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[54] **METHODS AND MATERIALS FOR
REPLENISHMENT OF DEVELOPERS
FOR COLOR PHOTOGRAPHIC FILMS**

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[57] **ABSTRACT**

Developer replenishers having buffer controlled high pH and high potassium/sodium weight ratio are effective at low replenishment rates; for example, developer replenishers having a pH of 10.5 to 11 containing a potassium/sodium weight ratio of at least 5.4/1, p-phenylenediamine developing agent and benzyl alcohol in weight ratio of between about 1/1.5 and 1/2 and sulfite are especially effective. Such replenishers are advantageously prepared from kits comprising at least two solutions, one a buffered aqueous alkaline solution containing alkali metal ions in a high potassium/sodium weight ratio and another an aqueous solution having low pH and containing p-phenylenediamine developing agent in high concentration. The replenishers are utilized in conjunction with the processing of imagewise exposed, multilayer, incorporated coupler, silver halide sensitized, color photographic film materials.

17 Claims, No Drawings

METHODS AND MATERIALS FOR REPLENISHMENT OF DEVELOPERS FOR COLOR PHOTOGRAPHIC FILMS

This invention relates to developer replenishers which can be effectively utilized in the continuous processing of imagewise exposed, silver halide sensitized, color photographic film materials. In one of its aspects this invention relates to methods and materials effectively used in preparing such developer replenishers. In another of its aspects this invention relates to continuous processes in which such developer replenishers are employed.

The processing of imagewise exposed, multilayer, incorporated coupler, silver halide sensitized, color photographic film materials of the positive-negative type (that is, those which on exposure to a subject or positive image and processing are designed to result in a negative color image which can be used as a negative from which photographic color prints are made, or conversely on exposure to a negative are designed to form a positive transparency) usually involves subjecting the film to a series of processing steps by, for example, passing the film through a number of different processing compositions. These steps include: developing the film in an aqueous alkaline solution which contains p-phenylenediamine developing agent to simultaneously form silver images and dye images in the exposed areas; stopping the development by treating the film with an acidic composition; hardening the developed film by treating the film with a gelatin hardening composition; bleaching the hardened film by treating the film with a bleach composition to convert developed silver to Ag^+ ; and fixing Ag^+ , including unexposed silver halide, from the bleached film by treating the film with a fixing composition.

Several of the compositions used in this type of process lose effectiveness in their intended function after use for a period of time. The developer loses its effectiveness, for example, because some of the developer components react with components of the film. The p-phenylenediamine developing agent, for example, reacts with incorporated color couplers of the film to form dyes in areas which have received exposure. Also, some of the developer is lost as carryover when film is passed through a bath or series of baths of developer. As a result of the loss in effectiveness of the developer, the composition must be replaced or treated to restore its effectiveness.

In a continuous process, i.e., one designed for operation for large quantities of film over an extended period of time, the effectiveness of such compositions is restored by adding developer replenisher to the original solution. The concentration of the developer replenisher components are thus controlled to maintain desirable developer component concentrations between predetermined limits, usually at a relatively constant value. The replenisher must not only make up for components used during processing and loss through carryover, but also overflow loss by volume increase when the replenisher is added. The replenishment can be accomplished while the developer is in use by adding replenishment in continuous fashion or at periodic intervals, usually at a specified amount of replenisher for each square foot of film processed.

In such processes it has heretofore been considered necessary to use a developer replenishment rate of at least about 325 ml. of developer replenisher per square foot of processed film (normally about 485 ml. per square foot of picture area) to assure high-quality, reproducible development.

We have found that by using developer replenishers having a buffer controlled high pH and high potassium/sodium weight ratio in processing multilayer, incorporated coupler, silver halide sensitized, color photographic film materials of the positive-negative type, high-quality development can be obtained at a replenishment rate which is a fraction (one-half and even less) of the rate previously considered necessary for satisfactory results. These surprisingly effective developer replenishers are advantageously prepared from replenisher kits having at least two solutions, one containing concentrated acidic developing agent solution and another containing a concentrated aqueous solution having a buffer controlled high pH with alkali metal ions in high potassium/sodium ratio.

According to the present invention there are provided developer replenisher kits and components thereof which are advantageously used for the production of developer replenishers which can be effectively utilized at a surprisingly low replenishment rate.

Also, in accordance with the present invention there are provided methods of making such developer replenishers.

Further, in accordance with the present invention there are provided improved developer replenishers.

Additionally, according to the present invention, there are provided methods and materials for use in conjunction with processing of multilayer, incorporated coupler, silver halide sensitized, color film materials which result in substantial decrease in the cost of chemicals used in developers and cost of pollution prevention with no detrimental effect on the overall quality of the process.

