(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 573 700 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **92201656.3**

(51) Int. Cl.5: **G03C 5/31**

(22) Date of filing: **09.06.92**

(43) Date of publication of application:
15.12.93 Bulletin 93/50

(84) Designated Contracting States:
BE DE FR GB

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(54) **Replenishment of a developer containing ascorbic acid and 3-pyrazolidone derivatives.**

(57) A method is disclosed for processing with constant activity image-wise exposed silver halide photographic material comprising the steps of :

(a) developing photographic material in a continuous automatic way by means of a developing solution containing an ascorbic acid analogue or derivative and a 3-pyrazolidone derivative as developing agents ;

(b) replenishing said developing solution by means of at least one replenishing solution having a higher pH than the developing solution.

In an alternative method the replenisher is added as a powder.

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1. Field of the invention.

The present invention relates to a method for processing silver halide materials with a developing solution containing an ascorbic acid derivative and a 3-pyrazolidone derivative as developing agents and more particularly to a method of replenishment of such a developing solution.

2. Background of the invention.

In general, the processing of black-and-white silver halide photographic materials is performed in the sequence of development, fixing and washing. Development is commonly carried out with aqueous alkaline developer compositions containing a developing agent, usually of the dihydroxybenzene type such as hydroquinone.

Due to the toxicity and environmental hazards posed by the use of hydroquinone, several substitutes which are less toxic by nature have been proposed. For example the development activity of ascorbic acid and some chemical analogues is known for quite some time in the photographic art. However ascorbic acid and derivatives are regarded as rather weak developers in the pH-range in which hydroquinone acts as a developing agent. Hence, since the first report of the developing activity of iso-ascorbic acid and its optical isomer in Berichte, Vol.67, p.1239 (1934) by Maurer et al., there have been several publications on developers containing a superadditive combination of a conventional developing agent and an ascorbic acid derivative used as auxiliary developer. So, US 2,688,549 discloses the combination of a 3-pyrazolidone developing agent and of an ascorbic acid derivative. GB 1 266 533 describes the combination of a p-hydroxybenzene developing agent, an ascorbic acid and sulphite ions. An equally good developing activity for both surface and internal latent images is claimed in US 3,826,654 which discloses a combination of a 3-pyrazolidone, an ascorbic acid, a heterocyclic thione or thiol and an alkali iodide at a pH of at least 12. Several superadditive compositions specifically for high contrast development are published. So US 3,942,985 discloses the combination of an iron chelate developer and an ascorbic acid derivative. US 4,756,997 claims a combination of a p-hydroxybenzene, an auxiliary developer, an anti-foggant, an antioxidant and an α-ketocarboxylic acid wherein the antioxidant can be ascorbic acid.

However developing solutions containing ascorbic acid derivatives which are themselves excellent antioxidants have a poor resistance against aerial oxidation and can not be left in continuous transport automatic processors for several days without undergoing a dramatic decrease in developing activity.

Only a few attempts have been made in order to increase the resistance against air oxidation of developing solutions containing ascorbic acid derivatives as developing agents. US 3,386,824 discloses the use of plastic microcapsules containing an ascorbic acid derivative in a photographic contact processing carrier material. Childers et al. mentions the protection against aerial degradation of ascorbic acid developers by means of high salt concentration in Phot. Sci. Eng. 16, p. 275 (1972). JP-A-55149936 discloses the combination of a naphthalene compound and an ascorbic acid derivative in order to form an image of sufficient density even in the case of small amount of coated silver; a high stability against aerial oxidation was claimed as an advantage.

These attempts however, do not sufficiently inhibit the pH decrease of developing solutions containing ascorbic acid derivatives as developing agents. The active developing species are likely to be the mono- and dianion of ascorbic acid as was described by Willis and Pontius in Phot. Sci. Eng. Vol. 14 (6), p.384 (1970), and their concentration is pH-dependent. When oxidation occurs due to aerial oxygen or due to development, the pH drops leading to a decrease in photographic activity. Contrary to automatic lith processing based on a polyhydoxybenzene as developing agent where aerial oxidation leads to a pH increase while development of silver haide leads to a pH decrease, so that several different replenishers are needed (see e.g. US 4,081,280, US 4,025,344 and US 4,228,234), both phenomena work in the same direction, in casu a pH decrease, in the case of ascorbic acid developers. The decrease in pH can be diminished by adding high quantities of buffering agent. However in continuous automatic processing with replenishment during film throughput for active developing substances using the same developing solution as the tank solution, as is often the case, a gradual decrease in pH will nevertheless still occur.

