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(54) **Colour photographic developer concentrate**

(57) A one-part, optionally multi-phase, colour developer concentrate which contains at least one colour developer substance, at least one auxiliary solvent, an

antioxidant, a buffer system and alkali, wherein the antioxidant is a mixture of 0.1 to 100 mmol of hydroxylamine and 0.01 to 4 mol of one or more substituted hydroxylamines, does not darken on storage.

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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 4-(N-ethyl-N-2-methylsulfonylaminoethyl)-2-methylphenylenediamine sesquisulfate (CD-3) and a third concentrate contains the buffer substance, alkali and a water softener.

[0003] 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.

[0004] 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).

[0005] 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. It is also disadvantageous to produce one-part concentrates which, while they contain no undissolved constituents, darken on storage.

[0006] The object of the invention was to provide a one-part, aqueous concentrate for a colour developer which contains no undissolved constituents and does not darken on storage.

[0007] This object is achieved in that the aqueous concentrate contains at least one colour development agent, at least one auxiliary solvent, alkali, a buffer substance and an antioxidant, wherein the antioxidant is a mixture of 0.1 to 100, preferably of 1 to 25 mmol of hydroxylamine and 0.01 to 4, preferably 0.1 to 2 mol of one or more substituted hydroxylamines.

[0008] In a preferred embodiment, the concentrate contains at most 0.1 mol of sulfate ions/L. The colour developer substance is, for example, added to the concentrate not as the sulfate, as is usual with CD-3, but instead as a phosphate, p-toluenesulfonate, chloride or as the free base.

[0009] CD-3 (sesquisulfate) may also be used and the sulfate ions removed by precipitation with metal ions and filtration.

[0010] A concentrate for the purposes of the invention is an aqueous preparation, 1 part by volume of which is diluted with 1 to 39 parts by volume of water in order to produce a ready-to-use solution; the concentrate contains at least 50 mmol, preferably 70 to 700 mmol of colour developer substance/L.

[0011] The present invention accordingly provides a one-part, optionally multi-phase, colour developer concentrate which contains at least one colour developer substance, an auxiliary solvent, a buffer system and alkali, characterised in that the concentrate contains an antioxidant, wherein the antioxidant is a mixture of 0.1 to 100, preferably 1 to 25 mmol of hydroxylamine and 0.01 to 4, preferably 0.1 to 2 mol of one or more substituted hydroxylamines.

[0012] The concentrate furthermore preferably contains at least one water softener.

[0013] Water-soluble organic solvents are in particular used as the auxiliary solvent.

[0014] Water-soluble organic solvents which may be considered are those from the range of glycols, polyglycols, alkanolamines, aliphatic and heterocyclic carbonamides, aliphatic and cyclic monoalcohols, wherein 50 to 95 wt.%, preferably 60 to 90 wt.% of the total of water and water-soluble solvent is water.

[0015] Suitable water-soluble organic solvents are, for example, carboxylic acid amide and urea derivatives such as dimethylformamide, methylacetamide, dimethylacetamide, N,N'-dimethylurea, tetramethylurea, methanesulfonamide, dimethylethyleneurea, N-acetyl glycine, N-valeramide, isovaleramide, N-butyramide, N,N-dimethylbutyramide, N-(2-hydroxyphenyl)acetamide, N-(2-methoxyphenyl)acetamide, 2-pyrrolidinone, ε-caprolactam, acetanilide, benzamide, toluenesulfonamide, phthalimide;

aliphatic and cyclic alcohols, for example isopropanol, tert.-butyl alcohol, cyclohexanol, cyclohexanemethanol, 1,4-cyclohexanedimethanol;

aliphatic and cyclic polyalcohols, for example glycols, polyglycols, polywaxes, trimethyl-1,6-hexanediol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol;

aliphatic and cyclic ketones, for example acetone, ethyl methyl ketone, diethyl ketone, tert.-butyl methyl ketone, diisobutyl ketone, acetylacetone, acetonylacetone, cyclopentanone, acetophenol;

aliphatic and cyclic carboxylic acid esters, for example trimethoxymethane, methyl acetate, allyl acetate, ethylene

glycol monomethyl ether acetate, ethylene glycol diacetate, glycerol 1-acetate, glycerol diacetate, methylcyclohexyl acetate, methyl salicylate, phenyl salicylate;

aliphatic and cyclic phosphonic acid esters, for example methylphosphonic acid dimethyl ester, allylphosphonic acid diethyl ester;