Also provided in accordance with the present invention are improved methods and materials for processing imagewise exposed, well-known incorporated coupler, silver halide sensitized, color photographic film materials of the positive-negative type and for utilizing replenisher compositions whereby the concentrations of desirable components in processing solutions are controlled between predetermined concentration limits.

Further advantages which result from the present invention will become apparent from the following description.

In one embodiment of the present invention a concentrated, buffered aqueous solution having a pH in excess of about 10.5, advantageously above about 10.75 when measured at about 75° F. (normally buffered solutions having a high pH decrease in pH with increase in temperature) and containing water; hydroxide; buffer, e.g., phosphate, carbonates, advantageously boric acid borate buffer; and alkali metal ions selected from the group consisting of sodium and potassium ions so that the potassium/sodium weight ratio is at least 2.5/1, especially at least 5.4/1.0, forms one component of a developer replenisher kit. This solution also desirably contains some sulfite (e.g., supplied as sodium or potassium sulfite or bisulfite) and/or sequestering agent, such as ethylenediamine tetraacetic acid and advantageously diaminopropanol tetraacetic acid. In some instances it is also desirable to have small amounts of bromide present in the buffered solution.

The buffered solution can be prepared in a number of ways but it is especially advantageous to add alkali metal hydroxides to water and then the weak acid to the alkaline solution to form the buffer. The alkali metal hydroxide/weak acid ratio used to from the buffer may vary to some degree but it is desirably about a 1/1 mole ratio and advantageously 1-1.1/1 to maintain the desired pH and buffer capacity. It is especially advantageous to use potassium hydroxide as the main source of hydroxide but some sodium hydroxide can be used with effectiveness.

The potassium/sodium weight ratio for the total solution to be used as the component for the developer replenisher kit should be at least about 2.5/1, advantageously at least about 5.4/1 and especially between 5.4-10/1. Thus, if alkali metal ions are introduced into the kit component as cations of the other salts, e.g., as sodium sulfite, the weight ratios of hydroxides may vary. In a preferred embodiment of the invention no cations other than sodium and potassium are present in the buffered solution in significant concentration.

The concentration of the ingredients in the buffered solution can vary considerably. However, the solutions are desirably concentrated so that shipping, packaging, and handling costs are reasonably low. However, the concentration should be sufficiently low so that no crystallization occurs since such crystals are often difficult to redissolve. Solutions having a cationic concentration of about 7-15 molar are generally desirable especially when the cations consist essentially of potassium and sodium in a potassium/sodium weight ratio of at least about 2.5/1, advantageously 5.4/1.0 and especially 5.4 to 10/1.0.

The hydroxide and weak acid concentrations desirable in such a solution will be dictated by the pH and buffer capacity desired but usually the alkali metal hydroxides constitute the main source of alkali metal. Accordingly, sufficient hydroxide is desirably used so that the hydroxide concentration also corresponds to about a 7-15 molar concentration were it not for the formation of the buffer. The weak acid concentration originally used will also vary depending upon the particular pH and buffer capacity desired. However, for formation of the boric acid-borate buffer it is advantageous to utilize the hydroxide-boric acid ratio indicated above.

The sulfite concentration of such a kit component is dictated by the amount of the sulfite necessary in the replenisher. A concentration of about 0.15 to about 0.4 molar in the kit component is usually desirable. Although, as mentioned above, it is sometimes desirable to have some bromide present in the kit component, it is important that the bromide content of the fresh, ready-to-use replenisher be no higher than about 0.010 molar and advantageously no higher than 0.009 molar. Thus, if the bromide were added, for example, as sodium bromide, the total sodium bromide used would be no greater than about 1.0 g. for sufficient concentrate to make one liter of replenisher or no greater than about 0.2 molar in the replenisher kit.

The buffered solution is advantageously one solution of a developer replenisher kit which includes at least another solution comprising p-phenylenediamine developing agent at high concentration in aqueous solution having a pH less than about 6, advantageously less than about 4. The p-phenylenediamine developing agents which are used in this solution are the color developing agents well known in the art, for example, U.S. Pat. Nos. 2,552,241 and 2,566,271, which form nondiffusing dyes with phenolic and reactive methylene couplers. These developing agents include N substituted or ring substituted p-phenylene-diamines, such as N,N-dialkyl-p-phenylenediamines wherein the alkyl groups and/or the aromatic nucleus may be substituted, for example, with a sulfonamido group. Examples of highly useful developing agents are 2-amino-5-diethylaminotoluene monohydrochloride; 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate; 4-amino-3-methyl-N-[β -hydroxyethyl]-aniline sulfate; and 4-amino-3-[β -methylsulfonamidoethyl]-N,N-diethylaniline. In an extremely advantageous embodiment of the present invention 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate is used as the color developing agent.

