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(54) **Photographic processing**

(57) A method of controlling the rate of replenishment of a developer solution used in photographic processing apparatus is provided wherein replenish-

ment is carried out as a function of the exposure of the photographic material being developed and the average amount of material being developed in unit time.

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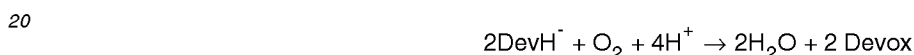
Description**Field of the Invention**

5 The invention relates to photographic processing. More particularly, it relates to the replenishment of a development solution used in the processing of a photographic material.

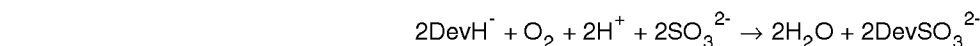
Background of the Invention

10 As the chemicals in the baths of a photographic processor are used up, replenishment chemicals must be added to the baths in order to keep the activities and concentrations of the chemicals constant. A number of factors affect the composition of the developer solution including the amount of photographic material processed, the degree of exposure of the photographic material, developer evaporation rate and developer oxidation rate.

15 This invention relates to the replenishment of photographic processors, especially for those processors designed for black and white processing and for those processes where the developer pH tends to rise on standing, by aerial oxidation. These developers usually contain hydroquinone or a derivative thereof and sulphite as the oxidised developer scavenger/anti-oxidant. This can be explained by reference to the following reactions in which DevH⁻ represents the mono anion of the developer, Devox represents oxidized developer and DevSO₃²⁻ represents sulphonated developer.



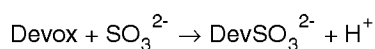
which can be summed to give the overall reaction



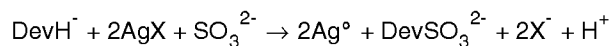
which consumes a proton for every oxygen atom reacted. In this case the pH of the developer tends to increase.

The composition of the developer can also be influenced by evaporation that takes place on standing. The concentrations of the components tend to increase.

35 It is well known in the art to change the replenishment in line with photographic material exposure as taught by EP-A-0,596,994; US-A-5,235,369; EP-A-0,500,278; EP-A-0,456,684 and US-A-4,486,082 as oxidation of developer with silver halide generally generates unwanted species such as bromide and protons, seen as a reduction in pH and increase in bromide concentration. This can be explained by the following reactions



45 which again can be summed to give an overall reaction as follows



50 which liberates a proton from every developer molecule consumed as well as two halide ions. In this case the pH of the developer tends to decrease.

Another proposed way of determining the amount of replenisher needed is by measuring the final image density and relating this back to the replenisher needed to hold the process activity constant for example as taught us by EP-A-0,596,991; US-A-5,315,337; US-A-5,073,464; GB-A-2,108,707 and GB-A-2,106,666.

55 The sensitometric sensitivity to developer composition is different for different photographic materials. For example, rapid access image setting materials which often contain silver halide emulsions which are predominantly silver chloride are sensitive to bromide concentration and so during seasoning the bromide concentration should remain constant. By comparison, materials which contain nucleators and boosters to achieve high contrast are sensitive to pH but are

relatively insensitive to bromide ions.

For a process used for a rapid access image setting material, the bromide level in the developer is affected by evaporation, the relative extent of which is determined by the utilisation of the process. If the process is not used much the evaporation will have more effect compared to the effect on a highly utilised process which will be more dependent on the film area processed and is exposure dependent.

Similarly, for a nucleated material, oxidation of the developer is an important factor. If there is a lot of oxidation or a process is not used much the pH of the developer tends to rise according to the first set of reactions discussed above as there is little pH loss caused by film developing. However, for processes that process much film, particularly with high exposure, the pH tends to drop as the effect of oxidation raising the pH cannot keep up with the pH drop caused by the silver developing. A method of replenishing, preferably with one solution, needs to be found that will reconcile both the process being used often and also with the process used occasionally.