aliphatic and cyclic oxyalcohols, for example 4-hydroxy-4-methyl-2-pentanone, salicylaldehyde;

aliphatic and cyclic aldehydes, for example acetaldehyde, propanal, trimethylacetaldehyde, crotonaldehyde, glutaraldehyde, 1,2,5,6-tetrahydrobenzaldehyde, benzaldehyde, benzenepropane, terephthalaldehyde;

aliphatic and cyclic oximes, for example butanone oxime, cyclohexanone oxime;

aliphatic and cyclic amines (primary, secondary or tertiary), for example ethylamine, diethylamine, triethylamine, dipropylamine, pyrrolidine, morpholine, 2-aminopyrimidine;

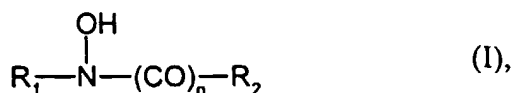
aliphatic and cyclic polyamines (primary, secondary or tertiary), for example ethylenediamine, 1-amino-2-diethylaminoethane, methyl-bis(2-methylaminoethyl)amine, permethyldiethylenetriamine, 1,4-cyclohexanediamine, 1,4-benzenediamine;

aliphatic and cyclic hydroxylamines, for example ethanolamine, 2-methylethylamine, 2-methylaminoethanol, 2-(diethylamino)ethanol, 2-(2-dimethylaminoethoxy)ethanol, diethanolamine, N-methyldiethanolamine, triethanolamine, 2-(2-aminoethylamino)ethanol, triisopropanolamine, 2-amino-2-hydroxymethyl-1,3-propanediol, 1-piperidineethanol, 2-aminophenol, barbituric acid, 2-(4-aminophenoxy)ethanol, 5-amino-1-naphthol.

[0016] Processing conditions, suitable colour developer substances, suitable buffer substances, suitable water softeners, suitable optical brighteners, auxiliary developers, wetting agents, development accelerators and antifogging agents are described on pages 102 to 107 of Research Disclosure 37 038 (February 1995).

[0017] Multi-phase means that the concentrate contains two or more liquid phases, but no precipitation. The liquid phases are, for example, an aqueous and an organic phase.

[0018] Suitable substituted hydroxylamines are of the formulae (I), (II) and (III).



in which

R_1 means optionally substituted alkyl,

R_2 means optionally substituted alkyl or optionally substituted aryl and

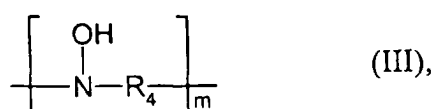
n means 0 or 1

preferably those in which at least one of the residues R_1 and R_2 contains at least one -OH, -COOH or -SO₃H group;



in which

R_3 means an optionally substituted alkyl or optionally substituted acyl group;



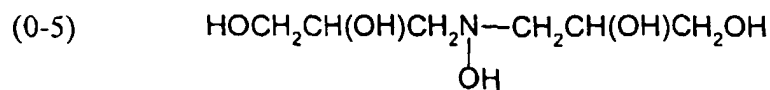
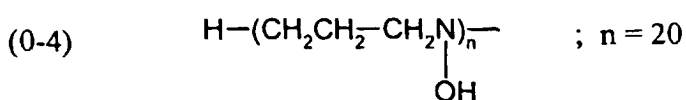
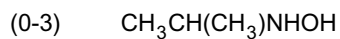
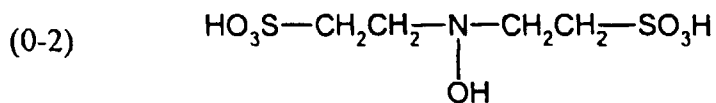
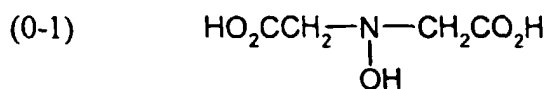
in which