The concentration of the developing agent will, of course, vary depending upon the specific developing agent selected, etc. Again, for economic reasons, it is advantageous to have a highly concentrated solution, particularly between about 1-6 g. diamine per 10 grams of water, for the replenisher kit component. When 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine is used as the developing agent it is desirable to use a concentration of about 5 g. diamine (i.e., about 7.8 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate) for each 10 g. water.

The developer replenisher kit according to the present invention also contains sulfite. As mentioned above, sulfite is advantageously included in the buffered solution. It is also desirable to include sulfite in the developing agent solution desirably in a diamine/sulfite mole ratio of about 1/0.08 to about 1/1.5, especially about 1/0.15 to about 1/0.5. (Mole ratios of diamine set forth herein relate to the moles of available diamine in the solution not necessarily moles of salt added, e.g., 846 g. of 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate, is considered to include 2 moles of diamine.)

Benzyl alcohol is also included in the developer replenisher kit according to the present invention and it, too, is advantageously included in the developing agent solution desirably at a phenylenediamine/benzyl alcohol weight ratio of no less than about 1/2 and especially between about 1/1.5

and 1/2. A highly advantageous method of incorporating the benzyl alcohol in the concentrated developing agent solution is by utilizing a simple liquid glycol with a carbon/oxygen ratio of about 0.75 to about 1.5/1 and molecular weight of from about 62 to about 150, desirably in a benzyl alcohol/glycol weight ratio between about 0.7/1 and about 1/1. Particularly advantageous glycols are propylene glycol, diethylene glycol, and triethylene glycol, and especially ethylene glycol. With such compounds the benzyl alcohol can be combined with acidic aqueous solutions to form clear solutions in a high benzyl alcohol concentration, a water/benzyl alcohol weight ratio of from 1/6 to about 5/1.

The developing agent solutions which contain benzyl alcohol may be prepared by simply combining the various ingredients. However, to obtain maximum concentration and convenience and minimize the necessity for rechecking the component quantity accuracy, the solution is formed by first combining water with the desired amount of sulfite, and then dissolving the p-phenylenediamine developing agent (usually as the acid salt) in the sulfite solution. The benzyl alcohol is then advantageously added to form a cloudy slurry after which at least sufficient glycol is added to convert the slurry into a clear solution, i.e., apparently a one phase composition.

The developer replenisher kit effectively may be a single package; for example, an outside container in which the concentrated solutions are compartmentalized. The compartments can be an integral part of the exterior packaging material but advantageously are, for example, glass or plastic bottles enclosed in the outside container, e.g., a cardboard box. The choices of sizes and shapes of the bottles, etc., which form the compartments, can vary with the selected ingredients, concentrations desired, etc. Usually it is desirable to choose the bottle size, shape, etc., which will result in a total package of minimum size and weight to minimize shipping and storage costs. As a result, it may in some instances be desirable to place a single component type in a plurality of compartments, e.g., to conserve space.

The developer replenisher kit ingredients should be separated during storage, shipping, etc., to the extent that the developing agent solution is in a separate compartment from the buffered solution and desirably so that the benzyl alcohol and some sulfite are in the developing agent solution as mentioned above. Other components which may form part of the developer replenisher kit, for example, additional sulfite; accelerators; and complexing agents, e.g., polyphosphates, sodium hexametaphosphates, nitrolo acetic acid, methylamino diacetic acid, dimethylethylene diamino diacetic acid, ethylenediamine tetraacetic acid, and diaminopropanol tetraacetic acid, are advantageously contained in the compartment containing the buffered solution, although placing the addenda in other or separate compartments may be desirable depending upon the particular ingredient chosen, etc.

The developer replenisher kit is then converted into a developer replenisher by combining the developing agent solution and the buffered solution with water, desirably by first mixing a concentrated developing agent solution which contains benzyl alcohol with a desired amount of water and subsequently adding the buffered solution and adjusting the final concentration by adding water.

The ready-to-use developer replenisher according to the present invention has a pH of about 10.5 to 11, desirably 10.6 to about 10.9, when measured at 75° F., and contains alkali metal cations, p-phenylenediamine developing agent, benzyl alcohol, and sulfite. The alkali metal ions utilized are generally potassium and sodium. Although it is often desirable to include some sodium ions in the replenisher, the alkali metal ions must be selected so that the potassium/sodium weight ratio is in excess of about 2.5/1, advantageously in excess of about 4/1, and especially above about 5.4/1. It is frequently advantageous to utilize a potassium/sodium weight ratio between about 4/1 and about 10/1 with ratios between 5.4/1 and 10/1 being especially efficacious.

The developing agents and concentrations used in the replenisher kit desirably result in a replenisher concentration of about 3 g. to about 5 g. per liter based on the weight of available diamine. (Thus, although about 6 g. of 2-amino-5-diethylaminotoluene monohydrochloride may be used, there would be less than 5 g. of available diamine.) In an especially desirable embodiment of the present invention about 3.8 to 4.5 g. of 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine are utilized per liter of replenisher solution.

