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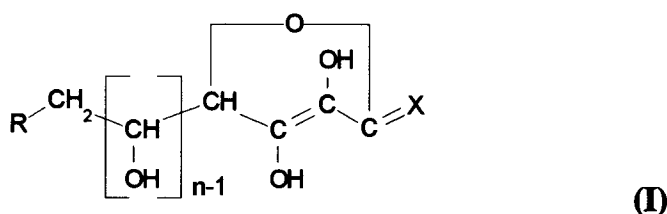
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(54) Photographic silver halide developer composition and method

(57) The present invention provides a black-and-white aqueous alkaline photographic developer composition and a method of processing an exposed photographic silver halide element comprising the steps of developing by means of a developer comprising a silver halide developing agent and treating the developed element with a fixer composition, wherein the developer composition, free of dihydroxybenzene developing agents, comprises :

a) a developing agent corresponding to general formula (I), its salts and mixture thereof:



wherein X represents an oxygen atom or an imino group;

n represents a positive integer from 1 to 4, and

R represents a hydroxy group when n is 1, and a hydroxy group or a hydrogen atom when n is 2 to 4;

b) a superadditive auxiliary developing agent; and

c) a combination of carbonate and borate compounds as buffering agents.

EP 0 736 802 A1

Description**FIELD OF THE INVENTION**

5 The invention relates to a black-and-white photographic developing composition free of dihydroxybenzene developing agent that is stable against aerial oxidation and to a process for forming a photographic image using said developing composition.

BACKGROUND OF THE INVENTION

10 Black-and-white photographic elements, such as for example photographic materials useful both in X-ray radiography and in Graphic Arts, are typically processed in aqueous alkaline developing solutions containing a dihydroxybenzene developing agent, such as hydroquinone, and a superadditive auxiliary developing agent. Example of useful superadditive auxiliary developing agents are aminophenols and 3-pyrazolidones. Thus, for example, in the working
 15 examples of US 4,975,354, the developing solution comprises hydroquinone and 1-phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone and in the working examples of US 4,914,003 and 5,030,547 the developing solution comprises hydroquinone and N-methyl-p-aminophenol.

While development processes based on the use of hydroquinone generally provide very good results, they are disadvantageous with regard to ecological and environmental considerations. In particular, hydroquinone and its derivatives, and the oxidized forms thereof, have become of increasing concern in recent years from the point of view of
 20 potential toxicity and environmental pollution. Thus, there is an urgent need in the art for a development process, useful with such elements, which utilizes a developing solution that is highly stable, which exhibits its high developing capacity and which is more ecologically favorable than the developing solutions utilized heretofore because it does not require the use of hydroquinone.

25 Ascorbic acid developing agents have been utilized heretofore in a wide variety of photographic developing processes. Thus, for example, US 2,688,548 and 2,688,549 disclose developing solutions containing a 3-pyrazolidone developing agent, an ascorbic acid developing agent, a sulfite preservative, such as sodium sulfite, and an alkaline buffering agent, such as sodium carbonate. GB 1,266,533 describes the combination of a p-hydroxybenzene developing agent, ascorbic acid and sulfite ions. US 3,826,654 discloses the combination of a 3-pyrazolidone, ascorbic acid and an
 30 heterocyclic thione or thiol and an alkali iodide at pH of at least 12. US 3,942,985 describes the combination of an iron chelate developer and an ascorbic acid developer. US 3,022,168 describes a developing composition containing ascorbic acid and an activating developer such as N-methyl-p-aminophenol. US 3,512,981 discloses developing composition containing a dihydroxybenzene developing agent, such as hydroquinone, a sulfite and an ascorbic acid developing agent. US 3,870,479 discloses a lithographic-type diffusion transfer developing containing an ascorbic acid developing
 35 agent. US 4,168,977; 4,478,928 and 4,650,746 disclose the use of an ascorbic acid developing agent in processes in which a high contrast photographic element is developed in the presence of a hydrazine compound.