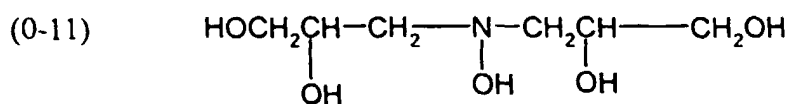
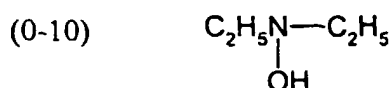
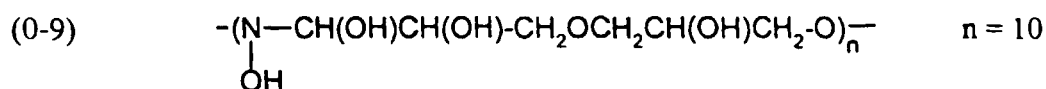
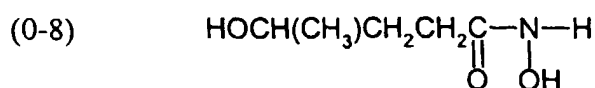
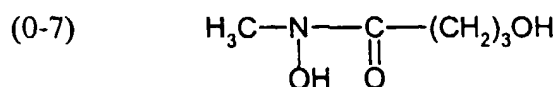
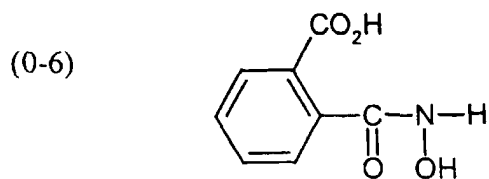
R_4 means an alkylene group optionally interrupted by O atoms and

m means a number of at least 2,

[0019] The alkyl groups R_1 , R_2 , R_3 , the alkylene group R_4 and the aryl group R_2 may bear further substituents in addition to the stated substitution.

[0020] Examples of suitable antioxidants are





[0021] Any phase boundaries which are present disappear on dilution of the concentrate with water to produce the ready-to-use colour developer or regenerator; the ready-to-use developer is one-phase.

[0022] For the purposes of storage 200 mL of concentrate are placed in a 250 mL beaker (tall form) and the beaker sealed with an air-tight film (for example PARAFILM "M" ® from American National Can, Chicago). The concentrates are stored for two months at room temperature or 4 weeks at 40°C.

Examples

Example 1 (Comparison)

[0023] The constituents listed below of a colour developer regenerator are combined in a concentrate (the ready-to-

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use regenerator is produced from the concentrate by dilution with water):

[0024] One-part, one-phase developer concentrate:

Diethylhydroxylamine, 85 wt.% aqueous solution (DEHX soln.)	35 mL
CD 3, base	31 g
Diethylene glycol	30 mL
Optical brightener W1	2 g
Ethylenediaminetetraacetic acid (EDTA)	10 g
Potassium carbonate	60 g
adjust to pH 13.5 with KOH and make up to 1 litre with water.	

[0025] The concentrate undergoes distinct darkening on storage.

Example 2 (Comparison)

[0026] One-part, one-phase developer concentrate:

Antioxidant O-2	35 g
CD 3, base	31 g
Diethylene glycol	30 mL
Optical brightener W1	2 g
EDTA	10 g
Potassium carbonate	60 g
adjust to pH 13.5 with KOH and make up to 1 litre with water.	

[0027] The concentrate undergoes distinct darkening on storage.

Example 3 (Comparison)

[0028] One-part, one-phase developer concentrate:

DEHX soln.	35 mL
Sodium sulfite	0.5 g
CD 3, base	31 g
Diethylene glycol	30 mL
Optical brightener	2 g
Polymaleic acid anhydride, 50% by weight aq. solution	15 mL
Potassium carbonate	60 g
adjust to pH 13.5 with KOH and make up to 1 litre with water.	

[0029] The concentrate undergoes distinct darkening on storage.

Example 4 (Comparison)

[0030] One-part, one-phase developer concentrate:

DEHX soln.	35 mL
Sodium sulfite	2 g
CD 3, base	31 g
Diethylene glycol	30 mL
Optical brightener	2 g
EDTA	10 g
Potassium carbonate	60 g

(continued)

adjust to pH 13.5 with KOH and make up to 1 litre with water.

5 [0031] The concentrate undergoes distinct darkening on storage.

Example 5 (according to the invention)

10 [0032] One-part, one-phase developer concentrate:

DEHX soln.	35 mL
CD 3, base	31 g
Hydroxylammonium sulfate	0.5 g
Diethylene glycol	30 mL
Optical brightener	2 g
EDTA	10 g
Potassium carbonate	60 g
adjust to pH 13.5 with KOH and make up to 1 litre with water.	

[0033] The concentrate is light yellow and does not darken on storage.

