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(54) **Control of replanishment during photographic development.**

(57) An improved developer and associated replenisher is provided which can be analyzed in a single non-invasive measurement. One advantage of the improved developer is the ability to indirectly measure the activity of the developer and replenisher and to determine if the solutions are properly prepared. These and other advantages are provided in a system for converting an image-wise exposed silver halide photographic film to a viewable image comprising: a development means wherein said image-wise exposed silver halide is reduced to elemental silver with subsequent depletion of said development means; a fixing means wherein unexposed silver halide is removed from said photographic film; a replenishing means for said development means wherein said replenishing means comprises at least two titratably distinct components.

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Related Application

The present patent application is a continuation -in-part of Serial No. 08/021,542 filed February 24, 1993.

Field of Invention:

This invention is related to chemical processing of photographic film. More specifically this invention is related to improved processing mixtures, and a diagnostic test therefore, which allows for accurate determination of replenishment and which provides a method for diagnosing improper replenishment.

Background of the Invention:

In the photographic process, an image-wise exposed film must be processed to convert the latent image into a viewable negative of the image. The processing operation requires a development step, wherein the exposed silver halide crystals are reduced to elemental silver, and a fix or bleach step wherein the unexposed silver halide crystals are removed from the film. It is also advantageous to wash the film prior to drying and viewing.

Development is accomplished by the reduction of exposed silver halide to silver metal. When hydroquinone, or an equivalent, is used as the reducing agent the reaction which occurs is represented by Equation 1.

$$2AgBr + HO\text{-}C_6H_4\text{-}OH + Na_2SO_3 \text{ ----> } 2Ag + HO\text{-}C_6H_4\text{-}OSO_3Na + HBr + NaBr \quad 1$$

The active ingredients, hydroquinone and sodium sulfite, are depleted by the silver reduction reaction. Because of the chemical depletions the effectiveness of the processing solution decreases with use. Also occuring is an increase in the bromide level and a decrease in the pH.

Ascorbic acid based developers are also used for reduction of exposed silver halide during development. Analogous depletion of active ingredients is observed with use.

Methods of replenishing the active ingredients are well known in the art and most modern processors are equipped with tanks of replenishment solution and an automatic replenishment mode based on various criteria as known in the art.

Hydroquinone developers are also susceptible to air oxidation. The chemical reaction associated with air oxidation is provided in Equation 2.

$$HO\text{-}C_6H_4\text{-}OH + 2Na_2SO_3 + O_2 \text{ ----> } HO\text{-}C_6H_4\text{-}O\text{-}SO_3Na + Na_2SO_4 + NaOH \quad 2$$

Air oxidation of a hydroquinone developer does not effect the bromide level but the pH increases due to liberation of hydroxide ion as the sodium salt.

Evaporation of water is also known to occur. Loss of solvent can alter the concentration of ingredients and the reactivity. Yet another detrimental phenomenon is the physical removal of developer solution by the film.

Under standard operating conditions decreases in developer activity are expected due to the development reaction, oxidation reaction, solvent evaporation and physical removal. All of these detrimental phenomenon occur, albeit at different rates. When a large amount of film is processed the development reaction is dominant and the problems which must be addressed are decreasing active ingredients, increasing bromide and decreasing pH. When a small amount of film is processed, or for periods of inactivity, the oxidation reaction and solvent evaporation are the dominant concerns.

Monitoring the bromide in the developer is advantageous for suggesting hydroquinone depletion as detailed in U.S. Patents 3,529,529 and 3,970,457 yet oxidation is not addressed with this method. In practice these automatic systems are known to fail which is blamed, in part, on the lack of an effective method for standardizing electrodes that are continuously monitored. Monitoring pH is not considered to be effective since competing development and oxidation reactions could balance with no substantial change in pH. Also, most modern developer solutions contain pH buffers which may mask changes. Monitoring both bromide and pH places a burden on the user and is typically neither feasible nor diagnostic.

Specific gravity is another analytical measurement which is often used during the initial makeup of the solutions. The inaccuracy and non-specificity of this method is well known in the art and diagnostic information is rarely obtained.

There has been a long felt need in the art to provide a diagnostic measurement whereby the chemicals and their replenishment can be optimized. Prefered is a single measurement which can provide the diagnostic information.