For highly effective replenishers according to the present invention, it is important that the benzyl alcohol in the ready-to-use replenisher be used at a concentration of no more than about 8 g. per liter, normally between about 4 to about 8 g. per liter, desirably about 6 to about 7.5 g. per liter. Similarly, if any bromide is utilized in the developer replenisher, it is important that no more than about 0.80 g. bromide be used per liter of replenisher. Thus, if the bromide is supplied to the solution as sodium bromide, no more than about 1.0 g. should be utilized per liter of replenisher.

The replenisher also contains sulfite desirably in concentration of about 1.25 g. to about 1.55 g. per liter of solution or in a total p-phenylenediamine/sulfite mole ratio of about 1/1.6. As with the bromide, the sulfite is desirably supplied to the solution as an alkali metal sulfite or bisulfite, desirably as sodium sulfite.

The replenisher also advantageously includes a buffer system as mentioned above. An especially effective buffer system is the boric acid-borate system, desirably supplied to the kit solution by incorporating therein the alkali metal hydroxides selected from the group consisting of potassium and sodium hydroxides so that the potassium/sodium ratio for the replenisher is at least 2.5/1, and 18 to 30 g. especially 25 to 30 g. boric acid per liter of replenisher solution to maintain the pH of the solution at the desired level. The resultant replenisher solution contains from about 19 to about 28.5 g. per liter borate in various states of dissociation, i.e., boric acid and/or the dissolved borate containing residues from the boric acid.

The other addenda indicated as being advantageously included in the developer replenisher kit can also be included in the replenishers according to the present invention. For example, in a highly effective embodiment of the present invention the dissolved residues from diaminopropanol tetraacetic acid are also included in the replenisher especially at a concentration of about 1 to about 1.5 g. per liter of solution.

According to another highly advantageous embodiment of the present invention the developer replenishers mentioned are used in a method for processing imagewise exposed silver halide photographic film materials of the positive-negative type having adhered to and superposed on a transparent support at least a red sensitized emulsion layer containing nondiffusing cyan dye-forming coupler, green sensitized emulsion layer containing nondiffusion magenta dye-forming coupler, and a blue sensitized emulsion layer containing nondiffusing yellow dye-forming coupler. Such elements are, for example, described in Hansen, U.S. Pat. No. 2,449,966. Suitable nondiffusing couplers are described in U.S. Pat. Nos. 2,956,876, 2,407,293, and 2,640,776.

The method for processing exposed films of the type mentioned and for utilizing replenishers, especially developer replenishers, whereby the concentration of desirable components in the various processing solutions, especially in the developer, are controlled between predetermined concentration limits involves:

a. applying to the exposed film an aqueous developer having a pH of from about 10.5-11, desirably between about 10.6 and 10.75 when measured at 75° F., and containing the p-phenylenediamine color-developing agent, benzyl alcohol, and sulfite to develop the exposed silver halide and to form dye images in the exposed area;

b. adding developer replenisher as described above to said developer whereby the concentration of desirable components of said developer is maintained between predetermined concentration levels;

c. contacting the developed film with an acidic composition, e.g., containing acetic acid, to stop development;

d. treating the film with a gelatin-hardening composition, e.g., containing formaldehyde and methanol;

e. treating the film with a bleach composition, e.g., containing ferricyanide and bromide, to oxidize the Ag^0 to Ag^+ ; and

f. treating the film with a fixing composition, e.g., hypo, to remove silver salts from the developed film.

Desirably, washing steps follow each of the hardening, bleaching, and fixing steps and, prior to drying the processed film, it is usually recommended that the film is treated in a final rinse composition to prevent the formation of "water spots" on the film. The times and temperatures for each of the processing steps may be varied. However, it is usually desirable to maintain the temperature of the developer relatively constant. Dwell times and bath temperatures which are generally used for continuous machine processing in standard solutions are as follows: Develop 12 minutes at 75° F. and stop 4 minutes; harden 6 minutes; wash 4 minutes; bleach 6 minutes; wash 4 minutes; fix 8 minutes; wash 8 minutes; and final rinse 1 minute, all at 73°-77° F. and drying at elevated temperature, e.g., 90°-110° F.

The developer advantageously contains substantially the same ingredients as the developer replenisher described above. The same developing agent, for example, is desirably used in both the developer and replenisher. Similarly, benzyl alcohol, sulfite, and buffer are desirably utilized in the developer. However, according to the present invention the concentrations of various ingredients in the developer vary considerably from those of the replenisher. Although the potassium/sodium ratio in the developer, for example, is desirably similar to that of the developer replenisher, the ratio in the developer is not very important. The potassium/sodium ratio is extremely important in the replenishers and replenisher kits of the present invention.

