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COLOR PHOTOGRAPHIC PROCESSING COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A liquid composition for color photographic liquid processing concentrate comprising

(1) benzyl alcohol or a homolog thereof,
(2) diethylene glycol,
(3) hydroxylamine hydrochloride, and
(4) water.

This invention relates to a composition of a component package for a color photographic processing. More particularly, the invention relates to an improved composition of a component package for the processing containing benzyl alcohol used for the development of color photographic materials.

A color photographic developer solution used for development of an exposed color photographic material contains generally a color developing agent which reduces silver halide having developing nuclei to form the oxidized developing agent which reacts with a coupler to form a dye, a preservative for preventing the deterioration of the developer solution by air oxidation, such as sodium sulfite or hydroxylamine; a suitable buffering agent to keep the pH of the solution constant and alkaline compounds for increasing the activity of the developing solution; an antifoggant for preventing the formation of undesirable fogs; and a solvent for couplers for accelerating the reaction of the developing agent with the couplers, such as benzyl alcohol. The developing solution may further contain a polyethylene glycol, a surface active agent, and an auxiliary developing agent.

In some cases, such a color photographic developing solution is prepared by mixing the necessary components before use and in other cases, commercially available prepared developer packages already containing the necessary components in correct weight ratios are used. The latter type of the developing composition is ordinarily called "prepared developer chemicals" or "prepared developer packages."

In the former case, it takes a fairly long and tedious time to prepare the color photographic developing solution by weighing correctly various kinds of components and dissolving them in water, the quality thereof is liable to be changed in each mix, and moreover the preparation of chemical mix requires much labor cost. Upon consideration of these points, the above-mentioned mixed developing composition is clearly profitable. In particular, a so-called liquid processing composition in which all the necessary components are dissolved in liquid is, as a matter of course, more profitable because a color photographic developing solution in a usable state can be readily prepared by only diluting the compositions with water before use. However, such a liquid-type prepared developer composition has the faults that the preservable period of it is short and in particular in a case of preparing the liquid-type prepared developer composition, the concentration thereof cannot be increased sufficiently owing to the restriction in solubility of each component.

A prepared developer composition is usually composed

of two to four component groups for the purpose of the preservability and the convenience for lab-working. By dissolving all the component parts or packages in water, a final use developer solution is prepared. The prepared developer composition is ordinarily composed of a component part containing a color developing agent and sodium sulfite, a component part containing an alkali and a buffering salt, and a component part containing benzyl alcohol and hydroxylamine.

This third composition part comprises a solvent for the coupler, hydroxylamine, a glycol, and water. As the solvent for the coupler, benzyl alcohol is usually used but phenylethyl alcohol of ω-phenylpropyl alcohol which is a homolog of benzyl alcohol may also be employed. Hydroxylamine for the composition has usually been used as the sulfate. The examples of the glycol are diethylene glycol, triethylene glycol, hexylene glycol and the like, and they are used for improving the solubility of the coupler solvent in water. It is far more advantageous to add the hydroxylamine to the third component part than to add it to another component part or parts from the point of stability but the component part has such a large fault that the highly concentrated composition is not prepared owing to the poor solubility of the components in each other.

Also, the third component part has such faults that the preservation temperature which is an important characteristic of the prepared liquid developing composition is largely influenced by the component part and the preservable period of time of the component part is short.

Therefore, an object of this invention to provide a prepared processing composition which contains an aqueous solution of benzyl alcohol and hydroxylamine in a highly concentrated state and can be stably preserved for a long period of time.

Another object of the invention is to provide a prepared composition for color photographic developer which can be stably preserved for a long period of time.

Still another object of the invention is to provide concentrated compositions for color photographic developers which can be stably preserved for a long period of time.

The above objects of our invention can be achieved by using the hydroxylamine as the hydrochloride thereof in the composition.

Hitherto, hydroxylamine sulfate has conventionally been employed in a color photographic developing solution, but the concentration of the component system is restricted to a very limited extent owing to the solubilities of benzyl alcohol, ethylene glycol, and water. And, the ratios of each component are also restricted from the solubilities of the components in each other, and hence the homogeneous solution can be prepared only in a definite range of the component ratios.