The prior art also suffers from the lack of diagnostic information provided by the above mentioned measurements. For example, a high bromide ion concentration in the developer would suggest more replenishment chemicals need to be added as described for hydroquinone systems in U.S. Pat. Nos. 3,529,529 and 3,970,457. If oxidation, or evaporation, has occurred in the replenishment solution, or if the replenisher is incorrectly prepared the bromide ion concentration alone may provide an inaccurate assessment of developer strength.

The ineffective quantitative means of determining chemical activity has led to the design of indirect methods to determine chemical activity of the developer. The standard method in the art has been to process film and monitor the photographic response as detailed in U.S. Patents 5,063,583; 4,508,686 and 4,365,895. A similar approach has been adopted by the American College of Radiology and is manifested in their recommendations for accreditation under the processing section of their Mammography Accreditation Program. These methods are all predicated on the assumptions that:

a) the film samples are identical and stable with time;
b) exposure and density readings are invariant;
c) the developer used at the start of the test is correct; and
d) changes in chemistry will have a predictable, or noticeable, effect on the film.

In actual practice all of these assumptions may, and do, fail.

The choice of film is also critical as realized in the art. Films which utilize tabular grains are known to exhibit sensitometric properties which vary with bromide level in the developer. Films with more conventional grains are known to be less sensitive to bromide level but sensitometric differences correlate more strongly to processing temperature and other changes in developer. This places a burden on the health care professional since different films could exhibit different properties in the same processor. To adequately use the indirect method a control film would have to be established for all types of films employed.

A particular deficiency of prior art tests is the lack of information on the activity of the replenisher chemicals. The bromide titration, or indirect film methods, only test the activity of the development solutions in the processor at the time of the test. A single test provides no information about the replenishment conditions. To obtain information on replenishment a subsequent test must be done and the data correlated to analyze for trends and/or the replenisher must be checked independently. Furthermore, a film method is intrusive since the test film itself initiates the development reaction and some replenishment occurs to compensate therefor. Immediately after the control film is processed the conditions in the development solution will be different.

An improperly prepared replenisher may take a considerable amount of time (several hours to several days) to displace a sufficient amount of developer to be observed by a film test. Nominal replenishment rates, as expected for moderate film use, are sufficient to replace approximately half of the chemicals in the developer tank with replenisher chemicals in approximately 8-10 hours. The full effect of incorrect replenishment, either rate or composition, may not be noticed until the developer has been replaced by at least one equal volume of replenisher. This creates a lag time between replenisher preparation, or a change in the rate of addition, and the actual sensitometric effect. The lag time can span several days in some instances. Once an actual problem is detected the entire replenisher and developer must be replaced to correct the situation.

It is not uncommon that specific chemical changes combine with film choice to generate a rapidly deteriorating problem. If the film is particularly sensitive to specific changes in chemistry a deterioration in performance may occur from the time the new replenisher is prepared. The deterioration in performance may not be realized for quite some time, particularly when large batches of film are processed. This problem is especially troublesome in cases such as mammographic exams where mobile units acquire the exposed films and return to a central processing center wherein all of the films are processed prior to being observed.

The tardiness of the test is especially critical if recommended procedures are followed in entirety. Corrective action is suggested only after three consecutive test are observed to generate a trend in any direction away from the norm. Typical test frequency is daily for most situations but the actual time can vary substantially. Therefore, many inferior films could be produced prior to running a control which may lead to an incorrect diagnosis or a need to repeat the exposure to the patient.

Faced with this chemical dilemma and the accepted American College of Radiography guidelines, the practitioner is forced into one of the following two situations. The first is a correct film measurement

indicating the current chemistry may be correct but replenishment conditions are unknown. In this situation the practitioner typically continues operating with no knowledge of potential problems. The second situation occurs when the film measurements are not correct. Based on the standard guidelines an initial check of obvious problems such as temperature, and the like, is suggested. If the problem is not resolved the processing and replenishment chemicals are usually discarded and replaced at a substantial financial and time burden to the medical professional.

There is a long felt need in the art to provide means for improved quality control in film processing. There is a further need to provide a developer and replenisher therefore which purposefully contain ingredients that can be accurately and rapidly analyzed to determine the chemical activity of the solution. Described herein is a chemical development system wherein specific ingredients can be added and a potentiometric titration performed to insure proper levels of developer, replenisher, color chromophores and the like.

Summary of the Invention:

It is an object of the present invention to provide an improved development method for silver halide films which can be easily monitored and can provide diagnostic information on the activity of the developer.