The problem of sensitivity to any component can be alleviated by increasing the developer replenishment rate, replenishing with a developer with the same composition as the processing tank aim, to such an extent that the changes caused by processing film, evaporation and oxidation are very small. With films sensitive to component changes, this results in high solution use and effluent.

One way around the problem of change in developer composition with oxidation and evaporation is to have a replenishment taking place related to time, sometimes known as time dependent replenishment or 'anti-ox'. This is carried out to add components lost or to dilute components gained. The problem with this means of control is replenishment takes place continually and liquid is displaced as effluent even though photographic material is not being processed.

To reduce the amount of developer used a tank solution is put in the processor and a replenisher of different composition used which is added at a rate to maintain the original tank composition. The replenishment rate has to be controlled dependent on the film exposure, oxidation and evaporation.

Problem to be solved by the Invention

A method of controlling the replenishment of the developer is required which overcomes problems associated with variation in the exposure of the photographic material, oxidation and evaporation outlined above.

Summary of the Invention

The invention provides a method of controlling the replenishment of a developer solution used in photographic processing apparatus characterised in that replenishment is carried out as a function of the exposure of the photographic material being developed and the average amount of material being developed in unit time.

The invention also provides photographic processing apparatus comprising (a) means for measuring the exposure of a photographic material, (b) means for measuring an average amount of photographic material processed in unit time, (c) means for controlling the supply of development replenisher to a development bath as a function of the exposure of the photographic material being developed and the average amount of material being developed in unit time, and (d) means for communicating the information measured by (a) and (b) to (c).

Advantageous Effect of the Invention

Photographic processing is rendered more stable to changes in sensitometry caused by variable utilisation and exposure. The amount of replenishment chemicals used is reduced. No continuous time dependent replenishment or "anti-ox" is required.

Detailed Description of the Invention

The method of the invention can be used in the processing of a variety of silver halide photographic materials. Examples of such materials are described in Research Disclosure, September 1994, Number 365 published by Kenneth Mason Publications Limited, (hereinafter referred to as Research Disclosure), Section I. The materials include black and white, colour and X-ray e.g. industrial and medical materials.

Developer composition will depend on the nature of the photographic material being processed. Examples of developer compositions are given in Research Disclosure, Section XIX. A typical developer composition comprises a dihydroxybenzene primary developer, an auxiliary developer such as a pyrazolidone or amino phenol, an alkali metal sulphite, a restrainer such as bromide, antifoggants such as benzotriazole and phenylmercaptotetrazole, and a buffer. The pH may be from 8 to 12, preferably from 9.5 to 11.5.

The invention may be applied to the processing of black and white silver halide materials and is particularly useful

when applied to the processing of graphic arts materials i.e. high contrast, black and white materials. The average gradient of the characteristic curve of a high contrast material is preferably at least 2 e.g. from 3 to 20 or for higher contrast materials from 10 to 20. The silver halide can be bromiodide, chlorobromiodide, bromide, chlorobromide, or chloride. A preferred silver halide emulsion layer has a silver chloride content of at least 50%. The photosensitive silver halide emulsions employed in the present materials may contain both silver bromide and silver iodide in addition to the silver chloride. Preferably the iodide content is less than 10 mole percent. Substantially pure silver chloride emulsions may be used although the preferred emulsions comprise 70 mole % chloride and 30 mole % bromide.

In a particular embodiment, the photographic material may be a nucleated or rapid access material e.g. for use in an imagesetter. Typically, such materials comprise silver chloride or silver chlorobromide emulsions in which the silver coating weight is from 1 to 10 g/m² and the contrast index is from 1 to 30.

Emulsions containing hydrazide nucleating agents may be used. These emulsions can be processed in a developer with conventional amounts of sulphite, hydroquinone and possibly metol or a pyrazolidone. Such developers also contain an amine additive as described in US-A-4,269,929. Other developers containing amines are described in US-A-4,668,605 and US-A-4,740,452.