In recent years there has been an increasing interest in the use of ascorbic acid. US 5,236,816 and 5,264,323 disclose a free of hydroquinone developing solution having a pH in the range of from 9.5 to 11.5 and comprising an ascorbic acid developing agent, a superadditive auxiliary developing agent and a carbonate buffering agent in a
 40 concentration of at least 0.5 molar. The developing solution is particularly useful in a process for forming a high contrast image utilizing a silver halide photographic element comprising a hydrazine compound which functions as a nucleating agent and an amino compound which functions as an incorporated booster.

US 5,098,819 and 5,278,035 disclose a non-toxic, non-hydroquinone and non-alkali metal hydroxide containing photographic developing composition comprising an ascorbic acid type developer together with a sulfite, a 3-pyrazolidone and an auxiliary developing agent. The composition has a pH in the range of from 9.75 to 10.6, the ascorbic acid
 45 type developer is in an amount of at least about 15 grams and the sulfite in an amount of from 2 to 20 grams. In the developing composition disclosed in US 5,098,819, an alkali metal carbonate in an amount of from 15 to 30 grams is also required, while an anti-swelling agent selected from the group consisting of sodium sulfate and glutaraldehyde is required in the developing composition disclosed in US 5,278,035.

50 EP Patent Application 603,586 discloses a concentrated photographic silver halide developing solution comprising ascorbic acid and at least one basic compound the anion of which is carbonate, sulfite or hydroxide, one basic compound the cation of which is sodium or potassium, and the sodium potassium ion ratio in the concentrated developing solution being from 50:50 to 0:100. A developing solution containing ascorbic acid and high potassium level is also described in US 5,376,510 and in Research Disclosure 35249, August 1993.

55 WO 93/11,456 describes an improved system for rapid access processing of photographic silver halide elements containing a hydrazine compound, the developing solution containing ascorbic acid.

US 5,196,298 describes a photographic developing solution for immersion development showing a pH higher than 12 and containing more than 0.4 moles/liter of a sugar derivative, such as ascorbic acid.

EP Patent Application 531,582 discloses a developing solution having a pH higher than 12.0 and containing ascorbic acid stabilized by a compound, such as a salicylic acid.

EP Patent Application 552,511 discloses a method for controlling the alkalinity of a developing solution containing ascorbic acid, maintaining it at a desired constant pH level by means of a redox potential measuring system.

EP Patent Application 573,700 discloses a method for processing with constant activity image-wise exposed silver halide photographic material comprising the steps of a) developing by means of a developing solution containing ascorbic acid and a 3-pyrazolidone derivative as developing agents and b) replenishing said developing solution by means of at least one replenishing solution having a higher pH than the developing solution.

EP Patent Application 588,408 discloses a photographic developing solution containing ascorbic acid and a mixture of at least two 3-pyrazolidone type developing agents.

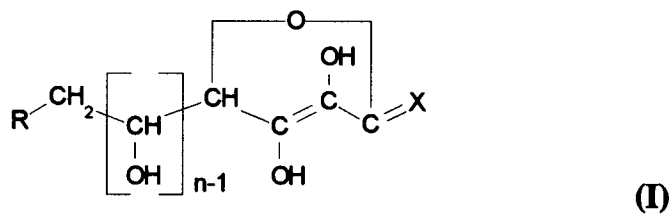
WO 95/00,881 discloses a non-hydroquinone developing composition comprising ascorbic acid, an auxiliary developing agent, an alkali metal sulfite in an amount less than or equal to 0.32 moles per liter, an alkali metal carbonate in an amount of 0.1 to 0.4 moles per liter and an alkali metal hydroxide in an amount less than 25 g per liter.

The photographic developing compositions free of hydroquinone, known in the art, have the problem of not being stable against aerial oxidation.