It is a further object to provide a developer solution, and replenisher therefore, which can provide diagnostic information on the activity of the developer and the replenisher from a single measurement.

It is a further object that the developer/replenisher solution can be monitored independent of the film thereby decreasing the effects of film, exposure and density measurements on the development conditions.

Yet another object is a diagnostic test method which can determine if the replenisher or developer is properly mixed and which can provide diagnostic information for correcting an improperly prepared solution.

A particular feature of the present invention is the ability to determine quantitative information rapidly and with minimal cost.

These and other advantages are provided in a method for converting an image-wise exposed silver halide photographic film to a viewable image comprising:

a development solution wherein said image-wise exposed silver halide is reduced to elemental silver with subsequent depletion of said development means;

a fixing solution wherein unexposed silver halide is removed from said photographic film;

a replenishing solution for said development means wherein said replenishing means comprises at least two titratably distinct components.

In a particularly preferred embodiment the titratably distinct components are independently defined to have a Ksp between 10^{-6} and 10^{-20}. It is also preferred that the Ksp of the titratably distinct ions differ by at least 10^{-2}. Particularly preferred as titratably distinct components are bromide and chloride.

Detailed Description of the Invention:

Chemical developers are specifically formulated to efficiently reduce image-wise exposed silver halide to elemental silver. The developer typically comprises a reducing agent, optional antifoggants, optional pH buffers, optional hardeners and optional stabilizers.

Each of at least two components of an inventive replenisher further comprise compounds which are analytically distinct one from the other when the components are mixed. The term analytically distinct preferably refers to compounds which are titratably distinct.

The term "titratably distinct" refers specifically to compounds which can be quantitatively distinguished in a single potentiometric titration with silver nitrate. The titration should be done at a pH of which is sufficient to insure that silver oxide formation does not occur. This pH is preferably no higher than approximately 8.0.

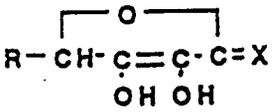
Preferred titratably distinct components are anions which form silver salts and which do not adversely interfere with the photographic development or fix process. It is particularly important that the silver salts formed are sufficient solubility that premature precipitation does not alter the results. Preferred is a salt with a solubility product (Ksp) of 10^{-6} to 10^{-20}. Specifically preferred are combinations of anions which form silver salts with sufficient differences in solubility product to be quantitatively seperatable in a potentiometric titration. The solubility products of the silver salts, measured as Ksp, are preferably different by at lease 10^{-2} using current titration abilities under ambient conditions. In a particularly preferred embodiment the bromide is one titrant and the other titrants are chosen accordingly. Chloride has been found to be particularly preferred as a second titrant due to the low cost, photographic inert properties, solubility and the like.

Preferred reducing agents are 4-hydroxymethyl-1-phenyl-3-pyrazolidone, 1-phenyl-3-pyrazolidone, or a derivative thereof such as 4-methyl or 4,4-dimethyl-1-phenyl-3-pyrazolidone; hydroquinone or a derivative thereof such as chlorohydroquinone or bromohydroquinone; ascorbic acid; sugar-type derivatives of ascorbic acid; stereoisomers and diastereoisomers of ascorbic acid and their sugar-type derivatives; or salts of ascorbic acid or their derivatives.

Preferred reducing agents are hydroquinone, 4-hydroxymethyl-1-phenyl-3-pyrozolindone, 1-phenyl-3-pyrazolidone, ascorbic acid, d-erythroascorbic acid (i.e. erythorbic or isoascorbic acid), d-glucosascorbic acid, 6-deoxy-l-ascorbic acid, d-glucoascorbic acid, d-galactoascorbic acid, l-glucoascorbic acid and l-alloascorbic acid.

Exemplary salts of ascorbic acid, which are useful for the teachings herein, include alkali metal salts, such as the sodium and potassium salts thereof (e.g. sodium or potassium ascorbate and sodium or potassium erythorbate).

The unsubstituted compounds of this class of compounds may be represented by the formula:



wherein X is an oxygen atom or imino group, R is any group which does not render the ascorbic acid water-insoluble and is a non-interfering group. Non-interfering is defined as not causing steric hindrance, is not chemically reactive with other portions of the molecule, is not a coordination group for the molecule, and is not more electropositive than a saturated hydrocarbon residue. R is preferably an aryl group of 6-10 carbons or a group of the formula $R^1(CH_2)(CH_2)_{n-1}$ wherein n is a positive integer from 1 to 4 and R1 is either a hydrogen atom or hydroxyl group when n is 2 to 4 and is hydroxyl when n is 1. Of these materials, ascorbic and erythorbic (iso-ascorbic) acid are preferred.

