l'eau; la pellicule radiologique est fixée, lavée et séchée, et le bain de développement est régénéré par une solution de régénération visant à maintenir constantes les propriétés photographiques du bain de développement pendant le traitement, caractérisé par l'utilisation d'une solution de traitement selon la revendication 1 pour constituer à la fois le bain de développement et la solution de régénération; avec la condition que la solution de régénération présente un pH plus bas que celui du développateur.

3. Utilisation ou procédé selon la revendication 1 ou 2 dans laquelle ou lequel l'antivoile organique est l'un au moins des corps suivants: benzimidazole, benzotriazole, benzothiazole, indazole, tétrazole, thiazole ou sel de l'acide anthraquinone sulfonique.

4. Utilisation ou procédé selon la revendication 1 ou 2 dans laquelle ou lequel l'antivoile et le modérateur de rapidité d'émulsion organique est un mélange de 5-nitroindazole et de benzotriazole.

5. Utilisation ou procédé selon l'une quelconque des revendications précédentes dans laquelle ou lequel la solution contient au moins un adjuvant choisi parmi les agents durcisseurs de gélatine, les inhibiteurs d'oxydation par l'air, les agents séquestrants, les agents tensioactifs et les colorants.