SUMMARY OF THE INVENTION

The present invention relates to a black-and-white aqueous alkaline photographic developer composition, free of dihydroxybenzene developing agents, comprising :

a) a developing agent corresponding to general formula (I), its salts or mixture thereof:



wherein X represents an oxygen atom or an imino group,

n represents a positive integer from 1 to 4, and

R represents a hydroxy group when n is 1, and a hydroxy group or a hydrogen atom when n is 2 to 4;

b) a superadditive auxiliary developing agent; and

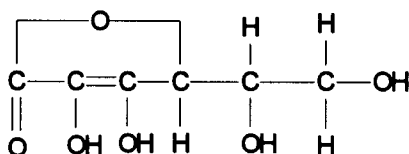
c) a combination of carbonate and borate compounds as buffering agents.

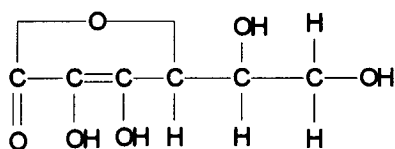
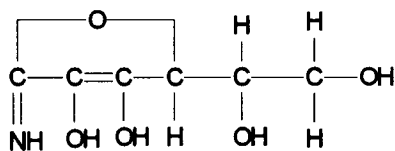
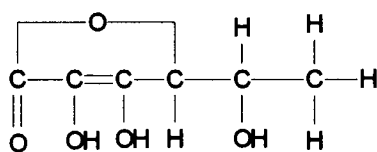
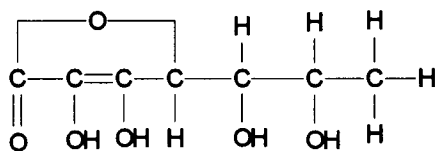
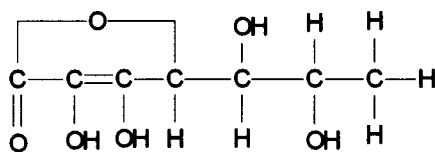
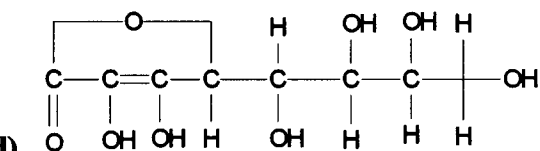
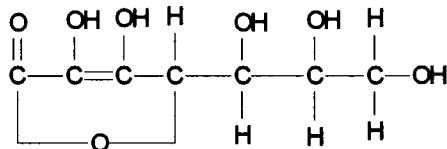
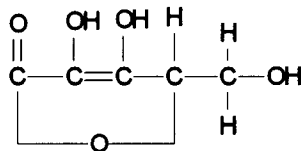
The developing composition of the present invention is more stable against aerial oxidation because there is only a little decrease in the pH level, when the developing composition is stored under room conditions in an open air storage container.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, preferred developing agents are 1-ascorbic acid and iso-ascorbic acid. Examples of developing agents corresponding to general formula (I) are hereinbelow reported, but the invention is not limited to these Examples.

1.1 (l-ascorbic acid)



1.2 (iso-ascorbic acid)**1.3 (imino-l-ascorbic acid)****1.4 (6-desoxy-l-ascorbic acid)****1.5 (l-rhamnoascorbic acid)****1.6 (l-fucoascorbic acid)****1.7 (d-glucoheptoascorbic acid)****1.8 (d-glucoascorbic acid)****1.9 (l-erythroascorbic acid)**

These compounds can be dissolved into the developing composition in their free acid form; alternatively, they can be incorporated as an alkali salt, preferably sodium, lithium or potassium salt or a mixture.

The useful amount of developing agents is from 0.01 to 0.9 moles per liter, preferably from 0.05 to 0.5 moles per liter, in ready-to-use composition.

The auxiliary developing agents showing a superadditive effect are well known in the art, as described in Mason *"Photographic Processing Chemistry"*, Focal Press, London 1975.