It is clear from the above that the pH value of the developing solution containing an ascorbic acid analogue or derivative as developing agent in automatic processing is very important and has to be kept under careful control. Otherwise a loss in development activity will occur in an uncontrollable way.

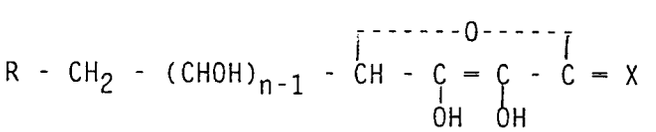
It is an object of the present invention to provide a method for processing image-wise exposed silver halide photographic material by a developer containing an ascorbic acid developing agent and a 3-pyrazolidone developing agent in such a way that very constant processing results are obtained during automatic continuous processing.

3. Summary of the invention.

The object of the present invention is realized by providing a method for processing with constant activity image-wise exposed silver halide photographic material comprising following steps :

(a) developing photographic material in a continuous automatic way by means of a developing solution containing an ascorbic acid analogue or derivative or a salt thereof represented by general formula (I), and a 3-pyrazolidone derivative as developing agents ;

(I)



wherein X represents an oxygen atom or an imino group, and
n represents a positive integer from 1 to 4, and
R represents a hydroxy group when n is 1, and R represents a hydroxy group or a hydrogen atom when n is 2 to 4.

(b) replenishing said developing solution by means of at least one replenishing composition, which is a solution having a higher pH than the developing solution and comprising essentially the same ingredients as the developing solution, so that the pH of said developing solution is maintained constant.

In a preferred embodiment the ascorbic acid analogue or derivative represented by general formula (I) is l-ascorbic acid, iso-ascorbic acid or a salt thereof.

In an alternative method the replenisher is added as a powder comprising substantially the same ingredients as the developer but having alkali in such an amount that the pH of the developer is maintained constant by adding this powder periodically to it.

In the preferred embodiment the replenisher is just one solution having a higher pH than the developer and having the same ingredients in the same or, if needed, in a different concentration.

4. Detailed description of the invention.

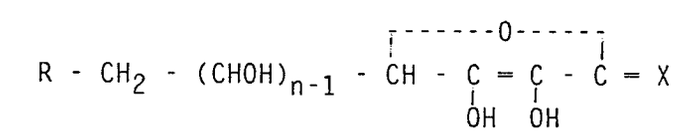
The replenishment can be performed by means of a single solution having a higher pH than the developing solution, two or more replenisher solutions from which at least one has a pH value higher than the developing solution, or by means of a powder composition containing alkali in such an amount that the pH of the developer is maintained constant by adding this powder periodically to it.

In the preferred embodiment of the replenishing composition being a solution, the composition of this solution is the same as the composition of the developing solution, except for the alkali compound, or is formulated so that the concentration of the important components of the developer solution is readjusted to a constant starting value during processing, e.g. an increase in concentration by replenishment for developing agent and anti-fogging agent, and a decrease for halide ion.

The minimal pH difference between replenisher and developer is about 0.2 units per g $AgNO_3$ coated per sq.m. of which 50 % is developable, for a replenishment amount of 250 ml/m^2. For a typical graphic arts film coated at a coverage of about 7 g $AgNO_3/m^2$ and requiring 250 ml/m^2 of replenishment volume the optimal pH difference is about 0.7 ; e.g. the pH of the developer is 10.0 and the pH of the replenisher is 10.7.

The ascorbic acid type developing agent can be represented by following general formula (I):

(I)



wherein X represents an oxygen atom or an imino group, and
n represents a positive integer from 1 to 4, and
R represents a hydroxy group when n is 1, and R represents a hydroxy group or a hydrogen atom when n

is 2 to 4.

Preferred compounds for use in accordance with the present invention are l-ascorbic acid and iso-ascorbic acid. Other useful compounds include imino-l-ascorbic acid, 6-desoxy-l-ascorbic acid, l-rhamnoascorbic acid, l-fucoascorbic acid, d-glucoheptoascorbic acid, d-glucoascorbic acid, l-erythroascorbic acid, and their stereoisomers. The developing agents can be incorporated in the developing solution in the free acid form or as a salt, preferably an alkali salt.

The ascorbic acid type developing agent is incorporated in the developer in a concentration ranging preferably between 0.1 and 0.8 mole/liter. In the replenishing solution the concentration is preferably the same or up to 20 % higher than in the developer.

Derivatives of 3-pyrazolidone for use as second developing agent in connection with the present invention include 1-phenyl-3-pyrazolidone (commonly designated as "Phenidone"), 1-phenyl-4-monomethyl-3-pyrazolidone, 1-phenyl-4,4'-dimethyl-3-pyrazolidone and 1-phenyl-4-hydroxymethyl-4'-methyl-3-pyrazolidone.