The developer may contain a multitude of conventional ingredients which serve functions well known in the art. Included are additional development agents, antifoggant agents, pH buffers, sequestering agents, swelling control agents, development accelerators, and the like. Materials which may be included in the processing solution, such as swelling control agents (i.e. gelatin hardening agents), aerial oxidation restrainers, sequestering agents, surfactants, dyes, etc., well known in the art are exemplified in U.S. Pat. No. 3,545,971 and Photographic Processing Chemistry, L.F.A. Mason, 1966, page 149 et seq.

Other reducing agents which may be used are organic agents such as catechols, aminophenols, phenylenediamines, tetrahydraquinolines, bis(pyridone)amines, cylcoalkenones, pyrimidines, reductones and coumarins. Inorganic development agents may also be mentioned to include metals having at least two distinct valence states and are capable of reducing ionic silver to metallic silver. Such metals include iron, titanium, vanadium and chromium and it is preferable to employ the metals with organic compounds such as polycarboxylic acids or aminopolycarboxylic acids.

The organic antifoggant may be any organic antifoggant or film speed restrainer. Such organic antifoggants are commonly employed in X-ray developer baths and include compounds such as benzimidazole, benzotriazole, benzothiazole, indazole, tetrazole, imidazole, mercaptotetrazole 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 or two antifoggants such as 5-nitroindazole and benzotriazole. Sodium or potassium bromides are also suitable.

Exemplary sequestering agents include but are not limited to aminopolycarboxylic acid compounds, ethylenediaminetetraacetic acid, and sodium salts thereof, diethylenetriaminepentaacetic acid, diaminopropanoltetraacetic acid, gluconic acid and its salts, hepto and borogluconates, citric acid and its salts.

Exemplary swell control agents are dialdehydes or diketones particularly glyoxal, or homologous of glyoxal in which the two aldehyde groups are separated by a chain of 2 or 3 carbon atoms. Preferred is glutaraldehyde. Other compounds which may be mentioned include diacetyl, acetyl benzoyl and dichlorodiacetyl.

It is imperative that a developer pH of approximately 9-12 be maintained. More preferred is a developer pH of approximately 9.7-10.6 and most preferred is a developer pH of 10.0±0.3. 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 quite suitable.

The replenisher solution is ideally formulated such that addition to the developer restores the chemical composition of the developer to optimal composition under steady state conditions. It is typically preferred

that the replenisher be substantially identical to the developer with the exception of the titratably distinct additives described herein.

The term Ksp is standard in the art and refers specifically to the solubility product constant. The solubility constant can be defined as the product of the concentration of the ions of a substance in a saturated solution of the substance. For purposes of this invention the solubility product in water, at ambient temperatures, is a sufficiently close approximation to the solubility product in processing chemicals.

If more than two replenisher components are to be monitored then multiple salts can be used with the proviso that at least two meet the criteria described above. Another embodiment includes the use of two salts with at least one salt used in multiple samples. In this embodiment the concentration of salt in the component would be such that when all of the components are added the deviations from ideal concentration would be detectable as shown in Example 1.

The preferred developer composition and replenisher therefore comprises, per liter: 0.5 to 5.0 g. of 1-phenyl-3-pyrazolidone or a derivative thereof; 15 to 35 g. of hydroquinone, or a derivative thereof; 0 to 10 g. of bromide ion; 0.01 to 6.0 mmoles of an organic antifoggant; 1.0 to 30.0 g. of a titratably distinct ion and 0 to 30 g. of a different titratably distinct ion. When bromide ion is present it is preferred that the second titratably distinct ion is chloride.

Another preferred developer composition and replenisher comprises, per liter, 15.0 to 75.0 g. of ascorbic acid; 0.5 to 5.0 g. of 3-pyrazolidone or a suitable derivative thereof; 2 to 20 grams of sulfite; 15 to 30 grams of carbonate; 0 to 10 g. of bromide ion; 0.01 to 6.0 mmoles of an organic antifoggant; 1.0 to 30.0 g. of a titratably distinct ion and 0 to 30.0 g. of a different titratably distinct ion.