In fact, in order to prevent the occurrence of precipitation, at room temperature, in an aqueous solution containing 4 g. of hydroxylamine sulfate and 15 ml. of benzyl alcohol, the amount of diethylene glycol (hereinafter, it is shown as DEG) to the amount of water must be in the range as shown in the following table.

TABLE 1

Critical concentration (25° C.)

Hydroxylamine sulfate, g.	Benzyl alcohol, ml.	DEG, ml.		Water, ml.
		Lower limit	Upper limit	
4	15	17	17	15
4	15	18	30	20
4	15	19	40	25
4	15	20	75	25
4	15	22	130	25

Similarly, the amount of water necessary for the preparation of a homogeneous solution to each amount of DEG is limited to a narrow range, and the relations therebetween are shown in the following table.

TABLE 2

Ratio of water/DEG (25° C.) capable of providing homogeneous solution

Hydroxylamine sulfate, g.	Benzyl alcohol, ml.	DEG, ml.	Water, ml.	
			Lower limit	Upper limit
4	15	20	25	25
4	15	25	25	45
4	15	30	30	70
4	15	35	30	105

Accordingly, the necessary amounts of DEG and water for the preparation of the homogeneous liquid composition are more than 10 times that of hydroxylamine sulfate.

The preservability of this type of concentrated liquid composition is remarkably influenced by the temperature of storage, and in particular, when the storage temperature is lower than 10° C., the bad phenomena such as white precipitation deposition, and liquid-phase separation usually occur. In such states, when a final use developing solution is prepared by mixing the liquid composition with other compositions, the developing solution is imperfect and hence any normal photographic property for the developing solution can not be obtained. Since the influence of temperature is gradually increased as the concentration reaches the critical value of solubility, the concentration near the critical value must inevitably be avoided if it is desired to expand the range of temperature for the preservation. Accordingly, it is also difficult to prepare the highly concentrated liquid composition.

Hydroxylamine oxalate has an insufficient solubility and hence it is difficult as in the case of hydroxylamine sulfate to increase the concentration of the liquid composition by using hydroxylamine oxalate. Moreover the use of hydroxylamine oxalate has the fault that the liquid composition is liable to be deteriorated by oxidation.

Hydroxylamine base which has no acid has a sufficient soluibility but is remarkably liable to be oxidized and hence the preservable period of time is short and the use of hydroxylamine is quite impractical.

As mentioned above, the use of various kinds of hydroxylamines is accompanied with the above-mentioned faults but, when the hydroxylamine is used as the hydrochloride, the improved liquid composition excellent in stability to the preservative temperature and to oxidation can be prepared.

The ratio of DEG to water when the liquid composition containing hydroxylamine hydrochloride can be present as a homogeneous phase is shown in the following table.

TABLE 3

The DEG/water ratio of providing homogeneous liquid composition when the hydrochloride is used (25° C.)

Hydroxylamide hydrochloride, g.	Benzyl alcohol, ml.	DEG, ml.	Water, ml.	
			Lower limit	Upper limit
2	15	10	3	7
2	15	20	5	13
2	15	4.5	10	3
2	15	7.5	20	5

It is necessary that the ratio of water to diethylene glycol (DEG) in the liquid composition is 1:1.5 to 1:4.0 by volume, and if the content of water is larger or smaller than the above value, insoluble matter is formed and a homogeneous liquid composition is not obtained.

In the liquid composition the amount of benzyl alcohol and hydroxylamine hydrochloride are almost the same as

the case of using the sulfate, and thus the liquid composition has the same photographic effect. However, while the total amount of water and DEG in the liquid composition can not be reduced lower than 32 ml. when the sulfate is used, the amount can be reduced to 13 ml. when the hydrochloride is used according to the present invention.

Furthermore, such a concentrated liquid composition for the mixed processing composition has a higher preservative stability and shows excellent resistance to the deterioration by temperature change (particularly the formation of insoluble matter at lower temperature) and oxidation during preservation. Practically, when the temperature coefficient to the solubility in the case of using the hydrochloride is compared with that of the case of using the sulfate, the temperature coefficient is reduced to about 30% in the proper contents of DEG, water, and benzyl alcohol.