For the purpose of the present invention, the preferred superadditive auxiliary developing agents are those described in US 5,236,816; particularly useful are the superadditive auxiliary developing agents such as, for example, 1-phenyl-3-pyrazolidone (also known as Phenidone), substituted pyrazolidones, such as, for example, 1-phenyl-4-methyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone (also known as Dimezone S) and 1-phenyl-4,4-dimethyl-3-pyrazolidone (also known as Dimezone), 1-p-tolyl-3-pyrazolidone, 1-m-tolyl-3-pyrazolidone, 1-p-chlorophenyl-3-pyrazolidone, 5-phenyl-3-pyrazolidone, 1-methyl-5-phenyl-3-pyrazolidone, 1-p-methoxyphenyl-3-pyrazolidone, and the like; aminophenols and substituted aminophenols, such as, for example, N-methyl-p-aminophenol (also known as Metol) and 2,4-diaminophenol.

The amount of such superadditive auxiliary developing agent used in the present invention is from about 0.0001 to 0.15 moles per liter, preferably from 0.0025 to 0.1.

According to the present invention, a combination of carbonate and borate compounds as buffering agents is required to prevent the pH decreasing due to the oxidation products of sugar type derivatives developing agents. The carbonate buffering agent can be sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, etc. The borate buffering agent can be boric acid, sodium borate, potassium borate, sodium tetraborate, potassium tetraborate, alkanolamine borate, such as diethanolamine borate or triethanolamine borate, and the like.

The amount of carbonate buffering agent is from 0.01 to 0.45 moles per liter, preferably from 0.1 to 0.4 moles per liter. The amount of borate buffering agent is from 0.01 to 1.0 moles per liter, preferably from 0.1 to 0.8 moles per liter in ready-to-use composition.

The developer composition of this invention contain an antioxidant compound in a quantity sufficient to give good stability characteristics, from about 0.001 to about 1 mole per liter. Useful antioxidant compounds include the sulfite preservatives, i.e. any sulfur compound capable of forming sulfite ions in aqueous solutions, such as alkali metal or ammonium sulfites, bisulfites, metabisulfites, sulfurous acid and carbonyl-bisulfite adducts. Typical examples of sulfite preservatives include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium bisulfite, lithium bisulfite, sodium metabisulfite, potassium metabisulfite, lithium metabisulfite, bisulfite formaldehyde addition compound sodium salt, and the like.

Antifoggant agents, known in the art to eliminate fog on the developed photographic silver halide films, can be used in the developer composition of this invention. They include, for example, organic antifoggant agents, such as derivatives of benzimidazole, benzotriazole, tetrazole, imidazole, indazole, thiazole, mercaptotetrazole, etc. used alone or in combination. The organic antifoggants are well known as discussed, for example, in Mees, *The Theory of the Photographic Process*, 3rd Edition, 1966, p. 344-346. Derivatives of benzotriazole are preferred in the practice of the invention, as described in EP 182,293. Said derivatives include lower alkyl groups (having 1 to 4 carbon atoms), such as 5-methyl-benzotriazole, lower alkoxy groups (having 1 to 4 carbon atoms) or halogen (chlorine) substituted benzotriazole antifoggant agents.

At least an inorganic alkali agent is used in the developer composition of this invention to achieve the preferred pH range which normally is above 10. The inorganic alkali agent includes KOH, NaOH, etc.

Other adjuvants well known in the art are comprised in the developer compositions of this invention. These include inorganic antifogging agents such as soluble halides (e.g., potassium or sodium bromide) and sequestering agents such as aminopolycarboxylic acid derivatives (e.g., nitriloacetic acid (NTA), ethylenediaminetetracetic acid (EDTA), diethylenetriaminopentacetic acid (DTPA), diaminopropanoltetracetic acid (DPTA), triethylenetetraminohexacetic acid, hydroxyethylenediaminotriacetic acid, ethylenediamino-N,N,N',N'-tetrapropionic acid (EDTP)), α -hydroxycarboxylic acid compounds (e.g., lactic acid), dicarboxylic acid compounds (e.g., oxalic acid and malonic acid), polyphosphate compounds (e.g., sodium hexametaphosphate) or polyphosphonic acid compounds (e.g., methylaminophosphonic acid, dimethylaminomethane diphosphonic acid, morpholino diphosphonic acid as described in US 4,873,180) and/or their salts.

