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(54) Colour photographic developer concentrate

(57) A two-part colour photographic developer concentrate in which part 1 contains at least one antioxidant, at least one auxiliary solvent, at least one optical brightener and at least one colour developer substance and part 2 contains at least one buffer substance, alkali and at least one water softener, may be produced by part 1 additionally containing 0.001 to 1 mol of hydroxylamine or a monoalkylated hydroxylamine or the salts thereof per litre of concentrate.

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Description

[0001] The developer solution for developing colour photographic materials, in particular for developing colour photographic paper, is prepared from or, in the case of continuous operation, replenished with concentrates which contain the necessary constituents.

[0002] It is conventional to provide three different concentrates, as certain constituents of the developer bath are not mutually compatible on extended storage. Thus, for example, one concentrate contains the antioxidant, an auxiliary solvent and an optical brightener, a second concentrate contains the colour developer substance, for example CD 3 (N-ethyl-N-(2-methylsulfonylaminoethyl)-3-methyl-p-phenylenediamine) and a third concentrate contains the buffer substance, alkali and a water softener.

[0003] The first concentrate is alkaline (approx. pH 10), the second is strongly acidic and thus stable with regard to colour developer concentration and the third is strongly alkaline. A small quantity of sulfite is generally added to the concentrate of the colour developer substance for stabilisation purposes. The quantity of sulfite must not be too large as it otherwise has a negative impact on sensitometry (inhibition of development and thus reduction of colour densities).

[0004] There has been no lack of attempts to develop stable, one-part colour developer concentrates as handling errors during preparation or replenishing of a developer solution may consequently be avoided.

[0005] Two one-part concentrates are currently commercially available, a) Monoline® RA-4 CD-R from Tetenal, a two-phase concentrate with a solid, undissolved phase deposited at the bottom and b) TriPhase® RA-4 CD-R from Trebla, a three-phase concentrate with undissolved constituents in the middle phase (c.f. also US 5 891 609).

[0006] In both cases, the presence of undissolved constituents is disadvantageous for the purposes of handling the concentrate. Especially when preparing the regenerating solution, problems may occur because the undissolved constituents dissolve only poorly.

[0007] The object of the invention was to provide a two-part concentrate for a colour developer, neither part of which contains any undissolved constituents, from which parts a regenerating solution may rapidly be produced and which parts comprise a single phase.

[0008] This object is achieved by part 1 of the two-part concentrate containing the antioxidant, the auxiliary solvent, the optical brightener, the colour developer substance and 0.001 to 1 mol of hydroxylamine or a monoalkylated hydroxylamine or the salts thereof per litre of concentrate.

[0009] Preferably, 0.005 to 0.3 mol of hydroxylamine or monoalkylated hydroxylamine or the salts thereof are used, particularly preferably hydroxylammonium sulfate.

Part 1 preferably has a pH of 1.5 to 6.

Part 2 of the two-part concentrate corresponds to the previous part 3, comprising the buffer substance, alkali and water softener.

[0010] Monoalkylated hydroxylamine is preferably of the formula

$$\text{HO-NH-R}$$

in which

R means C_1-C_{10}-alkyl, hydroxy-C_1 -C_{10}-alkyl, C_1-C_{10}-alkoxy-C_1 -C_{10}-alkyl, carboxy-C_2-C_{10}-alkyl, dicarboxy-C_1 -C_{10}-alkyl, carboxyhydroxy-C_1 -C_{10}-alkyl, hydroxy-C_1 -C_5-alkyl-(oxy-C_1 -C_5-alkyl)$_n$, C_1 -C_5-alkoxy-C_1 -C_5-alkyl-(oxy-C_1-C_5-alkyl)$_n$ or aryl and

n means a number from 1 to 4.

Examples

[0011] The following Examples describe concentrated (parts 1, 2 and 3, or parts 1 and 2), from which developer solutions were prepared in the stated manner. A portion of each of the concentrates was stored for 1 week at 60°C before use and then compared with the freshly produced concentrates. Table 1 shows the differences in yellow fog of a material based on silver chloride emulsions which was processed with these developer solutions.

Example 1 (Comparison)

Part 1

[0012]

Polyethylene glycol, average MW 400	300 ml
Diethylhydroxylamine, 85 wt.% aqueous solution (DEHX solution)	120 ml
Optical brightener	20 g
Water to make up to	1000 ml
pH 10	

Part 2

[0013]

CD 3	280 g
Sodium disulfite	10 g
Water to make up to	1000 ml
pH 1	

Part 3

[0014]

Potassium hydroxide	65 g
Potassium carbonate	600 g
EDTA	3 g
Water to make up to	1000 ml
pH 14	

[0015] The colour of the stored concentrates is unchanged in comparison with the fresh preparations.

[0016] A colour developer working solution was then prepared from these concentrates. 35 ml of part 1, 17.5 ml of part 2 and 35 ml of part 3 were used per litre. The pH is adjusted to 10.2 with potassium hydrogen carbonate. 2 g of potassium chloride were added per litre. The preparation is light yellow and clear and thus matches the preparation made from the fresh, unstored concentrates.

