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Iwano et al.

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[54] **VISCOUS DEVELOPER FOR SILVER HALID DIFFUSION TRANSFER PROCESSES**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **96/66 R,** 96/29 R, 96/61 M

[51] **Int. Cl.** **G03c 5/30,** G03c 5/54, G03c 5/38

[58] **Field of Search** ..... 96/66, 61 M, 29

[56] **References Cited**

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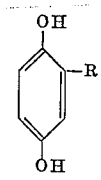
Attorney—Richard C. Sughrue et al.

[57] **ABSTRACT**

There is provided a viscous developer for a diffusion transfer process, which contains (a) a developing agent, (b) a silver halide solvent, (c) a thickening agent and (d) an alkali agent, said developing agent represented by the formula:



wherein R is a member selected from the group consisting of an ethyl group, a propyl group, and a butyl group.

12 Claims, No Drawings

VISCOUS DEVELOPER FOR SILVER HALID DIFFUSION TRANSFER PROCESSES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a processing of silver halide photographic material, in particular, to a developer composition for the diffusion transfer process of silver halide photographic material.

2. Description of the Prior Art

A negative material for the silver halide diffusion transfer process, is prepared by coating gelation silver halide emulsion layer on a support and a positive material therefor is prepared by coating a layer containing silver precipitating nuclei such as metal sulfide, colloidal silica (popularly called silica gel), etc. on a support. Usually, a developing agent, a solvent for silver halide, an alkali agent, an antifogging agent, an antioxidant, a toning agent, etc. are contained in a developer used for the diffusion transfer process.

According to the process of silver halide diffusion transfer, an exposed silver halide in the negative material is developed with a developing agent contained in a developer, while a non-exposed silver halide in the material is reacted with a silver halide solvent to form soluble silver complex, which is diffused to a positive material and is deposited on the silver-precipitating nuclei to give positive silver images.

As various kinds of diffusion transfer processes, there is known the process described in "Photography, Its Material and Process" fifth edition, at Pages 234 – 244 (1952) by C.B.Neblette, and others A process spreading a viscous developer in some thickness between a negative material and a positive material, is advantageous in many points.

While in the case of using a non-viscous liquid developer, the treatment is carried out by superposing, usually an exposed negative material on a positive material and dipping them in a developer, in the case of using a viscous developer, the negative and positive materials are not stained by the developer and can be quickly dried because the developer is not impregnated into supports of the negative material and the positive material. And the viscous developer is not split from the contacted materials and hence handly or portable processings is possible by the diffusion transfer process using such viscous developer.

However, when a viscous developer is used, there are many problems which are described below.

First, when stripping the positive material from the negative material, the viscous developer often adheres to the surface of the positive material to give a sticky print.

Second, a developing agent, a silver halide solvent and an alkali agent are contained in the developer remaining on the surface of the positive material, which cause stain and fading of images. Third, a viscous developer is usually so adhesive that it often becomes impossible to strip the positive material off the negative material.

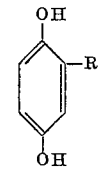
SUMMARY OF THE INVENTION

An object of the invention is to provide highly active viscous developer with which silver images of high density can be obtained.

Another object of the invention is to provide a developer which does not remain on the surface of a positive material upon stripping a negative material from the positive material.

A further object of the invention is to provide a developer that the negative material can easily be separated from the positive material. Still a further object of the invention is to provide a positive material so stable that no contamination or discoloration occurs after long storage.

The inventors have found that a viscous developer can be obtained by using the compound having the following general formula as a developing agent and using a cellulose derivative as a thickening agent;

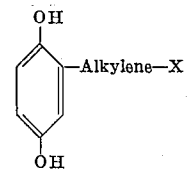


wherein R represents ethyl, propyl or butyl group.

The developing agents used in this invention are ethylhydroquinone, isopropylhydroquinone, n-butylhydroquinone, t-butylhydroquinone, etc.

It has already been known by the several patents to use hydroquinone derivatives for diffusion transfer process. These compounds, however, are far more complicated in structure than those of this invention. Judging from the examples, etc. described in the patented specification, they are quite different from the process of this invention in that they are used together with other developing agents or those compounds are used in a way different from that of this invention.

For example, a developing agent represented by the following formula



is described in U.S. Pat. No. 3,214,469. Structurally, this is a derivative of the compound of this invention, but, the compound of this invention which is simple in structure and can be prepared cheaply is far superior to the compound described therein.