The photographic developer composition of this invention can vary widely with respect to the concentration of the various ingredients included therein. Typically, the sugar type derivatives developing agent is used in an amount of from about 0.01 to about 0.9 moles per liter, preferably from about 0.05 to about 0.5 moles per liter; the superadditive auxiliary developing agent is used in an amount of from about 0.0001 to about 0.15 moles per liter, preferably from about 0.0025 to about 0.1 moles per liter; the carbonate buffering agent is used in an amount of from about 0.01 to about 0.45 moles per liter, preferably from about 0.1 to about 0.4 moles per liter; the borate buffering agent is used in an amount of from about 0.01 to about 1.0 moles per liter, preferably from about 0.1 to about 0.8 moles per liter; the inorganic antifogging agent is used in an amount of from about 0.001 to about 0.2 moles per liter, preferably from about 0.01 to about 0.05 moles per liter; the antioxidant compound (such as the sulfite preservative) is used in an amount of from about 0.001 to about 1 moles per liter, preferably from about 0.08 to about 0.7 moles per liter; the organic antifogging compound is used in an amount of from about 1×10^{-5} to about 5×10^{-2} moles per liter, preferably from about 5×10^{-4} to 0.01

moles per liter and the sequestering agent is used in an amount of from about 0.0001 to about 0.2 moles per liter, preferably from about 0.001 to about 0.1 moles per liter.

According to the present invention, it is deemed to be significant to evaluate the stability of the developer composition of the present invention as absorbance variation (measured at 450 nm) when a sample of 100 ml developer solution is stored under room conditions in a 1000 ml open "volumetric flask", a flat-bottomed flask with a long neck, in contact with air for significant times, for instance of one, two or three days (from a practical point of view two days and, still better, three days are a particularly significant time since they represent a week-end work stop).

Making reference to a three-day period of time, the stability of a developing bath can be said to be significantly improved according to the present invention when the absorbance, measured under the above specified conditions with a LAMBDA 5 spectrophotometer of Perkin Elmer, tends to remain at the same levels, i.e. with a variation lower than 0.1.

Of course, both the pH of the solution and the storing temperature will affect the obtained results. The higher the values of such variables, the higher in general the measured absorbance values.

Alternatively and preferably additionally, a developer composition can be considered to be stable when its pH is stable. In the present invention, a developer composition can be considered to be unstable when after three days under the above reported conditions its pH varies an absolute value of at least 0.2 units when the pH is measured four times after mixing: 1) at mixing (as the base pH), 2) 24 hours after mixing, 3) 48 hours after mixing, and 4) 72 hours after mixing. Each "change" being a measurement of the difference in pH from the previous pH reading. The developer composition can be considered to be stable when pH varies of an absolute value lower than 0.2 units. The term "absolute value" obviously means that the total variation and the single variation it consists of are counted independently from their sign: a first variation from 0 to -0.2 and a further variation from -0.2 to +0.2, for instance, herein mean a total variation in absolute value of 0.6.

The developer composition of the present invention can be usually made as single concentrated liquid part that is then diluted with water in automatic processors by the use of a mixer, to have a ready-to-use solution. A method of making a concentrated alkaline photographic composition packaged in a single concentrated part to be diluted with water to form a ready-to-use solution is skown, for example, in US 4,987,060.

The developer compositions of the present invention are useful in a process for treating a silver halide photographic element which can be used for any general black and white photography, graphic arts, X-ray, print, microfilm, coupler reversal (i.e., in the black and white development step of a color reversal process), and the like, as described, for example, in EP patent applications 632,323; 622,670; 618,490; 595,089; 591,747 and 581,065.

The following examples illustrates the present invention.

In the examples, percentages are by weight and solutions are water solutions, unless otherwise stated.