[0017] Photographic materials were processed in these two preparations. The two processed materials (in fresh, unstored concentration or in stored concentrate) exhibit no sensitometric differences (Table 1).

Example 2 (Comparison)

[0018] In this Example, parts 1 and 2 from Example 1 were combined to form a new part 1 of the following composition. Since not all the substances from part 1 of Example 1 dissolve at pH 1, the pH value was raised.

[0019] Part 2 is identical to part 3 of Example 1.

Part 1

[0020]

Polyethylene glycol of an average MW of 400	375 ml
DEHX solution	150 ml
Optical brightener	25 g
CD 3	250 g
Sodium disulfite	6.2 g
Water to make up to	1000 ml
pH 5	

[0021] The colour of the stored concentrate, part 1, is distinctly darkened and deep brown in comparison with the fresh preparations.

[0022] A colour developer working solution was then prepared from these concentrates. 28 ml of part 1 and 35 ml of part 2 were used per litre. The pH is adjusted to 10.2 with potassium hydrogen carbonate. 2 g of potassium chloride are added per litre. The preparation is dark and turbid, while the preparation made from the fresh, unstored concentrates is light in colour and clear.

Example 3 (Comparison)

[0023] As Example 2, but the part 1 concentrate is adjusted to pH 3.

[0024] The colour of the stored part 1 concentrate is distinctly darkened and deep brown in comparison with the fresh preparations.

[0025] The preparation is dark and turbid, while the preparation made from the fresh, unstored concentrates is light in colour and clear.

Example 4 (Comparison)

[0026] As Example 2, but the sulfite is omitted from the part 1 concentrate.

[0027] The colour of the stored concentrate, part 1, is distinctly darkened and deep brown.

Example 5 (According to the invention)

[0028] As Example 3, but the sodium disulfite is replaced by 5 g of hydroxylammonium sulfate.

[0029] The colour of the stored concentrate, part 1, is unchanged in comparison with the fresh preparation.

Example 6 (According to the invention)

[0030] As Example 2, but with 150 g of caprolactam instead of the polyethylene glycol and additionally with 5 g of hydroxylammonium sulfate.

[0031] The colour of the stored concentrate, part 1, is unchanged in comparison with the fresh preparation.

Example 7 (According to the invention)

Part 1

[0032]

Triethanolamine	250 ml
HADS*	120 g
Optical brightener	25 g
CD 3	250 g
Hydroxylammonium sulfate	5 g
Water to make up to	1000 ml
pH 3	

* Diethylhydroxylamine disulfo acid

[0033] Part 2 is identical to part 3 of Example 1.

[0034] The colour of the stored concentrate, part 1, is identical to that of the fresh preparation.

Table 1

(Yellow fog of processed material)

	Yellow D_{min} x 1000	
	fresh	stored
Example 1 (Comparison)	114	116
Example 2 (Comparison)	114	137
Example 3 (Comparison)	115	155
Example 4 (Comparison)	113	132
Example 5 (Invention)	114	116
Example 6 (Invention)	113	115
Example 7 (Invention)	114	116

Table 2

(CD 3 loss due to storage of concentrate for 1 week at 60°C)

	CD 3 content [g/l]	
	fresh	stored
Example 1 (Comparison)	5.0	4.8
Example 2 (Comparison)	5.0	4.1
Example 3 (Comparison)	5.0	3.8
Example 4 (Comparison)	5.0	4.3

Table 2 (continued)

(CD 3 loss due to storage of concentrate for 1 week at 60°C)		
	CD 3 content [g/l]	
	fresh	stored
Example 5 (Invention)	5.0	4.8
Example 6 (Invention)	5.0	4.7
Example 7 (Invention)	5.0	4.9

[0035] It is evident that only the two-part concentrates according to the invention achieve the performance of the three-part concentrate with regard to yellow fog and stability.

Claims

1. Two-part colour photographic developer concentrate in which part 1 contains at least one antioxidant, at least one auxiliary solvent, at least one optical brightener and at least one colour developer substance and part 2 contains at least one buffer substance, alkali and at least one water softener, characterised in that part 1 additionally contains 0.001 to 1 mol of hydroxylamine or a monoalkylated hydroxylamine or the salts thereof per litre of concentrate.

2. Developer concentrate according to claim 1, characterised in that part 1 additionally contains 0.005 to 0.3 mol of hydroxylamine or a monoalkylated hydroxylamine or the salts thereof per litre of concentrate.

3. Developer concentrate according to claim 1, characterised in that part 1 contains N-ethyl-N-(2-methylsulfonylaminoethyl)-3-methyl-p-phenylenediamine as colour developer substance.

4. Developer concentrate according to claim 1, characterised in that part 1 has a pH of 1.5 to 6.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 1918

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.7)
X	DE 29 10 251 A (MINNESOTA MINING & MFG) 20 September 1979 (1979-09-20) * see example 1 *	1-4	G03C7/407 G03C7/44
A	DE 38 01 536 A (AGFA GEVAERT AG) 27 July 1989 (1989-07-27) * see comparative example (diethylhydroxylamine) *	1-4	
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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	25 July 2000	Okunowski, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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