The Phenidone type developing agent is incorporated in the developer in a concentration ranging preferably between 0.002 and 0.025 mole/liter. In the replenishing solution the concentration is preferably the same or up to 20 % higher than in the developer.

The developing and replenishing solutions preferably further contain an anti-fogging agent. Many known compounds can be added as fog-inhibiting agent or stabilizer to a processing solution. Suitable examples are e.g. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione and oxazoline-thione. Other classes include triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278 and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide compounds. A preferred compound for use in accordance with the present invention is 1-phenyl-5-mercaptotetrazole.

The developing and repleshing solutions for use in accordance with the present invention preferably further contain a compound providing halide ions as development rate regulator, most preferably sodium or potassium bromide in a concentration between 0.01 and 0.2 mole/liter. Further sulphite ions, preferably provided as an alkali sulphite, are preferably present as antioxidant in a concentration between 0.1 and 0.5 mole/liter.

The alkali agent is preferably sodium or potassium hydroxide.

The developing and replenishing solutions for use in accordance with the present invention further contain buffering agents. Suitable buffer systems include carbonate buffer, phosphate buffer, metaborate buffer, etc. The concentration of these buffering agents is preferably about 0.4 mole/liter.

Other adjuvants well known to those skilled in the art can be incorporated into the developer solution. A survey of conventional developer addenda is given by Grant Haist in "Modern Photographic Processing" - John Wiley and Sons - New York (1979) p. 220-224. Examples of such addenda include complexing agents for calcium and magnesium ions, present in hard water, e.g. ethylene diamine tetraacetic acid and analogous compounds. Further can be present anti-foaming agents, surface-active agents, biocides, thickening agents like polystyrene sulphonate and antioxidants like benzoate and cyclodextrine, The developing liquid can contain so-called anti-sludge agents in order to reduce dirt streaks on developed photographic material. Finally the solution can contain development accelerating agents like polyalkyleneoxides and alkonolamines and hardening agents including latent hardeners.

The silver halide photographic materials which can be processed by the method of the present invention include all kinds of black-and-white materials, e.g. films and papers for amateur photography, films for cinematography, materials for radiographic recording and materials for graphic arts.

The replenishment can be performed on a regular time interval basis and/or based on film throughput, pH-measurement, halide ion concentration measurement and density measurements on test strips.

The present invention is illustrated by the following examples without however being limited thereto :

EXAMPLES

Example 1

Daily, 10 m^2 graphic arts silver halide film having a silver halide coverage equivalent to 7.3 g of silver nitrate per sq.m. and containing a silver chlorobromide emulsion with a halide composition of 83.6 mole % of chloride, 16 mole % of bromide and 0.4 mole % of iodide were exposed in such conditions that about 50

% of the silver halide was developable. Then the total amount film was processed in an Agfa Rapiline 66A processor having a tank solution volume of 17 l. The development time applied was 30 s and the temperature was kept constant at 35 C.

Replenishment of the developer solution was performed at the following rates : 250 ml of the replenisher were added per sq.m. of said film for compensation of developer exhaustion; an extra 250 ml of the replenisher were added per 24 h for compensation of aerial oxidation.

During a period of 28 days the pH of the developing solution was measured daily and the sensitometry was evaluated daily by means of test strips of the same film exposed through a continuous tone wedge. Different processing methods were used :

Processing method A : The composition of the developing solution (Da) was the same as the composition of the replenishing solution (Ra). This composition was :

Water	600ml
K_2CO_3	20g
K_2SO_3	65g
KBr	10g
Sodium iso-ascorbate . 1 aq.	45g
1-phenyl-3-pyrazolidone	0.5g
1-phenyl-5-mercaptotetrazole	0.006g
KOH	16.6g
Water to 1 l. pH = 10.70	

Processing method B : the same processing method was used as method A, but both solutions contained a higher concentration of buffering agent and ascorbic acid developing agent. The composition of developer Db and replenisher Rb was :

Water	600ml
K_2CO_3	61g
K_2SO_3	65g
KBr	10g
Iso-ascorbic acid	60g
1-phenyl-3-pyrazolidone	0.5g
1-phenyl-5-mercaptotetrazole	0.015g
KOH	17g
Water to 1 l. pH = 10.50	

Processing method C : following compounds differed in their concentration between the developing solution and the replenishing solution : 1-phenyl-3-pyrazolidone, 1-phenyl-5-mercaptotetrazole and KOH. These compositions were :