One embodiment, in accordance with the teachings herein, is the inclusion of one titratably distinct salt with the reducing agent and one titratably distinct salt with a second replenisher component. Particularly preferred is a composition with one titratably distinct salt added in an amount which is directly proportional to the reducing agent, and the second titratably distinct salt added in an amount which is directly proportional to the glutaraldehyde bisulfite.

It has long been the practice in the art to provide the customer with concentrated solutions which are then mixed prior to use or placed in an automatic mixer as detailed in U.S. Patent 4,741,991. In this embodiment it is particularly preferred that titratably distinct ions be included in each solution. A potentiometric titration can then be used to insure that mixing is accurate prior to replenishing the working developer.

A range of bromide ion can be used successfully in this invention. It is preferred that one of the titratably distinct ions be KBr in an amount equal to 1 to 10 g/liter. 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.

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 mixing 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 U.S. Pat. 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 without change in sensitometric properties of the film, and will be determined empirically, as well known. As a guide, when using an X-Omat Processor to process X-ray film, a suitable replenishment rate will be about 50-70 mls per 240 square inches of film (40% exposed) for development to normal radiographic density, using the processing solution of the invention as properly prepared.

Substantially all processors have some type of a standby replenishment mode. There are a lot of differences based on the manufacturer but the concept is usually similar. The standby mode typically 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 the 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.

Potentiometric titrations are well known in the art as exemplified in Instrumental Analysis, Bauer, Christian, O'Reilly, Alyyn and Bacon, 1979, Chapter 2.

The following examples are intended to further illustrate and demonstrate the teachings of this invention. These examples are not intended to limit the scope of the claims in any way.

EXAMPLE 1

An example of the use of three components with two salts is as follows:
Solution 1 would contain salt A at a level sufficient to equal 4 g/l in the final mixture, Solution 2 would contain salt B at a level sufficient to equal 4 g/l in the final mixture, Solution 3 would contain salt A at a level sufficient to equal 1 g/l and salt B at a level sufficient to equal 1 g/l in the final mixture. A properly prepared replenisher would be expected to contain 5 g/l of both salt A and salt B. If Solution 1 is added incorrectly then salt A will deviate from 5 g/l but salt B will be correct and so forth.

EXAMPLE 2

Three stock solutions were prepared in accordance with U.S. Patent 4,741,991. Sodium chloride was added to Solution C to demonstrate the utility of the current invention. For this example diagnostic analysis is restricted to two solutions only to facilitate understanding of the inventive concept. Expansion to more solutions could be accomplished as detailed in Example 1.

Ingredients	Amt (g)
Solution A	
Dist. Water	ca. 3785
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
Solution B	
Triethylene Glycol	402
Acetic Acid	270
Phenidone	60
5-nitroindazole	6
Benzotriazole	8
Dist. Water to	1 liter
Solution C	
Water	500
Glutaraldehyde (50% aq.)	267
Sodium Bisulfite (anhydr.)	106
Sodium Chloride	67.56
Dist. Water to	1 liter

Specific mixtures of these ingredients were prepared as replenishment solutions which are chosen to simulate actual operating conditions commonly encountered in a processor. This mixture is intended for use with a replenisher which has a constant bromide level of 3.0 g/l, as sodium salt, and a pH of 10.0 ± 0.3. The specific solutions are detailed below.

R1 - representing a properly prepared replenisher solution	
Water	700 mls
Solution A	250 mls
Solution B	25 mls
Solution C	25 mls

R2 - representing a replenisher which is 10% overdiluted	
Solution R1	250 mls
Water	25 mls

R3 - representing a replenisher which is 15% overdiluted	
Solution R1	250 mls
Water	37.5 mls

R4 - representing replenisher with proper dilution but 10% shortage of Solution A	
Water	725 mls
Solution A	225 mls
Solution B	25 mls
Solution C	25 mls

R5 - representing replenisher with proper dilution but 10% shortage of Solution C	
Water	702.5 mls
Solution A	250 mls
Solution B	25 mls
Solution C	22.5 mls

R6 - representing a solution which is properly mixed but underdiluted by 10%	
Water	600 mls
Solution A	250 mls
Solution B	25 mls
Solution C	25 mls

Standard pH and specific gravity measurements were taken and the halides were titrated using the following procedure. A 10 ml sample was taken from each solution. The sample was diluted to 120 mls with 0.1 N sulfuric acid. The samples were then titrated for bromide ion and chloride ion, in triplicate, using the two endpoint potentiometric method on a Brinkman Model 702 automatic titrator using a silver billet electrode. The halide ion concentration was reported as a sodium salt. The pH was measured with a Fisher Accumet 915 pH meter equipped with a combination glass electrode as known in the art. Specific gravity was determined by weighing 10 ml samples. The results are listed in Table 1.