Example 6 (according to the invention)

25 [0034] One-part, one-phase developer concentrate:

Antioxidant O-2	35 g
Hydroxylammonium sulfate	0.5 g
CD 3, base	31 g
Diethylene glycol	30 mL
Optical brightener	2 g
EDTA	10 g
Potassium carbonate	60 g
adjust to pH 13.5 with KOH and make up to 1 litre with water.	

[0035] The concentrate is light yellow and does not darken on storage.

40 **Example 7** (Comparison)

[0036] One-part, multi-phase developer concentrate:

DEHX solution	60 mL
CD 3, base	45 g
Caprolactam	100 g
Triethanolamine	80 mL
Optical brightener	10 g
Diethylenetriamine pentaacetic acid	40 g
Potassium carbonate	165 g
KOH	42 g
adjust to pH 11.2 with KOH and make up to 1 L with water.	

55 [0037] The upper phase of the concentrate undergoes distinct darkening on storage.

Example 8 (Comparison)**[0038]** One-part, multi-phase developer concentrate:

5	DEHX solution	60 mL
	Sodium sulfite	2 g
	CD 3, base	45 g
	Caprolactam	100 g
10	Triethanolamine	80 mL
	Optical brightener	10 g
	EDTA	30 g
	Potassium carbonate	165 g
15	KOH	42 g
	adjust to pH 11.2 with KOH and make up to 1 L with water.	

[0039] The upper phase of the concentrate undergoes distinct darkening on storage.**Example 9** (according to the invention)**[0040]** One-part, multi-phase developer concentrate

25	DEHX solution	60 mL
	Hydroxylammonium sulfate	0.6 g
	CD 3, base	45 g
	Caprolactam	100 g
	Triethanolamine	80 mL
30	Optical brightener	10 g
	EDTA	30 g
	Potassium carbonate	165 g
	KOH	42 g
35	adjust to pH 11.2 with KOH and make up to 1 L with water.	

[0041] The upper phase of the concentrate is light yellow and does not darken on storage.**Example 10**

[0042] A colour photographic recording material was produced by applying the following layers in the stated sequence onto a layer support of paper coated on both sides with polyethylene. Quantities are stated in each case per 1 m². The silver halide application rate is stated as the corresponding quantities of AgNO₃.

Layer structure 1

- [0043]**
- 1st layer (substrate layer):
0.1 g of gelatine
- 2nd layer (blue-sensitive layer):
Blue-sensitive silver halide emulsion (99.5 mol% AgCl, 0.5 mol% AgBr, average grain diameter 0.9 µm) prepared from
0.50 g of gelatine
0.42 g of yellow coupler GB-1
0.18 g of yellow coupler GB-2
0.50 g of tricresyl phosphate (TCP)
0.10 of stabiliser ST-1

3rd layer (interlayer):

1.1 g of gelatine

0.06 g of scavenger SC-1

0.06 g of scavenger SC-2

0.12 g of TCP

4th layer (green-sensitive layer):

Green-sensitive silver halide emulsion (99.5 mol% AgCl, 0.5 mol% AgBr, average grain diameter 0.47 μm) prepared from

0.40 g of AgNO_3

0.77 g of gelatine

0.21 g of magenta coupler PP-1

0.15 g of magenta coupler PP-2

0.05 g of magenta coupler PP-3

0.06 g of colour stabiliser ST-2

0.12 g of scavenger SC2

0.23 g of dibutyl phthalate

5th layer (UV protective layer):

1.15 g of gelatine

0.03 g of scavenger SC-1

0.03 g of scavenger SC-2

0.5 g of UV absorber UV-1

0.10 g of UV absorber UV-2

0.35 g of TCP

6th layer (red-sensitive layer):

Red-sensitive silver halide emulsion (99.5 mol% AgCl, 0.5 mol% AgBr, average grain diameter 0.5 μm) prepared from

0.30 g of AgNO_3 with

1.0 g of gelatine

0.40 g of cyan coupler BG-1

0.05 g of cyan coupler BG-2

0.46 g of TCP

7th layer (UV protective layer):

0.35 g of gelatine

0.15 g UV-1

0.03 g UV-2

0.09 g of TCP

8th layer (protective layer):