Also, the liquid composition in which the hydrochloride has been used has a sufficient acid property as in the case of using the sulfate and has a sufficient and practically usable stability to oxidation during preservation as compared with the case of using other salts of hydroxylamine such as the oxalate thereof or using hydroxylamine base.

The liquid composition for producing 1 liter of the mixed developing solution contains usually 0.5–4 g. of hydroxylamine hydrochloride, 4–20 ml. of benzyl alcohol, 10–100 ml. of DEG and water in the above-mentioned ratio and especially the liquid composition of this invention shows better effect when the total volume of the concentrated liquid is less than 50 ml.

Other composition to be used together with the liquid compositions containing benzyl alcohol and hydroxylamine hydrochloride of this invention may be conventional ones used generally for the purposes, which may be in the form of a liquid or solid and may be packaged in one or more parts.

Since the composition or part of the invention is in the liquid form, it may be only mixed, in use, with the other components or parts in the powder or liquid form.

For instance, the composition containing a developing agent contains as the developing agent at least one p-phenylenediamine type color developing agent such as

N,N-diethyl-p-phenylenediamine,
2-amino-5-diethylaminotoluene,
4-amino-N-ethyl-N-(β-methanesulfoamidoethyl)-m-toluidine,
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline,
N-ethyl-N-hydroxyethyl-p-phenylenediamine,

or the acid-addition salts thereof. Two or more developing agents may be used. The liquid composition usually contains further at least one preservative such as sodium sulfite, potassium sulfite, or potassium pyrosulfite. In some cases, the liquid composition contains further an antifoggant such as 6-nitrobenzimidazole, etc.

When the developing agent-containing composition mentioned above is a liquid composition, it is in a state that the components have been dissolved, in high concentration, in a proper solvent such as water, a mixture of water and triethylene glycol, a mixture of water and glacial acetic acid, or a mixture of water, glacial acetic acid and triethylene glycol.

The developing agent-containing composition for preparing 1 liter of the mixed developing solution contains usually about 1–12 g., preferably 4–8 g. of the developing agent and less than 5 g., preferably 0.5–2 g. of the sulfite.

The alkali-containing group or composition contains 1–50 g. of an alkaline salt such as sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium metaborate, potassium metaborate, sodium tertiary phosphate, potassium tertiary phosphate, disodium hydrogen phosphate, dipotassium hydrogen phosphate, borax or mixture thereof. The composition

further contains a buffering agent and a small amount of an alkali metal chloride, a bromide, an iodide, and aminopolycarboxylic acids such as ethylenediaminetetraacetic acid. This part may be in the form of a powder or an aqueous solution.

If necessary, other compositions containing other components for the developer solution may be employed.

The prepared processing liquid concentrates of this invention may be widely used for color photographic light-sensitive materials using silver halides, such as color papers, color negative films, reversal color films for color slides, reversal color papers for duplicates, color cinnefilms, and color positive films. That is to say, the photosensitive silver halide may be silver chloride, silver bromide, silver iodobromide, silver chlorobromide, and silver chloroiodobromide and also the coupler contained in the light-sensitive material may be a so-called oil protective type coupler or a coupler with a ballasting group and a water-solubilizing group.

The invention is explained in detail by the following examples.

EXAMPLE 1

The three component groups for preparing the developing solution are shown below.

Composition A:

Water	ml	3
Hydroxylamine hydrochloride	g	2
Benzyl alcohol	ml	15
Diethyl glycol	ml	4.5

Composition B:

Water	g	20
Potassium metaborate	g	30
Sodium sulfite	g	2
Potassium bromide	g	0.5
Sodium hydroxide	g	3.0
Sodium hexametaphosphate	g	2.0

Composition C:

4-Amino - N - ethyl-N-(β - methanesulfoamidoethyl) - m - moluidinesesquisulfate monohydrate	g	5

By dissolving 18 ml. of the composition A, 22 ml. of composition B and 5 g. of composition C in water to make the total volume to 1 liter, a developing solution for color photographic papers having excellent properties was obtained.