Composition of the developing solution (Dc) :

Water	600ml
K_2CO_3	61g
K_2SO_3	65g
KBr	10g
iso-ascorbic acid	60g
1-phenyl-3-pyrazolidone	0.5g
1-phenyl-5-mercaptotetrazole	0.039g
KOH	11g
Water to 1 l. pH = 9.90	

Composition of the replenishing solution (Rc) :

Water	600ml
K_2CO_3	61g
K_2SO_3	65g
KBr	10g
iso-ascorbic acid	60g
1-phenyl-3-pyrazolidone	0.6g
1-phenyl-5-mercaptotetrazole	0.045g
KOH	20.7g
Water to 1 l. pH = 10.70	

In table 1 the values of the pH of the developing solution and the gradations of the test strips (measured between densities 3 and 3.8) are compared in function of time for the three processing methods.

TABLE 1

Time (days)	Method A		Method B		Method C	
	pH	grad.	pH	grad.	pH	grad.
0	10.70	8.35	10.50	9.27	9.99	8.51
7	9.84	7.84	10.10	8.84	10.00	8.15
14	9.66	5.13	9.97	8.56	10.03	8.50
21	-	-	9.96	8.60	10.01	8.49
28	-	-	9.90	8.50	10.00	8.48

Only processing method C gives satisfactory results. The increase of buffering agent concentration decreases the pH drop in the developing solution. A constant pH value is only reached by means of replenishment with a solution at a higher pH value than the developing solution (method C).

Example 2

In an automatic continuous processor, having a tank solution volume of 1 l, 6 m^2 exposed silver halide film, the same as in example 1, were processed. The development time applied was 30 s and the temperature was kept constant at 35 C.

The pH of the developer was measured after every sq.m. of developed film. Different processing methods were used :

Processing method D : the composition of the developing solution is the same as the composition of the replenishing solution. The replenishment amounted to 250 ml per sq.m. developed film. The composition of developer Dd and replenisher Rd was :

Water	600ml
K_2CO_3	61g
K_2SO_3	65g
KBr	10g
Ascorbic acid	50g
1-phenyl-4-hydroxymethyl-4'-methyl-3-pyrazolidone	4.2g
1-phenyl-5-mercaptotetrazole	0.08g
KOH	8.5g
Water to 1 l.	
pH = 10.15	

Processing method E : replenishment was performed with a solution at a higher pH than the pH of the developing bath at an amount of 250 ml per sq.m. developed film. The compositions were :

Composition of the developing solution De :

Water	600ml
K_2CO_3	61g
K_2SO_3	65g
KBr	10g
Ascorbic acid	50g
1-phenyl-4-hydroxymethyl-4'-methyl-3-pyrazolidone	4.2g
1-phenyl-5-mercaptotetrazole	0.08g
KOH	8.0g
Water to 1 l.	
pH = 10.10	

Composition of the replenishing solution Re :

Water	600ml
K_2CO_3	61g
K_2SO_3	65g
KBr	10g
Ascorbic acid	60g
1-phenyl-4-hydroxymethyl-4'-methyl-3-pyrazolidon	4.2g
1-phenyl-5-mercaptotetrazole	0.08g
KOH	20.7g
Water to 1 l.	
pH = 10.73	

Processing method F : the amount of replenishing solution per sq.m. developed film was decreased from 250 ml (processing method E) to 200 ml and the pH of the replenishing solution was incrased from 10.73 to 10.83. The compositions were :

Composition of the developing solution Df : the same as De.

Composition of the replenishing solution Rf :

Water	600ml
K_2CO_3	61g
K_2SO_3	65g
KBr	10g
Ascorbic acid	60g
1-phenyl-4-hydroxymethyl-4'-methyl-3-pyrazolidon	4.2g
1-phenyl-5-mercaptotetrazole	0.08g
KOH	23g
Water to 1 l. pH = 10.83	

The pH values of the developing solutions in function of the amount of the developed film are compared for processing method D, E and F. The results are summarized in table 2.

TABLE 2

Film area (sq.m.)	pH		
	Method D	Method E	Method F
1	10.15	10.10	10.05
2	10.04	10.11	10.05
3	9.99	10.09	10.07
4	9.77	10.07	10.06
5	9.72	10.12	10.06
6	9.41	10.11	10.06

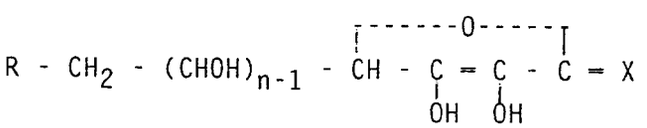
Replenishment with a solution having the same composition as the developing solution leads to a gradual decrease in pH of the developer. From table 2 it follows that the amount of replenishing solution per sq.m. film can be decreased without affecting the stability of the developer if the pH of the replenisher is raised sufficiently.