0.9 g of gelatine

0.3 g of hardener HM

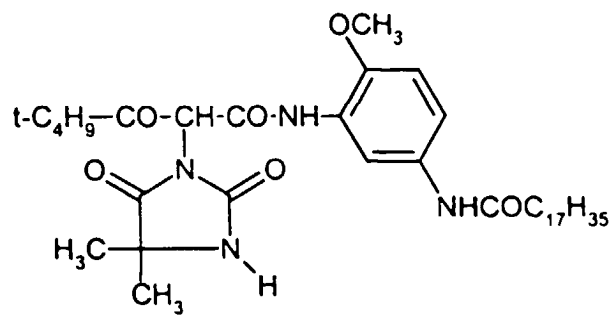
0.05 g of optical brightener W-1

0.07 g of vinylpyrrolidone

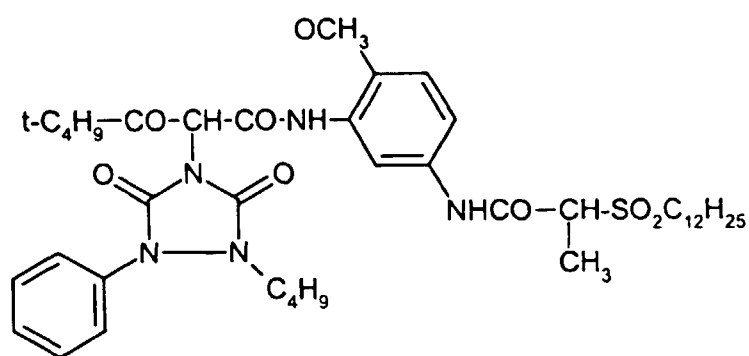
1.2 mg of silicone oil

2.5 mg of polymethyl methacrylate microspheres with an average particle diameter of 0.8 μm .