Since the composition A had been highly concentrated, the transportation and handling of the compositions for preparing the final use developer solution were very easy. Also, the composition for the developer solution could be stably stored at temperatures higher than 5° C. and thus could be stored for a long period of time at ordinary storing conditions.

On the other hand, when hydroxylamine sulfate or oxalate was used in place of hydroxylamine hydrochloride in the composition A, the volume of the composition became 60 ml. and could not be highly concentrated.

EXAMPLE 2

A liquid developer solution was prepared by dissolving the following three components to make one liter.

Composition A:

Water	g	3
Hydroxylamine hydrochloride	g	2
Benzyl alcohol	ml	15
Diethylene glycol	ml	4.5

Composition B:

Water	ml	20
Potassium metaborate	g	30
Sodium sulfite	g	1.8
Potassium bromide	g	0.5
Sodium hydroxide	g	3.0
Sodium hexametaphosphate	g	2.0

Composition C:

Water	ml	16
Sodium sulfite	g	0.2
4-Amino - N - ethyl-N-(β-methanesulfoamidoethyl) - m - toluidinesesquisulfate monohydrate	g	5

The developer solution gave good results for color paper as in Example 1.

The above composition A could be stored stably for longer than 6 months at room temperature and also for longer than 2 months at high temperatures varying between 35° C. and 45° C. and further it could be stored for a short period of time at a low temperature of 5° C.

EXAMPLE 3

The following liquid composition and powder compositions were dissolved in water to make 1 liter of developer solution in final use. The developing solution for color photographic films showed good photographic properties. The liquid and powdery compositions could be stored stably even at 0° C.

Composition A:

Water	ml	5
Hydroxylamine hydrochloride	g	2
Benzyl alcohol	ml	15
Diethylene glycol	g	20

Composition B:

Sodium sulfite	g	5
Sodium tertiary phosphate	g	40
Potassium bromide	g	1
Potassium iodide	g	0.05
6-Nitrobenzimidazole	g	0.02

Composition C:

Para-diethyl-aminoaniline	g	5

EXAMPLE 4

When the developing agent in the composition C of Example 2 was replaced by 3 g. of 4-amino-N-ethyl-N-(β-hydroxyethyl)-m-toluidine sulfate, the composition C could be further concentrated to 11 ml. and the developing solution prepared by dissolving the compositions in water showed the same photographic properties as in Example 2.

EXAMPLE 5

The following compositions were dissolved in water to make 1 liter of developer solution for negative color photographic films having good photographic properties.

Composition A:

Water	ml	3
Hydroxylamine hydrochloride	g	1.5
Benzyl alcohol	ml	9
Diethylene glycol	ml	4.5
6-Nitrobenzimidazole	g	0.02

Composition B:

Water	ml	20
Potassium metaborate	g	30
Sodium sulfite	g	2
Potassium bromide	g	0.5
Sodium hydroxide	g	3.0
Ethylenediaminetetraacetic acid	g	2

Composition C:

4-Amino - N - ethyl-N-(β-methanesulfoamidoethyl) - m - toluidinesesquisulfate monohydrate	g	6

What is claimed is:

1. A liquid composition for color photographic liquid processing concentrate comprising:

(1) a member selected from the group consisting of benzyl alcohol, phenylethyl alcohol, and ω-phenylpropyl alcohol,

(2) diethylene glycol,
(3) hydroxylamine hydrochloride, and
(4) water,

wherein said composition contains from 0.5 to 4.0 parts by weight of hydroxylamine hydrochloride, from 4.0 to 20.0 parts by volume of benzyl alcohol, phenylethyl alcohol or ω-phenylpropyl alcohol, and from 10.0 to 100 parts by volume of diethylene glycol in water, the volume ratio of said diethylene glycol to water ranging from 1.5 to 4.0.

2. The liquid composition of claim 1, further comprising a p-phenylenediamide type developing agent.

3. The liquid composition of claim 2, further comprising an alkali.

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