TABLE 1

Replenisher	pH	SG	Br	Cl
R1	10.10	1.81	3.05	1.69
R2	10.10	1.72	2.81	1.51
R3	10.11	1.71	2.68	1.46
R4	10.02	1.72	2.75	1.69
R5	10.13	1.79	3.02	1.55
R6	10.16	1.90	3.42	2.00
SG is specific gravity in g/l, Br and Cl are both in g/l as sodium salt.				

Expected values for pH are 10.1 ± 0.1 which suggest that all of these solutions are within the normal operating range and are therefore considered acceptable for use even though they were purposely prepared incorrectly.

Except for the sodium chloride, the replenisher illustrated is substantially identical to that described in U.S. Pat. No. 4,741,991. This replenisher is intended to be used with a developer which has a steady state bromide level of approximately 6.0 to 7.0 g/l as the sodium salt. As expected the development reaction would cause the bromide ion level to increase as film is developed in accordance with Equation 1. The combined teachings of U.S. Pat. No. 4,741,991 and U.S. Pat. No. 3,970,457 would suggest that the replenisher is added in an amount sufficient to return the bromide ion level to the predetermined level. Addition of a replenisher with a bromide ion level of approximately 3.0 g/l as the sodium salt would effectively dilute the bromide ion concentration thereby counteracting the effect of use as described herein. Using only a bromide ion titration on the developer, and a replenisher with an expected bromide level of 3.0 g/l as the sodium salt, the replenishment for each sample would yield different results. The developer replenished with R2, R3 or R4 would be under replenished since not as much solution would be required to lower the bromide ion concentration to a predetermined level. Even though the bromide ion level would be corrected the $HOC_6H_4OSO_3Na$ would not be replaced with unreacted hydroquinone and sulfite. Therefore, a continuous bromide ion titration on the developer would not offer any diagnostic information. The developer replenished with R5 would have the proper amount of hydroquinone added but would be deficient of sulfite and glutaraldehyde. The deficiency in sulfite and glutaraldehyde would be completely transparant from the bromide ion titration alone. The developer replenished with R6 would also be incorrectly replenished since the bromide ion concentration added to the developer would be higher, on a volume basis, than expected.

Depending on the film used a processor upset may be detected for each of R2 through R6 with no diagnostic information available based on the bromide ion titration alone.

Using identical solutions and analyzing both the bromide and chloride ion solutions, in accordance with this invention, provides an immediate indication of improper mixing. The four distinct possibilities which exist for the replenisher in this example are:

1) both halide ions are on aim (i.e. R1)
2) both halides are either above or below aim (i.e. R2, R3, R6)
3) one halide ion is high and the other is low
4) one halide ion is off aim or missing (i.e. R4, R5).

A titration of the developer replenished with R1 would have the predetermined level of bromide ion and chloride ion. A titration of the developer replenished with a set amount of R2 or R3 would have a bromide ion level which is lower than the predetermined level and a chloride ion level which is below the predetermined level. A developer replenished with a set amount of R4 would have a bromide ion level which is lower than the predetermined level and a chloride ion level which is at the predetermined level. A developer replenished with a set amount of R5 would have a bromide ion level which is at the predetermined level and a chloride ion level which is low. A developer replenished with a set amount of R6 would have a bromide and chloride level which is above the predetermined levels. In all cases the incorrect solution could be immediately corrected by changing replenishment amount or adding one component of replenisher.

These diagnostics could then be used to properly adjust the solutions and/or the replenishment rate to achieve the appropriate results. Based on these examples the replenishment rate could be increased by the appropriate factor when samples such as R2 and R3 are observed. R4 and R5 could be remixed with additional ingrediants to achieve the proper balance of bromide ion to chloride ion and the replenishment adjusted accordingly. R6 could be diluted to the appropriate level and the problem alleviated. In each of these examples the current practice of replacing the entire chemical charge and remixing could be avoided since the mixture could be corrected.