To obtain optimum effectiveness it is very important that the concentration of benzyl alcohol in the replenisher be at least 0.2 g. per liter greater than the concentration of benzyl alcohol in the developer. In the developer, a benzyl alcohol concentration of 3.8 to about 7.8 g. per liter is suitable. A concentration of benzyl alcohol in the developer of about 5.6 to about 6.0 g. per liter is especially effective while a concentration of about 6.2 to about 7.2 per liter benzyl alcohol would be suitable for a corresponding replenisher solution.

It is also important to optimum effectiveness that the developing agent be present in a higher concentration in the replenisher than in the developer by at least 0.4 g. per liter based on the weight of available diamine especially when the replenisher contains about 3 g. to about 5 g. developing agent selected from the group consisting of 2-amino-5-diethylaminotoluene; 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine; 4-amino-3-methyl-N-ethyl-N-[β -hydroxyethyl]-aniline; and 4-amino-3-[β -methylsulfonamidoethyl]-N,N-diethylaniline. About 3.2 to about 3.8 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine per liter is especially effective for the developer, while the corresponding concentration for a replenisher used with such a developer is about 3.9 to about 4.5 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine per liter.

It is extremely important to maximum effectiveness of the system that the bromide concentration of the replenisher be substantially lower than the concentration of bromide in the developer. For example, the developer bromide concentration is nearly always at least 1 g. per liter (corresponding to at least about 1.3 g. sodium bromide per liter) whereas for optimum effectiveness the replenisher bromide concentration, if any is present, should be no greater than about 0.80 g. per liter (corresponding to about 1 g. sodium bromide). In one advantageous embodiment of the present invention the bromide concentration is between about 0.60 and 0.80 g. per liter.

Sulfite concentrations for the developer can vary somewhat but for maximum effectiveness should be between about 1.2 g. (e.g., supplied as about 1.9 g. sodium sulfite) to about 1.5 g. per liter. The corresponding replenisher then would desirably

contain slightly more than the developer, about 1.25 to about 1.55 g. per liter. As with the replenisher, the sulfite is normally supplied to the solution as an alkali metal sulfite or bisulfite.

The developer also desirably contains a buffer system which is provided in a manner analogous to that for the replenisher except that the resultant pH is desirably slightly lower for the developer. Highly suitable buffer systems result from the dissolution of boric acid and alkali metal hydroxides so that the total borate concentration, including boric acid and/or dissociated residues thereof, is about 26.5 to about 27.0 g. per liter. A replenisher for such a developer desirably would have a total borate concentration of about 27.2 to about 27.8 g. per liter.

The developer also desirably contains sequestering agent, desirably the dissolved residues from about 0.8 to about 1.3 g. per liter of diaminopropanol tetraacetic acid. With such a developer, a replenisher having the same sequestering agent in a concentration of about 1.0 to about 1.5 g. per liter would advantageously be utilized.

As mentioned above the rate of replenishment can be decreased substantially by the use of the developer replenishers of the present invention. Accordingly, rates of less than 300 ml. per square foot of processed film are easily accomplished. Since decreasing the replenishment rate can result in processing which compares favorably, with substantial reduction in cost of chemicals and pollution prevention, in a highly advantageous embodiment of the present invention the developer replenishment rate is less than about 163 ml. replenisher per square foot of processed film (corresponding to about 243 ml. replenisher per square foot of picture area processed). The replenishment rate can, of course, be decreased even further in which case the differences in concentration between developer ingredients and replenisher ingredients is even greater.

The following examples are intended to illustrate our invention and/or advantages thereof:

EXAMPLE 1

A three-component developer replenisher kit is prepared containing Parts A, B, and C as follows:

Part A

About 6.3 ml. benzyl alcohol.

Part B

A concentrated buffer solution which is prepared by: dissolving 3.4 g. NaOH and 22.8 g. KOH in about 63 g. water; then, slowly adding about 29 g. boric acid; and adjusting the pH of the resultant solution to about 10.75 at 80° F. by the addition of small amounts of potassium hydroxide (45 percent solution).

Part C

A concentrated acidic solution containing developing agent which is prepared by dissolving about 2 g. sodium sulfite in about 11 g. water, and adding about 6.4 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate with stirring.

EXAMPLE 2

A photographic developer replenisher is prepared by: adding the 6.2 g. benzyl alcohol (Part A, Example 1) with vigorous stirring to about 800 ml. water; adding to the resultant solution with stirring the solution from Part B (Example 1); after Part B is fully dissolved, adding Part C (Example 1) with stirring and adding water to adjust the volume to one liter at 80° F.