Many hydrazides have been proposed for use in such materials, for example in US-A-4,323,643, US-A-4,278,748, US-A-4,031,127, US-A-4,030,925 and in EP-A-0,333,435.

More recently, it has been proposed to incorporate amine boosters in high contrast materials with the advantage that it is not necessary to have a special developer in order to obtain the very high contrast that is demanded by much graphic arts work. Such amine boosters are described in JP-140340/85 and 222241/87 and in EP-A-0,364,166.

Preferably, the emulsion layer comprises two or more emulsion grain types. For example, more than one type of latent image-forming grain may be present. Grains sensitive to different regions of the spectrum may thus be used providing a material suitable for more than one exposing radiation type. When there are grains present which are sensitised to distinct wavelength ranges and exposure is to a source of limited wavelength, some of the sensitised grains will not respond to this wavelength and are thus non-latent image forming grains under these conditions of use.

The invention is particularly beneficial in respect of developers whose pH tends to rise on standing because of aerial oxidation. These developers usually contain hydroquinone or a derivative thereof and sulphite ions which react with oxidised developing agent.

The composition of the replenishment solution will depend on the developer composition. Preferably, the replenishment solution is the same as the developer solution or a more concentrated version thereof with less bromide.

The invention may be employed in any photographic processing apparatus comprising means for imagewise exposing a photographic material and means for processing the exposed material to produce the recorded image. The processing means will normally comprise development, fixing and one or more washing stages.

Any photographic processor known in the art can be used to process the photosensitive materials described herein. For example, large volume processors, and so-called minilab and microlab processors may be used. Other examples include the Low Volume Thin Tank processors described in such references as WO 92/10790, WO 92/17819, WO 93/04404, WO 92/17370, WO 91/19226 and 91/12567.

Replenishment of processing solutions e.g. the developer solution may be carried out manually or, preferably, by other controlled means of addition. A preferred means for controlling the supply of development replenisher to a development bath comprises a computer which receives information relating to photographic material exposure and usage and calculates the amount of replenishment required. The computer may be used to control the operation of a pump supplying replenisher to a tank of developer solution. Preferably, replenishment is performed using a single solution but use of a plurality of solutions is possible.

Developer replenishment is carried out using an algorithm or look up table which contains terms relating to the degree of exposure of the photographic material to activating radiation and the average amount of photographic material processed in unit time. In this way the constitution of the developer can be kept near that desired as the process matures.

The exposure term in the algorithm or look up table may be determined in any convenient way e.g. by obtaining information from the exposure device, by visual estimation or, if replenishment was made for the film after processing, by scanning the final image and using a density to exposure function.

The average amount of material processed in unit time may be calculated also by any convenient method e.g. by an assessment of the workload for the day, by assuming that the current days work will be similar to the last working day or by using the time since the last sheet was processed and its area.

The algorithm or look up table might also have additional terms relating to the rate of oxidation of the developer and solution evaporation in a particular processor. These rates would be determined by measurement or by models considering the geometry of the processor.

The algorithms or look up tables may be determined by experiment or by model calculations.

In a specific embodiment of the invention, a high contrast silver halide film e.g. Kodak Focus HeNe film is exposed by a scanning laser in an imagesetter e.g. a Herkules imagesetter (Linotype-Hell AG). Appropriate hardware and software is used to calculate the number of exposed pixels per page i.e. a signal is derived which is indicative of the

exposure of the film.

The exposed film is conveyed to a processor e.g. a Multiline 550 processor (Glunz & Jensen International A/S) which provides a four stage (develop/fix/wash/dry) rapid access process. The processor comprises a chemical management system including a computer which calculates and supplies the required amount of developer replenisher based on information received relating to the exposure of the photographic material and processor usage. A communication link is provided between the imagesetter and the processor so that the exposure information generated in the imagesetter can be provided to the chemical management system. Information relating to the average amount of photographic material processed in unit time can be generated in the processor from sensors which detect the number of sheets of a given area passing through the processor in a given time.

