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PHOTOGRAPHIC DEVELOPER COMPOSITIONS

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2 Claims. (Cl. 96—66)

This invention relates to developer compositions for photographic silver halide emulsions, especially concentrated solutions which before use merely require to be diluted with water.

The use of the developing agent 1-phenyl-3-pyrazolidone is known. This agent is, however, unstable in alkaline solution and compositions containing it have tended to suffer from considerable loss in activity on storage. This loss of activity is very marked at high temperatures (for example 40–60° C.) and this causes considerable difficulty when the developer is required for use in a tropical climate. This instability is discussed in a paper by Alletag, Phot. Sci. Engng., 1959, 2, 213.

It is an object of the present invention to provide developer compositions of enhanced stability, which are suitable for use in tropical countries.

According to one aspect of the present invention, there is provided a developer composition in the form of a solution comprising at least one alkali metal normal sulphite as a preservative, at least one alkali and, as developing agents, 1-phenyl-3-pyrazolidone and both hydroquinone and chlorohydroquinone, said composition being capable of being prepared for use by mere dilution with water to yield a solution having a pH of 11.0 to 11.8. These compositions which are prepared for use merely by dilution with water are referred to hereinafter as developer concentrates.

Although the compositions of the invention are preferably in the form of the developer concentrate because this form is more economical to transport and store, they may, if desired, be sold as solutions which are sufficiently dilute to be ready for use and need not be diluted with water, and such solutions are included within the scope of the invention.

The developer compositions ready for use preferably have a pH of 11.0 to 11.5; a particularly convenient pH is 11.3. These pH values and the others in this specification are measured on a pH meter using a standard calomel electrode as a reference electrode and a glass electrode.

The compositions may with advantage contain in solution one or more of the following additional ingredients: a fog restraining agent, e.g. benzotriazole; a buffering agent, e.g. lactic acid or boric acid; and a silver halide solvent (i.e. a compound which converts the silver halide to a soluble complex ion), e.g. a thiocyanate or thiosulphate. Solutions containing such silver halide solvents and commonly known as monobaths perform a dual function, that is to say they develop and fix the photographic images. It is also advantageous that potassium compounds constitute the main source of alkali metal ions in the composition.

The alkali metal normal sulphite, which may be added as such or formed in situ by reaction of a bisulphite with an alkali metal hydroxide, is preferably sodium or potassium sulphite or a mixture of these. The alkali is preferably sodium or potassium hydroxide.

The solutions which are ready for use usually contain at least 0.2 gram per litre of 1-phenyl-3-pyrazolidone, at least 9 grams per litre of a mixture of hydroquinone and chlorohydroquinone, and at least 12 g. per litre of the alkali metal normal sulphite. In the concentrate, or in the working solution if it is sold as such, the maximum concentration of each of the ingredients must not exceed the solubility thereof in the composition within the temperature range of conditions of storage and use. The minimum concentration is, of course, dependent on the extent to which the composition is to be diluted before use, which in turn depends on the solubility of the ingredients and the purpose for which the developer is intended.

In a preferred embodiment of the invention, the developer composition comprises, besides 1-phenyl-3-pyrazolidone, chlorohydroquinone and hydroquinone as developing agents, caustic potash as the sole source of alkali, and potassium sulphite as preservative, the composition preferably including a buffering agent, e.g. lactic or boric acid.

Preferably, the developer concentrate contains as developing agents, 1-phenyl-3-pyrazolidone in an amount at least equal to 1 gram per litre, chlorohydroquinone in an amount at least equal to 25 grams per litre, hydroquinone in an amount at least equal to 25 grams per litre and potassium sulphite in amount at least equal to 200 grams per litre, the maximum concentration of all these ingredients not exceeding the solubility thereof in the concentrate within the temperature range of conditions of storage and use. Where, as is preferred, the composition comprises lactic acid, the amount of the additive in the formulation is preferably at least 10 grams per litre.

The invention is illustrated in the following examples.

Example I

A developer concentrate is formulated as follows:

Trisodium salt of N-hydroxyethylenediaminetriacetic acid (in the form of a 34% w./w. aqueous solution)	ml	20
Potassium sulphite	g	400
Chlorohydroquinone	g	51
Hydroquinone	g	51
1-phenyl-3-pyrazolidone	g	2.44
Benzotriazole	g	3.45
Potassium hydroxide	g	94.5
Lacetic acid	g	23.3

Water to make 1000 cc.

On dilution of 1 part by volume of the developer concentrate with 9 parts by volume of water, solutions of pH 11.3 suitable for developing photographic silver halide emulsions are obtained.

Four different batches tested at random over a period of about seven months confirmed the high degree of stability of the concentrate. The photographic activity of these batches was measured both before and after storage at 40° C. for six weeks. The loss of activity found was approximately forty times less than that occurring in one commercial brand of developer concentrate which possessed similar photographic properties, and which was known to contain 1-phenyl-3-pyrazolidone.

Examples II–VII

Developer concentrates similar to those of Example I are prepared merely by altering the amount of potassium hydroxide therein so as to obtain on dilution with nine times their volume of water compositions of various pH values which are ready for use.

Example No.	Concentration of potassium hydroxide, g./litre	pH of diluted composition
II	86.0	11.0
III	89.0	11.1
IV	91.5	11.2
V	96.5	11.4
VI	99.0	11.5
VII	102.0	11.6

The following data compare the stability of the diluted compositions of Examples I to VII against control composition which are identical with them except that they contain lesser quanties of potassium hydroxide giving solutions of pH below 11.0. The fall on storage in the value of the contrast (determined as gamma by conventional means) and speed (determined as Rel log *E* by conventional means) is an indication of the stability of the developer.

Composition	Gamma		Rel log *E*		pH
	Pre-storage	After storage for 12 weeks	Pre-storage	After storage for 12 weeks	
Control A	3.3	1.2	2.0	1.32	10.02
Control B	3.3	1.62	2.0	1.42	10.3
Control C	3.3	1.96	2.0	1.53	10.5
Control D	3.3	2.4	2.0	1.63	10.7
Example II	3.3	2.7	2.0	1.75	11.0
Example III	3.3	2.74	2.0	1.78	11.1
Example IV	3.3	2.8	2.0	1.80	11.2
Example I	3.3	2.9	2.0	1.83	11.3
Example V	3.3	3.0	2.0	1.87	11.4
Example VI	3.3	3.12	2.0	1.91	11.5
Example VII	3.3	3.26	2.0	1.97	11.6

We claim:

1. A developer concentrate comprising an aqueous solution of at least 1 gram per litre of 1-phenyl-3-pyrazolidone, at least 25 grams per litre of hydroquinone, at least 25 grams per litre of chlorohydroquinone, at least 200 grams per litre of an alkali metal sulphite of the formula M_2SO_3 (where M represents an alkali metal atom), at least 10 grams per litre of lactic acid and 86 to 108.5 grams per litre of potassium hydroxide.

2. A developer concentrate having the following composition for each 1000 cc.

A 34% by weight aqueous solution of the trisodium salt of N-hydroxyethylenediaminetriacetic acid	ml	20
Potassium sulphite	g	400
Chlorohydroquinone	g	51
Hydroquinone	g	51
1-phenyl-3-pyrazolidone	g	2.44
Benzotriazole	g	3.45
Potassium hydroxide	g	94.5
Lactic acid	g	23.3

Water to make 1000 cc.

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