EXAMPLE

Ready-to-use developer compositions (samples 1 to 6) were prepared according to the following Table 1:

Table 1

	1 g/l	2 g/l	3 g/l	4 g/l	5 g/l	6 g/l
Water up to liter	1	1	1	1	1	1
KOH sol. 35%	15	90	-	-	-	-
NaOH sol. 35%	-	-	110	110	110	110
4-Morpholinyl-Methylene Diphosphonic Acid sol. 40%	-	-	5	5	5	5
DTPA.Na sol. 40%	2	2	5	5	5	5
Potassium Sulfite	30	30	-	-	-	-
Sodium Sulfite	-	-	25	25	25	25
Potassium Bromide	4	4	4	4	4	4
Potassium Hydrogen Carbonate	-	-	40	40	-	-
Potassium Carbonate	100	54	-	-	-	-
Benzotriazole	0.2	0.2	0.2	0.2	0.2	0.2
Dimezone S	2.5	2.5	2.5	0.2	0.2	0.2
Ascorbic Acid	35	35	30	30	30	30
Boric Acid	-	30	30	-	30	54
pH at 20°C	10.3	10.3	10.2	10.2	10.2	10.2

Developer composition 1 is a reference composition containing ascorbic acid as developing agent, Dimezone S as superadditive auxiliary developing agent and a carbonate compound as only buffering agent, as described in Research Disclosure 35,249, August 1993. Developer composition 2 (invention) is made as reference composition 1, with the addition of borate compound to have a double buffering system including both carbonate and borate compounds. Developer composition 3 (invention) is another example of composition containing ascorbic acid as developing agent, Dimezone S as superadditive auxiliary developing agent and a double buffering system including both carbonate and borate compounds. Developer compositions 4 to 6 (comparison) are made as developer composition 3, but containing only a single buffering agent (carbonate or borate compounds).

Developer compositions 1 to 6 were checked through the following test: samples of 100 ml of each developer were put into an open glass calibrated flask (capacity 1000 ml) and the oxidation test through a continuous air contact was made in stressed conditions by the use of Dubnoff thermostatic bath 38°C and constant agitation for 8 hours/day. At regular intervals, pH at 20°C and absorbance at 450 nm were measured. The higher and faster the increasing of these characteristics, the lower the stability against air oxidation of the developer composition. A developer composition is considered useful against aerial oxidation when it shows good results both considering the pH test and the absorbance test.

The values of the pH and of the absorbance at 450 nm for the developer compositions stored for different hours are respectively reported hereinbelow in Tables 2 and 3.

Table 2

Developer Compositions	pH Values			
	Fresh	24 hours	48 hours	72 hours
1 (reference)	10.30	10.15	10.05	9.88
2 (invention)	10.20	10.14	10.07	10.03
3 (invention)	10.20	10.16	10.12	10.05
4 (comparison)	10.25	9.99	9.82	9.68
5 (comparison)	10.20	10.02	9.83	9.74
6 (comparison)	10.22	10.06	9.93	9.88

Table 3

Developer Compositions	Absorbance			
	Fresh	24 hours	48 hours	72 hours
1 (reference)	0.05	0.07	0.20	0.36
2 (invention)	0.01	0.01	0.02	0.02
3 (invention)	0.01	0.02	0.03	0.03
4 (comparison)	0.05	0.12	0.27	0.30

Table 2 shows that reference developer composition 1 and comparison developer compositions 4 to 6 have a pH decrease. The only samples having a little decreasing of pH values are developer compositions 2 and 3 of the present invention, containing a double buffering system (carbonate and borate). Also the absorbance test confirmed the good properties of sample 2 and 3 of the present invention, compared with the bad results of reference developer composition 1 and of comparison developer composition 4, both not containing borate buffering agents in combination with carbonate buffering agents.

Developer compositions of the present invention, showing a very little decreasing in the pH value, also allow to use a replenishing composition having the same pH value of the basic developer composition, while in the art the replenishing developing composition using ascorbic acid as developer agent have a pH higher than the basic developer composition, as showed in EP 573,700, due to the decrease of the pH values of such basic developer composition.