The invention is further illustrated by way of example as follows.

Example 1

The developer used for this experiment was of the following composition.

Hydroquinone	15g/l
Sodium Bromide	2.5g/l
Hydroxymethyl Methyl	0.5g/l
Phenidone	
Benzotriazole	0.06g/l
Phenyl Mercapto Tetrazole	0.008mg/l
Sodium metabisulphite	25g/l
Diethylene glycol	21mls/l
pH	10.30
Potassium Carbonate (47%)	25g/l

A matrix of experiments was designed to give an experiment with varying exposure and processor utilisation. A4 size sheets of 'Kodak' IMAGELITE ESY Scanner Film were exposed to different amounts of area according to the first column of the table given below with white light source and processed in a processor of the type described in EP-A-0 614 545, at 35°C for 30 seconds, filled with 150mls of the developer solution. The processor was replenished with a measured amount of replenisher of the same formulation as the developer. The number of sheets processed per day was varied such that the utilisation as described by the second column of the table below was met. Sheets of film were processed until at least 500mls of replenisher had been added to the tank, by which time the process should have reached equilibrium. A control strip was put through, fixed in 'Kodak' 3000 fixer diluted 1+3 for 30 seconds at 35°C and the speed measured and compared to 220±1*, the aim. If the aim was met the replenishment rate was recorded. If it was not met a new replenishment rate was estimated from the measured sensitometry and the addition of sheets at the same daily rate and with the new replenisher rate, repeated. This was repeated until the aim speed for the material was met. This was repeated for all the conditions found in the table. The determined replenishment rates are given in the third column of the table below.

The experiment was repeated with the replenishment rate being fixed for utilisation at 11 m²/day, determined by the table for each exposure condition. This simulated the effect of not taking into account the effect of utilisation. Control strips were processed after 500mls of replenisher had been added and the speed determined. The results are shown in the last column of the table below.

Exposure (%)	Utilisation (m ² /day)	Optimum Replenisher Rate for Speed = 220	Relative Speed* with no allowance for Utilisation
10	2	850	Insufficient density
80	2	1090	218
10	20	166	220
80	20	1040	220
10	11	200	219
80	11	1070	220
45	2	980	215
45	20	605	220
45	11	640	220

* Speed is defined as 100x exposure required to give a density of 0.6 above fog density related to an arbitrary standard exposure.

The replenishment rate for a particular exposure and utilisation condition can be determined by reference to the table which is in effect a look up table. By using these replenisher rates the speed of the material will be 220±1*. If no account had been taken of the utilisation the speed would have varied considerable as shown by the fourth column of the table above and indeed with low exposure and low utilisation there was very little image unless account had been taken of the utilisation according to the look up table.

The intermediate processing conditions can be extrapolated from the table above but it is sometimes convenient to use an algorithm or mathematical model. These can be obtained by finding the best fit equation to fit the measured replenishment rates using exposure (E in %) and utilisation (U in m²/day) as factors. The best quadratic equation, ignoring the insignificant terms to the experimental results is:

$$\text{Replenishment rate} = 913 + 3.9E - 84.4U + 0.5EU + 1.8U^2 \text{ mls/m}^2$$

Example 2

An alternative to determining the replenishment rate by experiment is to calculate it using a model based on the usage rate of the developer component of interest and other factors which cause it to change. The method of deriving the model is set out in some detail below.