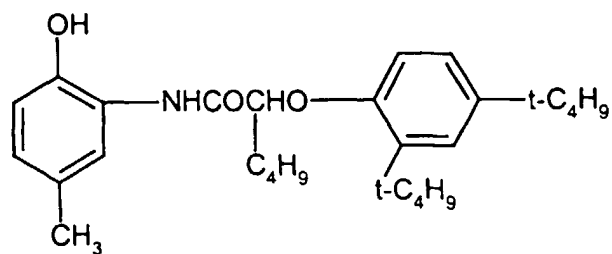
GB-1



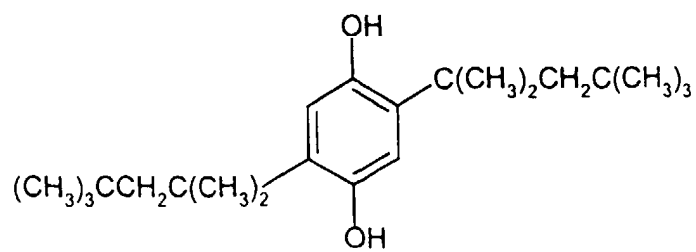
GB-2



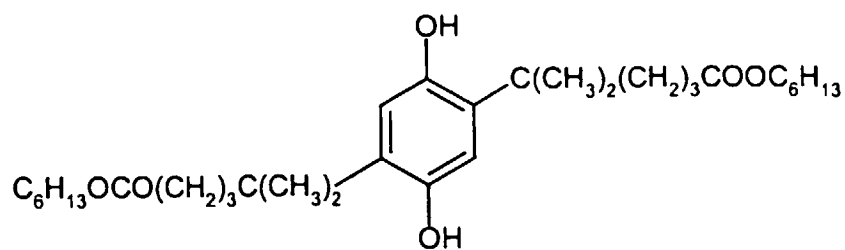
ST-1



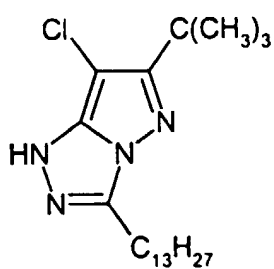
SC-1



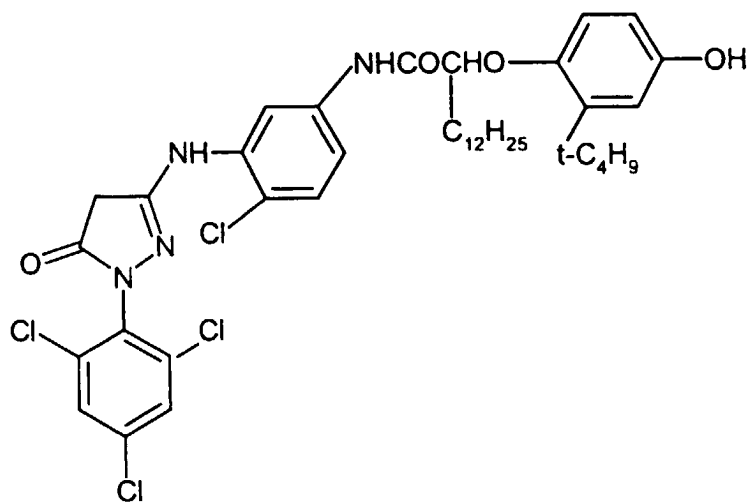
SC-2



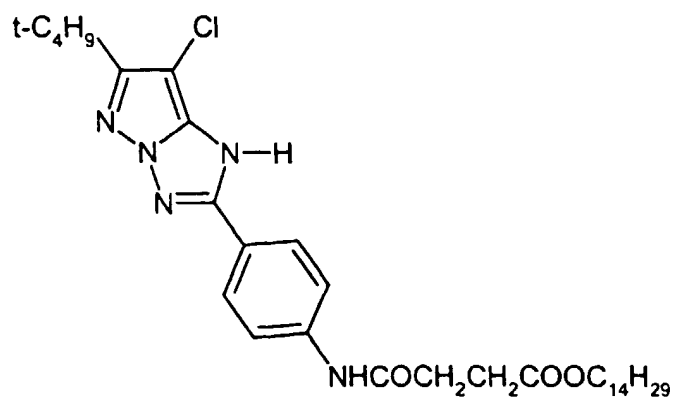
PP-1



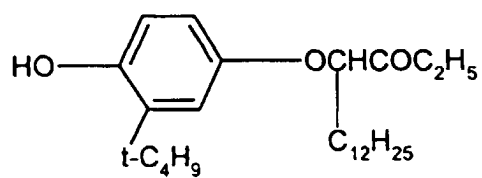
PP-2



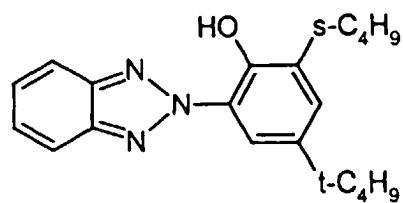
PP-3



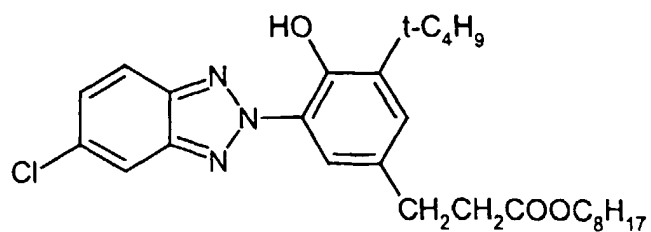
ST-2



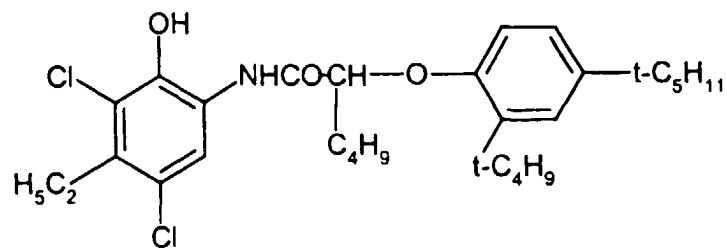
UV-1



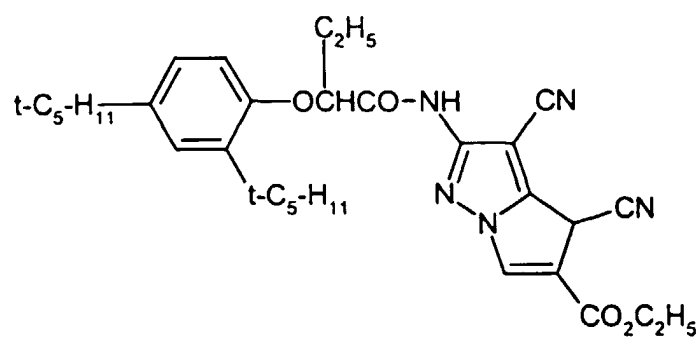
UV-2



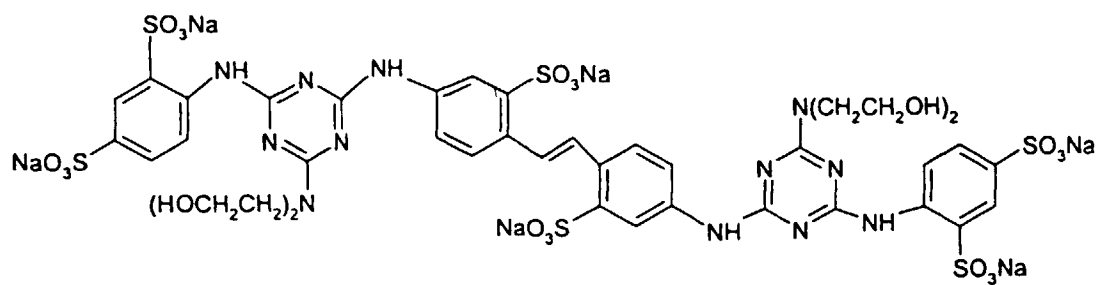
BG-1



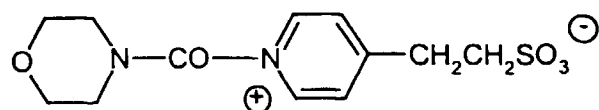
BG-2



W-1



HM



[0044] The colour photographic recording material is exposed and processed under the following conditions:

Step	Time	Temperature
Development	27 sec	39°C
Bleach/fixing	27 sec	35°C
Stabilisation	54 sec	33°C

[0045] The colour developers used were ready-to-use developers prepared from the concentrates according to Examples 1 to 9.

Bleach/fixing bath	
Ammonium thiosulfate solution, 58 wt. %	100 mL
Sodium disulfite	5 g
Ammonium-iron EDTA, 48 wt. %	100 mL
make up with water to 1000 mL, adjust pH value to 6.0 with ammonia or acetic acid.	

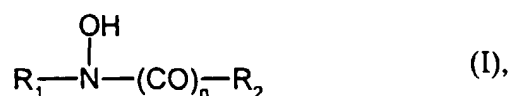
Stabilising bath	
Water	900 mL
Sodium sulfite	2 g
Hydroxyethanediphosphonic acid disodium salt	4 g
Sodium benzoate	0.5 g
make up with water to 1000 mL, adjust pH value to 5 with acetic acid.	

Drying

[0046] The resultant images exhibited no significant differences with regard to their sensitometric properties.

Claims

1. One-part, optionally multi-phase, colour developer concentrate which contains at least one colour developer substance, at least one auxiliary solvent, an antioxidant, a buffer system and alkali, characterised in that the antioxidant is a mixture of 0.1 to 100 mmol of hydroxylamine and 0.01 to 4 mol of one or more substituted hydroxylamines.