In addition, similar hydroquinone derivatives are described in U.S. Pat. Nos. 3,003,876, 3,019,107, 3,131,219, 3,236,893, 3,240,810, etc.

As is described above, quite many hydroquinone derivatives are known. However, it has not been known that lower alkyl hydroquinone which is far simpler than those described in these specifications is effective for the high speed diffusion transfer process using such kind of viscous developer as is used in this invention. The superior characters of the compound of this invention compared with the known hydroquinone derivatives are as follows.

First, a film which can be easily stripped off is formed by the mutual action of the cellulose derivative and the oxidized product of said alkylhydroquinone. Therefore, the surface of the positive image is smooth and clean. This action is especially remarkable when t-butylhydroquinone is used, and other hydroquinone derivatives are inferior in this point.

Second, supplementary developing agents are not used, and quite high transfer density to the image-receiving layer can be obtained by the independent use. In addition, white part of the resulting image fully keeps its whiteness, and a good gradation can be obtained.

The photographic characteristics of alkylhydroquinone in the usual developing process was reported by Van Veelen in "The Journal Of Photographic Science" 14 [1], 48(1966), but, said special effects thereof in the diffusion transfer process were not expected at all.

As is obvious from the above description, alkylhydroquinone exhibits especially great effects in a developer wherein cellulose derivative is used as a thickening agent.

When substituent R in the alkylhydroquinone is hydrogen atom or methyl group, such derivative has no film-forming ability, has a weak activity as a developing agent for diffusion transfer treatment and the transfer density thereby obtained is low. When substituent R is alkyl group having more than 4 carbon atoms, the solubility thereof is small and cannot be dissolved in such an amount that gives sufficient transfer density.

Examples of the cellulose derivatives used in this invention are methyl cellulose, hydroxyethyl cellulose, and carboxymethyl cellulose. These may be used independently or in combination.

The developing agent of this invention is, as is illustrated in the following Examples, active especially as a developing agent for diffusion transfer treatment. The developing agents used in a usual photographic treatment such as hydroquinone, etc. do not give contrast high transfer density.

The oxidized product of the developing agent used in this invention has the capability to react with the cellulose derivative and form a film. Therefore, when the viscous developer is spread between the negative material and positive material, the developer is exposed to air and the developing agent therein is oxidized. For this reason, upon stripping the negative material off the positive material after the treatment, the developer layer adheres to the surface of the gelatin protective layer of the negative material in a form of film and is stripped off the positive material without remaining on the surface thereof. Therefore, prints stable for storage can be obtained. Besides, the developer loses its adhesivity because of the film formation due to the above-mentioned reason, and there is no possibility that it becomes impossible to strip the negative material off the positive material.

The viscosity of the viscous developer suitable to spread it uniformly is in the range of from 1,000 cp to 200,000 cp (at 25°). The amount of the thickening agent added is adjusted so as to give the viscosity within this range.

Sodium thiosulfate is the most effective as a silver halide solvent. Potassium thiocyanate may be used together.

Potassium hydroxide, sodium hydroxide, sodium triphosphate, triethanolamine, etc. are used as alkali agents.

Potassium bromide, 6-nitrobenzimidazole, etc. are used as antifogging agents. Potassium sulfite, sodium sulfite, sodium bisulfite, metapotassium metabisulfite, sodium benzene-sulfonate, ascorbic acid, diethylhydroxylamine, etc. are used as antioxidants. As a toning agent, any kind of toning agent used for conventional diffusion transfer treatment is used. Especially, triazole compounds described in the specification of the Japanese Patent No. 523,043 are effective. 3-morpholinomethyl-1-phenyl-1,3,4-triazole, 5-methyl-3-morpholinomethyl-1-phenyl-1,3,4-triazole-4-in-2-thione, 3-hydroxymethyl-5-methyl-1,3,4-triazole-4-in-2-thione and the like are used as such compounds.

A better understanding of the present invention will be attained from the following examples, which are merely illustrative and not limitative of the present invention.

EXAMPLE 1

Exposure is conducted stepwise using Neopan SSS (made by Fuji Photo Film Co., Ltd.) as a negative material. A positive material is prepared by coating a solution having the following composition onto a baryta paper, and drying it.