Definitions for model:

- Mass_in - the mass of a component entering the process tank in unit time(e.g. g/day)
- Mass_out - the mass of a component leaving the process tank in unit time(e.g. g/day)
- Volume_in - the volume of liquid entering the process tank in unit time(e.g. mls/day)
- Volume_out - the volume of liquid leaving the process tank in unit time(e.g. mls/day)
- Usage - the amount of the component being considered that is consumed by 1m² of material (a positive number indicates a loss of material) (e.g.g/m²)
- Tank_conc - the concentration of the component being considered in the processor tank(e.g. g/l)
- Tank_conc_initial - the concentration of the component being considered at time = 0(e.g. g/l)

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Area	- the area of photographic material processed in unit time (e.g. m ² /day)
Rep_rate	- replenishment rate per unit area(e.g. mls/l)
Anti_ox	- volume of additional replenisher added per unit time that is independent of processed area (sometimes known as time dependent replenishment (TDR)) (e.g. mls/day)
5 Top_up	- Additional volume of replenisher added to tank at the beginning of unit time to make up for evaporation. This is set to zero in mass equations only if top-up is with water(e.g. mls/day)
Time	- the time elapsed in appropriate units (e.g. days)
Overflow_mass	- mass of component lost by tank overflow to drain in unit time (e.g. g/day)
Overflow_vol	- volume of liquid lost by tank overflow to drain in unit time(e.g. mls/day)
10 Carryout_mass	- mass of component carried out on material web in unit time (e.g. mls/day)
Carryout_vol	- volume of liquid carried out on material web in unit time(e.g. mls/day)
Oxidation	- the total mass of the component being considered lost in unit time(tank size dependent) (e.g. g/tank/day)
15 Evaporation	- the volume of liquid lost from the processing tank being considered in unit time (e.g. mls/tank/day)
Tank_volume	- the volume of the tank being considered (e.g. mls)

The Model:

20 Mass in = (Area*Rep_rate + Anti_ox + Top_up)*Rep_conc
 Volume_in = Area*Rep_rate + Anti_ox + Top_up
 Mass_out = (Carryout_mass + Overflow_mass) + Area*Usage + Oxidation
 Volume_out = (Carryout_vol + Overflow_vol) + Evaporation
 Rate of change of mass with time = (Area*Rep_rate + Antiox + Top_up)*Rep_conc - (Carryout_mass + Overflow_mass) - Area*Usage - Oxidation
 If Volume_in = Volume_out (Carryout_vol + Overflow_vol) = Area*Rep_rate + Anti_ox + Top_up - Evaporation
 25 (Carryout_mass + Overflow_mass) = (Carryout_vol + Overflow_vol) * Tank_conc
 (Carryout_mass + Overflow_mass) = (Area*Rep_rate + Anti-ox + Top-up - Evaporation) * Tank_conc
 Rate of change of mass with time = (Area*Rep_rate + Anti ox + Top_up)*Rep_conc - Area*Usage - Oxidation - (Area*Rep rate + Anti_ox + Top_up - Evaporation) * Tank_conc
 Let a = (Area*Rep_rate + Anti_ox + Top_up)*Rep_conc - Area*Usage - Oxidation
 30 Let b = (Area*Rep_rate + Anti_ox + Top_up - Evaporation) Rate of change of mass with time = a - b*Tank_conc
 Rate of change of concentration with time = (a - b*Tank_conc)/Tank_volume
 Integrating with respect to the limits Tank_Conc = (a - (a - b*Tank_conc_initial)*exp((-b*time) /tank_volume))/b
 When time is infinite, i.e. a totally seasoned process, Tank_conc = a/b

35 Using this concentration model for a particular component or components that need to be fixed or within certain bounds, in the tank solution, to produce the desired sensitometry for a given product e.g. pH and to a lesser extent bromide and benztriazole for a material containing a nucleator, and determining the usage rates, evaporation rate and oxidation rates for a given processor, the optimum replenishment rate can be determined related to the amount of material processed per day, exposure and also perhaps machine variables although these are confounded with the machine usage.
 40

The usage rates for all components in the following developer replenisher were determined for 'Kodak' Focus HeNe film:

45	Hydroquinone (HQ)	33g/l
	Sodium Bromide	1.9/l
	Hydroxymethyl Methyl Phenidone	0.8g/l
	Benzotriazole (BTAZ)	0.22g/l
	Phenyl Mercapto Tetrazole	0.013mg/l
50	Sodium metabisulphite	42g/l
	Diethylene glycol	35mls/l
	Potassium Carbonate (47%)	42g/l
	pH	10.56

55 The tank solution had the following composition:

Hydroquinone (HQ)	25g/l
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(continued)

Sodium Bromide	3.8/l
Hydroxymethyl Methyl Phenidone	0.8g/l
Benzotriazole (BTAZ)	0.20g/l
Phenyl Mercapto Tetrazole	0.013mg/l
Sodium metabisulphite	38g/l
Diethylene glycol	35mls/l
Potassium Carbonate (47%)	42g/l
pH	10.56

The following conditions of the tank solution were determined to be important for keeping the sensitometry of the film on aim:

BTAZ > 0.18 and NaBr < 4.8 and pH >= 10.40 (as near to pH 10.40 as possible)

The evaporation rate of a Glunz and Jensen Multiline 550 processor was found to be 450mls/day and the oxidation rate 12g HQ/day.

These figures were incorporated into the model and optimum replenishment rates determined for different exposures and daily usage rates. From this data an optimum replenishment algorithm was obtained.

$$\text{Replenisher rate} = 7 + 3.40E + 2.5U - 0.016U^2 \text{ mls/m}^2$$

This algorithm can be used to determine the replenishment rate for this processor knowing the film exposure, e.g. from data derived from the imagesetter, and usage data, e.g. from data derived from the use on the last working day.

Claims

1. A method of controlling the rate or replenishment of a developer solution used in photographic processing apparatus characterised in that replenishment is carried out as a function of the exposure of the photographic material being developed and the average amount of material being developed in unit time.
2. A method according to claim 1 wherein the photographic material is a black and white silver halide material.
3. A method according to claim 1 wherein the photographic material is a high contrast black and white silver halide material.
4. A method according to any one of the preceding claims wherein the developer solution comprises a dihydroxybenzene developing agent.
5. A method according to any one of the preceding claims wherein the rate of replenishment is calculated from an algorithm comprising terms representing the exposure of the photographic material being developed and the average amount of material being developed in unit time.
6. A method according to claim 5 wherein the term representing the exposure of the photographic material being developed is derived from exposure data provided by an exposing device.
7. A method according to claim 6 wherein the exposing device is an imagesetter.
8. A method according to any one of claims 5 to 7 wherein the term representing the average amount of material being developed in unit time is derived from data relating to the area of photographic material processed in a measured time which is provided by an exposing device, the processing apparatus or both.
9. Photographic processing apparatus comprising (a) means for measuring the exposure of a photographic material, (b) means for measuring an average amount of photographic material processed in unit time, (c) means for controlling the supply of development replenisher to a development bath as a function of the exposure of the photographic material being developed and the average amount of material being developed in unit time, and (d) means

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for communicating the information measured by (a) and (b) to (c).

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 1164

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO-A-93 03415 (KODAK LTD ;EASTMAN KODAK CO (US)) 18 February 1993 * abstract; claims 1,7 *	1-9	G03C5/31 G03D3/06
A	EP-A-0 082 628 (VICKERS PLC) 29 June 1983 * abstract *	1-9	
A	US-A-5 025 279 (ELLSWORTH ROGER D) 18 June 1991 * abstract *	1-9	
A	EP-A-0 348 512 (FUJI PHOTO FILM CO LTD) 3 January 1990 * claims 1-6 *	1-9	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 301 (P-1069) [4244] , 28 June 1990 & JP-A-02 096138 (FUJI PHOTO FILM CO LTD), 6 April 1990, * abstract *	1-9	
A	US-E-RE30123 (J A CROWELL ET AL) 23 October 1979 * abstract; figure 1 *	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C G03D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 August 1996	Examiner Bolger, W
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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