Strips of a Graphic Arts 3M DRC (Daylight Rapid Contact) Film (Film 1), comprising a chlorobromide emulsion $\text{AgBr}_{0.02}\text{Cl}_{0.98}$ of narrow grain size distribution and mean grain size of 0.20 micrometers, prepared by the conventional double jet procedure and coated onto a subbed polyester base at a silver coverage of 2.5 grams per square meter, were exposed in a sensitometer consisting of a 500 watt tungsten filament light source attenuated by a 0-4 continuous neutral image density wedge in contact with the film sample. Sensitometric tests were made by developing the exposed strips at a temperature of 35°C and development time of 38 seconds using developer compositions 1 and 2 in a Durr-Processor 260 Type, a developing processor made by Durr-Dental GmbH & Co.K.G., then fixing at a temperature of 35°C and fixing time of 30 seconds in a 3M Fix-Roll fixing solution. Sensitometric results include Dmin, Dmax, Speed, Toe contrast, Average contrast and Shoulder contrast. The Toe contrast corresponds to the absolute value of the slope of the line joining the density points of 0.07 and 0.17 above Dmin. The Average contrast corresponds to the absolute value of the slope of the line joining the density points of 0.10 and 2.50 above Dmin and the Shoulder contrast corresponds to the absolute value of the slope of the line joining the density points of 1.60 and 4.00 above Dmin. The sensitometric test was carried out measuring each day the sensitometric values, without replenishment for five days. Table 4 reports the sensitometric values of the fresh developer composition and after five days.

Table 4

Developer Compositions	Dmin	Dmax	Speed	Toe	Average	Shoulder
1 (fresh)	0.03	5.49	0.72	0.97	6.10	8.90
1 (after 5 days)	0.03	5.43	0.68	1.20	6.02	8.70
2 (fresh)	0.03	5.50	0.78	0.98	5.96	8.70
2 (after 5 days)	0.03	5.52	0.77	0.91	6.23	8.83

Table 4 shows that developer composition 2 of the present invention had more stability in the sensitometric values than reference developer composition 1, in particular with reference to Dmax, Speed and Toe contrast.

Strips of a hard dot Graphic Arts Kodak 2000 Film (Film 2), comprising a chlorobromide emulsion $\text{AgBr}_{0.30}\text{Cl}_{0.70}$ of narrow grain size distribution and mean grain size of 0.23 micrometers, a hydrazine compound which functions as a nucleator and an amino compound which functions as an incorporated booster, were exposed and developed as Film 1, the developing time being in this case 50 seconds. The sensitometric results are shown in Table 5.

Table 5

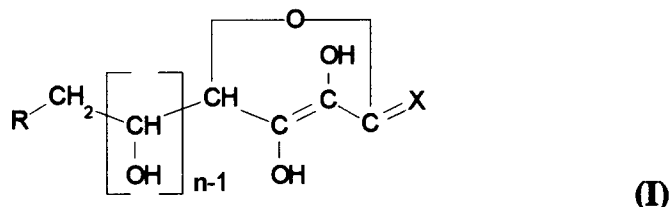
Developer Compositions	Dmin	Dmax	Speed	Toe	Average	Shoulder
1 (fresh)	0.03	5.32	3.40	2.51	18.3	22.4
1 (after 5 days)	0.03	5.30	3.41	2.55	17.8	21.6
2 (fresh)	0.03	5.20	3.38	2.32	12.2	15.3
2 (after 5 days)	0.03	5.28	3.39	2.51	15.2	20.0

Table 5 shows that developer composition 2 of the present invention had more stability in the sensitometric values than reference developer composition 1.

Claims

1. Black-and-white aqueous alkaline photographic developer composition, free of dihydroxybenzene developing agents, comprising :

a) developing agent corresponding to general formula (I), its salts or mixture thereof:



wherein X represents an oxygen atom or an imino group;

n represents a positive integer from 1 to 4, and

R represents a hydroxy group when n is 1, and a hydroxy group or a hydrogen atom when n is 2 to 4;

b) a superadditive auxiliary developing agent; and

c) a combination of carbonate and borate compounds as buffering agents.