2. Colour developer concentrate according to claim 1, characterised in that it contains one or more water-soluble organic solvents as auxiliary solvent, wherein 50 to 95 wt. % of the total of water and solvent is water.
3. Colour developer concentrate according to claim 1, characterised in that the colour developer substance is 4-(N-ethyl-N-2-methylsulfonylaminoethyl)-2-methylphenylenediamine.
4. One-part colour developer concentrate according to claim 1, characterised in that the substituted hydroxylamine is of one of the formulae (I), (II) or (III):



in which

R_1 means optionally substituted alkyl,

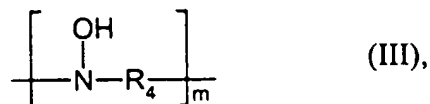
R_2 means optionally substituted alkyl or optionally substituted aryl and

n means 0 or 1;



in which

R_3 means an optionally substituted alkyl or optionally substituted acyl group;



in which

R_4 means an alkylene group optionally interrupted by O atoms and

m means a number of at least 2.

5. One-part colour developer concentrate according to claim 1, characterised in that it contains at most 0.1 mol of sulfate ions/L.
6. One-part colour developer concentrate according to claim 1, characterised in that it contains at most 0.05 mol of sulfate ions/L.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 20 3480

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)
D,A	US 5 891 609 A (PAPAI LASZLO) 6 April 1999 (1999-04-06) * see examples 1-2 and column 9, lines 3-22 *	1-6	G03C7/413 G03C7/44 G03C5/26
A	EP 0 528 406 A (KONISHIROKU PHOTO IND) 24 February 1993 (1993-02-24) * see claim 1 and page 2, lines 3-5 *	1-6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 18 December 2000	Examiner Okunowski, F
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			

EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 3480

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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