EXAMPLE 3

The solution from Example 2 is then utilized as a developer replenisher in processing an imagewise exposed commercially available silver halide sensitized color negative film material having respectively superposed on and adhered to a transparent support a red sensitized gelatinous emulsion layer containing nondiffusing cyan dye-forming coupler, a green sensitized gelatinous emulsion layer containing nondiffusing magenta dye-forming coupler, a yellow filter layer, and a blue sensitized emulsion layer containing nondiffusing yellow dye-forming coupler. The developer which is replenished contains

the dissolved residues from approximately 5.8 g. benzyl alcohol, 28.1 g. boric acid, 5.4 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate, 1.9 g. sodium sulfite, 3.2 g. sodium hydroxide, 20.5 g. of potassium hydroxide, and about 1.5 g. sodium bromide per liter of solution.

The process involves developing the film as described above for a period of about 14 minutes at about 75 $\pm$ 0.5° F. (about 24° C.), and the following steps in the order indicated at 75 $\pm$ 2° F.: stopping the development by treating the developed film in an acetic acid stop bath for about 4 minutes; treating the film in a gelatin hardener solution containing formaldehyde and methanol for about 4 minutes; washing the film in running water for about 4 minutes; treating the film in a bleach bath containing ferricyanide and bromide for about 6 minutes; washing the film in running water for about 4 minutes; treating the film in a hypo fix bath for about 8 minutes; washing the fixed film for about 8 minutes; and then drying the film at about 90° F.

The developer replenisher functions effectively when added to the developer at a rate of about 243 ml. per square foot of picture area produced (about 163 ml. per square foot of film processed).

EXAMPLE 4

The procedure according the Example 3 is followed except that the developer replenisher contains about 0.9 g. sodium bromide. High-quality development is obtained.

EXAMPLE 5

The procedure according to Example 3 is followed except that the developer contains the dissolved residues from about 1.16 g. diaminopropanol tetraacetic acid and the replenisher contains the dissolved residues from about 1.3 g. of the same compound plus about 0.9 g. sodium bromide. Consistent, high-quality development is obtained at a replenishment rate of about 242 ml. per square foot of picture area processed.

EXAMPLE 6

A two-component developer replenisher is prepared containing Parts A and B as follows:

Part A

An acidic aqueous developing agent which is prepared by: adding about 0.3 g. sodium sulfite (about 0.19 g. sulfite) to about 8 g. distilled water and stirring until the sodium sulfite is completely dissolved; then dissolving about 6.4 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate in the sulfite solution; adding to the resultant acidic solution about 6.6 g. benzyl alcohol with vigorous stirring to form cloudy slurry; and then gradually adding ethylene glycol to the slurry until a clear solution forms, about 7.8 g. This solution exhibits excellent storage stability.

Part B

A buffered aqueous alkali solution which is prepared by: dissolving about 3.4 g. of sodium hydroxide and about 23.3 g. of potassium hydroxide in about 42 g. water; gradually adding to this solution about 29 g. boric acid, about 1.7 g. sodium sulfite, about 1.3 g. diaminopropanol tetraacetic acid, and about 0.8 g. sodium bromide and adjusting the pH to about 10.75 $\pm$ 0.05 at 80° F. by the addition of small amounts of potassium hydroxide. The solution is stable for long periods of time at varying temperatures.

EXAMPLE 7

A developer replenisher is prepared by slowly adding the solution from Example 6A to about 800 ml. of water and stirring to assure complete dissolution; slowly adding the solution from Example 6B with stirring; and adding sufficient water to bring the total volume to one liter.

EXAMPLE 8

The procedure according to Example 3 is followed except that the solution from Example 7 is utilized in place of the replenisher from Example 2. Satisfactory results are achieved with a developer replenisher rate of about 243 ml. per square foot of picture area processed.

EXAMPLE 9

The procedure according to Example 8 is followed except that the developer of Example 3 also contains the dissolved residues from about 1.2 g. of diaminopropanol tetraacetic acid. Excellent results are achieved with a developer replenisher rate of about 243 ml. per square foot of picture area processed (about 160 ml. per square foot of film processed).

EXAMPLE 10

A developer replenisher is prepared containing the dissolved residues from about 7 g. benzyl alcohol, about 29 g. boric acid, about 3.4 g. sodium hydroxide, about 23.5 g. potassium hydroxide, about 2.1 g. sodium sulfite, about 1.3 g. diaminopropanol tetraacetic acid, about 0.4 g. sodium bromide, and about 7.9 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate per liter of aqueous solution. The resultant solution has a pH of about 10.78 at 80° F. and shows no signs of crystallization or precipitation at temperatures ranging as low as 50° F.

EXAMPLE 11

The procedure according to Example 3 is followed except that the solution from Example 10 is utilized in place of the solution from Example 2 and the developer which is replenished contains about 1.2 g. diaminopropanol tetraacetic acid and about 5 mg. potassium iodide. Satisfactory results are achieved at a replenishment rate of about 121 ml. per square foot of picture area processed (about 80 ml. per square foot of preprocessed film).