2. Black-and-white aqueous alkaline photographic developer composition of claim 1 wherein the developing agent is a 1-ascorbic acid or iso-ascorbic acid or a salt thereof.

3. Black-and-white aqueous alkaline photographic developer composition of claim 1 wherein the developing agent is used in an amount of from about 0.01 to about 0.90 moles per liter.

4. Black-and-white aqueous alkaline photographic developer composition of claim 1 wherein the superadditive auxiliary developing agent is a 3-pyrazolidone derivative.

5. Black-and-white aqueous alkaline photographic developer composition of claim 1 wherein the superadditive auxiliary developing agent is a 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone.

6. Black-and-white aqueous alkaline photographic developer composition of claim 1 wherein the carbonate buffering agent is used in an amount of from about 0.01 to about 0.45 moles per liter.

7. Black-and-white aqueous alkaline photographic developer composition of claim 1 wherein the borate buffering agent is used in an amount of from about 0.01 to about 1.00 moles per liter.

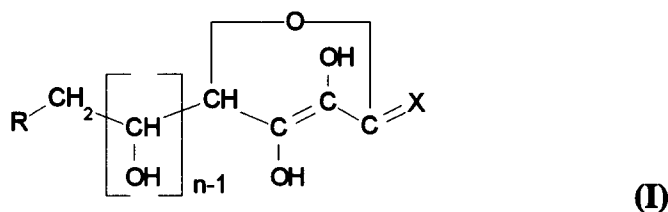
8. Black-and-white aqueous alkaline photographic developer composition of claim 1 comprising at least a sequestering agent selected from the group consisting of aminopolycarboxylic acid and polyphosphonic acid.

9. Black-and-white aqueous alkaline photographic developer composition of claim 1 comprising :

- a) a developing agent of formula (I) in an amount of from about 0.01 to about 0.9 moles per liter;
- b) a superadditive auxiliary developing agent in an amount of from about 0.0001 to about 0.15 moles per liter;
- c) a carbonate buffering agent in an amount of from about 0.01 to about 0.45 moles per liter;
- d) a borate buffering agent in an amount of from about 0.01 to about 1.0 moles per liter;
- e) an inorganic antifogging agent in an amount of from about 0.001 to about 0.2 moles per liter;
- f) an antioxidant compound in an amount of from about 0.001 to about 1 moles per liter;
- g) a sequestering agent in an amount of from about 0.0001 to about 0.2 moles per liter;
- h) an organic antifogging agent in an amount of from about 1×10^{-5} to about 5×10^{-2} moles per liter;
- i) an inorganic alkali agent to have a pH in the range 9 to 13, and
- l) water to make one liter.

10. Process for forming a black-and-white photographic silver image comprising the steps of (1) imagewise exposing a silver halide photographic element and (2) developing the exposed element, said developing being effected with a black-and-white aqueous alkaline photographic developer composition, free of dihydroxybenzene developing agents, comprising :

- a) a developing agent corresponding to general formula (I), its salts or mixture thereof:



wherein X represents an oxygen atom or an imino group;

n represents a positive integer from 1 to 4, and

R represents a hydroxy group when n is 1, and a hydroxy group or a hydrogen atom when n is 2 or 4;

b) a superadditive auxiliary developing agent; and

c) a combination of carbonate and borate compounds as buffering agents.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 10 4995

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)
Y	EP-A-0 588 408 (AGFA-GEVAERT NV) * page 3, line 49 - line 51 * * page 2, line 24 - line 30 * ---	1-10	G03C5/30 G03C5/305
Y	US-A-5 236 816 (M D PUROL ET AL) * column 3, line 40 - line 55; claim 1 * ---	1-10	
Y	US-A-3 022 168 (O N STJÄRNKVIST) * column 3, line 51 - line 64 * ---	1-10	
Y	EP-A-0 632 323 (MINNESOTA MINING AND MANUFACTURING CO.) * page 5, line 27; claim 1; table 4 * * page 11, line 53 - line 55 * * page 12, line 48 - line 58 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		5 September 1995	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 P : intermediate document 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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