Furthermore, once the above mentioned corrections are made a retest can be used to certify that the replenishment, and development are correct without the use of film.

Claims

1. A method for converting a series of image-wise exposed silver halide photographic films to a viewable images comprising the steps of:

(a) developing an image-wise exposed silver halide film in a first developer, comprising at least two titratably distinct components present in a first concentration ratio, whereby the exposed silver halide is reduced to elemental silver and the activity of said first developer is depleted concurrently altering the concentration ratio of the titratably distinct components forming a distinct components;

(b) removing unexposed silver halide from said photographic film;
(c) titrating the second developer to determine the second concentration ratio of titratably distinct components;
(d) adding a replenishment solution comprising at least two titratably distinct components to the second developer in an amount sufficient to change the second concentration ratio of titratably distinct components to the first concentration ratio of titratably distinct components;
(e) repeating steps (a) through (d) for at least one additional image-wise exposed silver halide film.

2. The method recited in Claim 1 wherein said titratably distinct components independently form silver salts with a Ksp value between 10^{-6} and 10^{-20}.

3. The system method recited in Claim 1 wherein said titratably distinct components have a Ksp value which differs by at least 10^{-2}.

4. The method recited in Claim 1 wherein at least one said titratably distinct component is bromide.

5. The method recited in Claim 1 wherein at least one said titratably distinct component is chloride.

6. The method recited in Claim 1 wherein said developer and said replenisher comprise at least one compound chosen from the set consisting of 4-hydroxymethyl-1-phenyl-3-pyrazolidone, 1-phenyl-3-pyrazolidone, 4-methyl-1-phenyl-3-pyrazolidone; 4,4-dimethyl-1-phenyl-3-pyrazolidone; hydroquinone, chlorohydroquinone and bromohydroquinone.

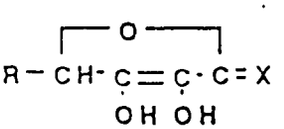
7. The method recited in Claim 1 wherein said replenisher compromises. per liter, 0.5 to 5.0 g. of 1-phenyl-3-pyrazoline; 15-35 g. of hydroquinone; 0.01 to 6.0 mmoles of an organic antifoggant; 1.0 to 30.0 g. of a first titratably distinct component and at least one titratably distinct component chosen from the group consisting of:
(a) up to 10 g. of bromide ion; and
(b) up to 30 g of a second titratably distinct compound.

8. The method recited in Claim 1 wherein said developer and said replenisher comprises at least one compound chosen from the set consisting of ascorbic acid, sugar derivatives of ascorbic acid, stereoisomers of ascorbic acid, diastereoisomers of ascorbic acid, salts of ascorbic acid and mixtures thereof.

9. The method recited in Claim 8 wherein said developer and said replenisher comprises at least one compound chosen from the set consisting of ascorbic acid, d-erythro-ascorbic acid [i.e. erythorbic or isoascorbic acid)], d-glucosascorbic acid, 6-deoxy-1-ascorbic acid, d-glucoascorbic acid, d-galactoascorbic acid, 1-glucoascorbic acid and 1-alloascorbic acid.

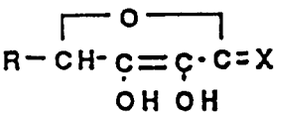
10. The method recited in Claim 1 wherein said replenisher comprises, per liter, 15.0 to 75.0 g. of ascorbic acid; 0.5 to 5.0 g. of 3-pyrazolidone or a suitable derivative thereof; 2 to 20 grams of sulfite; 15 to 30 grams of carbonate; 0 to 10 g. of bromide ion; 0.01 to 6.0 mmoles of an organic antifoggant; 1.0 to 30.0 g. of a titratably distinct ion and 0 to 30.0 g. of a different titratably distinct ion.

11. The method recited in Claim 1 wherein said developer and said replenisher comprises



wherein:
X is an oxygen atom or imino group;
R is an aryl group or a group of the formula $R^1CH_2(CH_2)_{n-1}$ where in
n is a positive integer from 1 to 4 and R^1 is either a hydrogen atom or hydroxyl group when n is 2 to 4 and is hydroxyl when n is 1.

12. The method recited in Claim 1 wherein said developer and said replenisher comprises



wherein:
X is an oxygen atom or imino group;
R is any group which does not render the ascorbic acid water-insoluble and is a non-interfering group.