EXAMPLE 12

The procedure according to Example 11 is followed except that a developer replenisher containing about 7.7 g. benzyl alcohol, about 8 g. ethylene glycol, about 1.3 g. diaminopropanol tetraacetic acid, about 29 g. boric acid, about 3.4 g. sodium hydroxide, about 23.5 g. potassium hydroxide, about 2.2 g. sodium sulfite, no bromide, and about 9.4 g. 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate per liter of solution is used in place of the replenisher from Example 10. Satisfactory results are achieved at a developer replenishment rate of about 77 ml. per square foot of picture area processed (about 52 ml. per square foot of processed film).

EXAMPLE 13

The procedure according to Example 11 is followed except that a replenisher solution is prepared from a two-component replenisher kit by procedures outlined in Example 7. Part A of the replenisher kit is identical to Example 6, Part A. Part B of the replenisher contains the same ingredients but about 11 g. more water than Example 6, Part B. The replenisher functions extremely effectively at a replenishment rate of about 243 ml. per square foot of picture area processed.

EXAMPLE 14 (Comparative Example)

A composition is prepared by combining about 0.25 moles (10 g.) sodium hydroxide, about 0.25 moles (14 g.) potassium hydroxide, about 6.4 g. 4-amino-N-ethyl-N-[β -methanesulfonamido-ethyl]-m-toluidine sesquisulfate monohydrate, about 2 g. sodium sulfite, about 6.6 g. benzyl alcohol, about 7.8 g. ethylene glycol, about 29 g. boric acid, about 1.3 g. diaminopropanol tetraacetic acid, and 0.8 g. sodium bromide and sufficient water to make one liter total volume. The composition functions poorly and is impractical as a developer replenisher for processing color film products according to the procedure of Example 3.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A unitary concentrated liquid developer replenisher kit comprising an outside container having a plurality of separate compartments therein containing at least two solutions adapted to be separately combined to form developer replenisher, a first compartment containing water, p-phenylenediamine developing agent and benzyl alcohol in a phenylenediamine/benzyl alcohol weight ratio of between about

1/1.5 and about 1/2, and having a pH less than about 6, a second compartment containing a buffered aqueous solution having a pH in excess of about 10.5 when measured at 75° F. and sulfite, said buffered aqueous solution comprising:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer, and
- d. alkali metal ions selected from the group consisting of sodium and potassium ions in a potassium/sodium weight ratio of at least 2.5/1.

2. The invention according to claim 1 and wherein said first compartment containing said developing agent solution also contains at least part of the total sulfite of the replenisher.

3. The invention according to claim 1 and wherein said first compartment containing said developing agent solution also contains sulfite in a diamine/sulfite mole ratio of about 1/0.08 to about 1/1.5.

4. The invention according to claim 1 and wherein said first compartment containing said developing agent solution also contains sulfite in a phenylenediamine/sulfite mole ratio between about 1/0.15 to about 1/0.5 and said kit also contains additional sulfite so that the total diamine/sulfite mole ratio is at least about 1/1.6.

5. The invention according to claim 1 and wherein said developing agent solution in said first compartment also contains said benzyl alcohol and simple liquid glycol with a carbon/oxygen ratio of about 0.75 to about 1.5/1 and molecular weight of from about 62 to about 150 and wherein the water/benzyl alcohol weight ratio is from about 1/6 to about 5/1.

6. The invention according to claim 1 and wherein said developing agent solution in said first compartment also contains said benzyl alcohol and at least one simple liquid glycol selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, and triethylene glycol, and wherein the water/benzyl alcohol weight ratio is from about 1/6 to about 5/1.

7. The invention according to claim 1 and wherein said developing agent is selected from the group consisting of 2-amino-5-diethylaminotoluene monohydrochloride; 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate; 4-amino-3-methyl-N-ethyl-N-[β -hydroxyethyl]-aniline sulfate; and 4-amino-3-[β -methylsulfonamidoethyl]-N,N-diethyl-aniline.

8. The invention according to claim 1 and wherein the developing agent is selected from the group consisting of 2-amino-5-diethylaminotoluene monohydrochloride; 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate/monohydrate; 4-amino-3-methyl-N-ethyl-N-[β -hydroxyethyl]-aniline sulfate; and 4-amino-3-[β -methylsulfonamidoethyl]-N,N-diethyl-aniline; and said developing agent solution in said first compartment contains:

- a'. benzyl alcohol in sufficient concentration so that the water/benzyl alcohol weight ratio is from about 1/6 to about 5/1;
- b'. at least one simple liquid glycol selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, and triethylene glycol; and
- c'. sulfite in an amount so that the phenylenediamine/sulfite mole ratio is between about 1/0.15 to about 1/0.5.