Claims

1. Method for processing with constant activity image-wise exposed silver halide photographic material, comprising following steps :

(a) developing photographic material in a continuous automatic way by means of a developing solution containing an ascorbic acid analogue or derivative or a salt thereof represented by general formula (I), and a 3-pyrazolidone derivative as developing agents ;

(I)



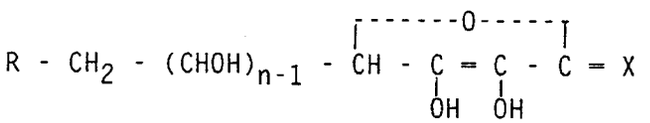
wherein X represents an oxygen atom or an imino group, and
n represents a positive integer from 1 to 4, and
R represents a hydroxy group when n is 1, and R represents a hydroxy group or a hydrogen atom when n is 2 to 4.

(b) replenishing said developing solution by means of at least one replenishing composition, which is a solution having a higher pH than the developing solution and comprising substantially the same ingredients as the developing solution, so that the pH of said developing solution is maintained

constant.

2. Method for processing with constant activity image-wise exposed silver halide photographic material, comprising following steps :
   (a) developing photographic material in a continuous automatic way by means of a developing solution containing an ascorbic acid analogue or derivative or a salt thereof corresponding to general formula (I), and a 3-pyrazolidone derivative as developing agents ;

(I)



   wherein X represents an oxygen atom or an imino group, and
   n represents a positive integer from 1 to 4, and
   R represents a hydroxy group when n is 1, and R represents a hydroxy group or a hydrogen atom when n is 2 to 4.
   (b) replenishing said developing solution by means of at least one replenishing composition which is a powder comprising substantially the same ingredients as the developing solution and alkali in such an amount that the pH of said developing solution is maintained constant by adding said powder periodically to said developing solution.

3. Method according to claim 1 wherein the pH of said developing solution is comprised between 9.5 and 10.8, and the pH of the replenishing solution is comprised between 9.7 and 11.5, with the proviso that the pH of said replenishing solution is at least 0.2 units higher than the pH of said developing solution.

4. Method according to claim 1 or 3 wherein said developing and replenishing solutions further contain buffering agents chosen from the list of carbonate, phosphate and metaborate.

5. Method according to any of claims 1, 3 or 4 wherein said developing and replenishing solutions further contain anti-fogging agent in a concentration between $5x10^{-5}$ and $8x10^{-3}$ mole/liter.

6. Method according to claim 5 wherein said anti-fogging agent is 1-phenyl-5-mercaptotetrazole.

7. Method according to any of claims 1 and 3 to 6 wherein said developing and replenishing solutions further contain a sulphite ions providing compound in a concentration between 0.1 and 2 mole/liter.

8. Method according to any of claims 1 and 3 to 7 wherein said developing and replenishing solutions further contain a halide ions providing compound in a concentration between 0.01 and 0.2 mole/liter.

9. Method according to any of claims 1 and 3 to 8 wherein said ascorbic acid analogue or derivative represented by said general formula (I) is l-ascorbic acid or iso-ascorbic acid, or a salt thereof, in a concentration in said developing and replenishing solutions between 0.1 and 0.8 mole/liter.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 1656

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.5)
Y	EP-A-0 461 783 (AUDENRIED W KNAPP) * page 6, line 20 - line 28 *	1-9	G03C5/31
Y	T.H.JAMES (ED) 'The theory of the photographic process fourth edition' 1977 , MACMILLAN PUBLISHING CO.,INC , NEW YORK USA *Page 291,equation (11.1)* * page 291, left column, paragraph 3 *	1-9	
D,Y	US-A-4 228 234 (E OKUTSU ET AL) * column 7, line 11 - line 12 * * column 7, line 57 - line 60 *	1-9	
D,Y	US-A-4 081 280 (H J CORLUY ET AL) * column 2, line 58 - line 65 * * column 3, line 29; example 1 *	1-9	
A	JOURNAL OF IMAGING TECHNOLOGY vol. 10, no. 6, December 1984, SPRINGFIELD US pages 212 - 216 T N HENDRICKSON ET AL 'The critical role of sulfite in the re-use of photographic solutions' * page 214, right column, line 1 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C
Y	US-A-3 826 654 (G R WEISS ET AL) * column 3, line 28 - line 30; example 1 *	6	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 FEBRUARY 1993	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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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

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