9. The invention according to claim 1 and wherein the developing agent is 4-amino-N-ethyl-N-[β -methanesulfonamido-ethyl]-m-toluidine and said developing agent solution in said first compartment contains:

- a'. benzyl alcohol in sufficient concentration so that the benzyl alcohol/water weight ratio is from about 1/6 to about 5/1;
- b'. ethylene glycol in sufficient concentration so that the benzyl alcohol/ethylene glycol weight ratio is between about 0.7/1 to about 1/1; and
- c'. sulfite in an amount so that the phenylenediamine/sulfite mole ratio is between about 1/0.15 to about 1/0.5.

10. The invention according to claim 1 and wherein said buffered solution in said second compartment has a pH in excess of about 10.75 when measured at 75° F. and comprises:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer, and
- d. alkali metal ions selected from the group consisting of sodium and potassium ions so that the potassium/sodium weight ratio is at least 5.4/1.0.

11. The invention according to claim 1 and wherein said buffered solution in said second compartment has a pH in excess of about 10.75 when measured at 75° F. and comprises:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer,
- d. alkali metal ions selected from the group consisting of sodium and potassium ions so that the potassium/sodium weight ratio is in excess of about 5.4/1.0.
- e. sulfite, and
- f. diaminopropanol tetraacetic acid.

12. The invention according to claim 1 and wherein said developing agent solution in said first compartment contains at least some sulfite and said buffered solution has a pH in excess of about 10.75 when measured at 75° F. and comprises:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer, and
- d. alkali metal ions selected from the group consisting of sodium and potassium ions so that the potassium/sodium weight ratio is in excess of about 5.4/1.0.

13. The invention according to claim 1 and wherein said developing agent solution in said first compartment contains at least some sulfite and benzyl alcohol, and said buffered solution has a pH in excess of about 10.75 when measured at 75° F. and comprises:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer,
- d. alkali metal ions selected from the group consisting of sodium and potassium ions so that the potassium/sodium weight ratio is at least 5.4/1.0, and
- e. sulfite.

14. A unitary concentrated liquid developer replenisher kit comprising an outside container having a plurality of separate compartments therein containing at least two separate solutions adapted to be combined to form developer replenisher, a first compartment containing water, 4-amino-N-ethyl-N-[(β -methanesulfonamidoethyl)-m-toluidine]sesquisulfate monohydrate, developing agent, and benzyl alcohol in a phenylenediamine/benzyl alcohol weight ratio of between about 1/1.5 and about 1/2, a second compartment containing a buffered aqueous solution having a pH in excess of about 10.75 when measured at 75° F. and sulfite, said first compartment containing said developing agent in aqueous solution having a pH less than about 4 and also containing:

a'. benzyl alcohol in sufficient concentration so that the benzyl alcohol/water weight ratio is between about 1/6 to about 5/1;

b'. ethylene glycol in sufficient concentration so that the benzyl alcohol/ethylene glycol weight ratio is between about 0.7/1 to about 1/1; and

c'. sulfite in an amount so that the phenylenediamine/sulfite mole ratio is between about 1/0.15 to about 1/0.5;

said buffered aqueous solution in said second compartment comprising:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer, and
- d. alkali metal ions selected from the group consisting of sodium and potassium ions in a potassium/sodium weight ratio of at least 5.4/1.0.

15. A concentrated buffered aqueous solution for preparing a developer replenisher to be used in solutions for processing silver halide color photographic film materials, said solution having a pH at least about 10.75 when measured at 75° F. and comprising:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer, and
- d. alkali metal cations selected from the group consisting of sodium and potassium ions so that the potassium/sodium weight ratio is between about 5.4/1.0 and 10/1.

16. A concentrated buffered aqueous solution for preparing a developer replenisher to be used in processing silver halide color photographic film materials, said solution having a pH at least about 10.75 when measured at 75° F. and comprising:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer,
- d. alkali metal ions selected from the group consisting of sodium and potassium ions so that the potassium/sodium weight ratio is in excess of about 5.4/1.0,
- e. sulfite, and
- f. diaminopropanol tetraacetic acid.

17. A unitary concentrated liquid developer replenisher kit comprising an outside container having a plurality of separate compartments therein containing at least three separate solutions adapted to be combined to form developer replenisher; a first compartment containing water, p-phenylenediamine developing agent, and sulfite, and having a pH less than about 6; a second compartment containing a buffered aqueous solution having a pH in excess of about 10.5 when measured at 75° F., said buffered aqueous solution comprising:

- a. water,
- b. hydroxide,
- c. boric acid-borate buffer, and
- d. alkali metal ions selected from the group consisting of sodium and potassium ions in a potassium/sodium weight ratio of at least 2.5/1;

a third compartment containing benzyl alcohol.

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