Silica gel (SANTOCEL C, made by Monsanto Chemical Co.)	300 g
Sodium sulfide (1% aqueous solution)	2800 cc
Cadmium acetate·$2H_2O$	30 g
Water	100 cc

Viscous developers are prepared by mixing ingredients described in Table 1 under nitrogenous atmosphere. Samples to which hydroquinone and methyl hydroquinone alone is added are set forth for comparison.

TABLE 1

	Sample: A	B	C	D
Carboxymethyl cellulose (sodium salt) (of medium Viscosity)	42 g	42 g	42 g	42 g
sodium thiosulfate	76 g	76 g	76 g	76 g
potassium sulfite	30 g	30 g	30 g	30 g
potassium hydroxide	36 g	36 g	36 g	36 g
n-propylhydroquinone	32 g			
t-butylhydroquinone		35 g		
Hydroquinone			23 g	
Methylhydroquinone				26 g
Water	700cc	700cc	700cc	700cc

The emulsion layer of the negative material is superposed on the image-receiving layer of positive material, and the viscous developer given in Table 1 is spread between them so that the developer will be about 30μ in thickness. The positive material is stripped off 20 seconds after the spreading. The comparisons of the quality of prints thus obtained are given in Table 2.

TABLE 2

	Sample: A	B	C	D
Reflection density at a part of maximum density	1.78	1.81,	1.02	0.76
State of the surface of prints after the treatment	No. developer remains	No. developer remains	Developer remains	Developer remains

The transfer density obtained by using n-propylhydroquinone or t-butylhydroquinone is higher than that obtained by using hydroquinone or methylhydroquinone. Besides, n-propylhydroquinone and t-butylhydroquinone have a property to react with cellulose and form film. Accordingly, the developer is stripper off adhering to the surface of the negative material in a film form, and no developer remains on the positive print.

EXAMPLE 2

In the Example 1, a solution having the following composition is used as viscous developer.

Hydroxyethyl cellulose (high viscosity)	40 g
Sodium thiosulfate	74 g
Sodium sulfite	14 g
Sodium hydroxide	32 g
t-butylhydroquinone	20 g
Potassium bromide	0.8 g
5-Hydroxymethyl-5-methyl-1,3,4-triazole-4-in-2-thione (3×10^{-2} mol methanol solution)	20 cc
Water	600 cc

The emulsion layer of the negative material is superposed on the image-receiving layer of positive material, and the viscous developer above-mentioned is spread between them so that the developer will be about 30μ in thickness. The positive material is stripped off 20 seconds after the spreading. No developer remains on the prints thus obtained. Prints with high density and without any stain are obtained. Even after spreading the developer and superposing the negative layer on the positive layer for 3 minutes, the positive layer could easily be stripped off.

EXAMPLE 3

In the Example 1, a solution having the following composition is used as a viscous developer.

Hydroxyethyl cellulose	41 g
Methyl cellulose	2 g
Sodium thiosulfate	60 g
Sodium sulfite	32 g
Sodium hydroxide	30 g
n-Propylhydroquinone	32 g
1-Phenyl-5-mercaptotetrazole (0.1% methanol solution)	10 cc
3-Morpholinomethyl-1-phenyl-1,3,4-triazole (3×10^{-2} mol methanol solution)	20 cc
Water	700 cc

In the same way as is described in Example 1 and 2, prints with high density and without any stain can be obtained.

Although the present invention has been adequately described in the foregoing specification and examples included therein, it is readily apparent that various changes and modifications can be made without departing from the spirit and scope thereof.

What is claimed is:

1. A viscous developer for the diffusion transfer process, which contains:

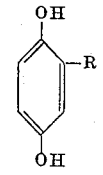
a. a developing agent,

b. a silver halide solvent,

c. a thickening agent selected from the group consisting of methyl cellulose, hydroxyethyl cellulose, and carboxymethyl cellulose,

d. an alkali agent, and

e. a toning agent, said developing agent represented by the formula:



wherein R is a member selected from the group consisting of an ethyl group, a propyl group, and a butyl group.

2. The developer of claim **1**, wherein said developing agent is a member selected from the group consisting of ethylhydroquinone, isopropylhydroquinone, n-butylhydroquinone and t-butylhydroquinone.

3. The developer of claim **1**, wherein the viscosity of said developer ranges from 1,000 to 20,000 cp.

4. The developer of claim **1**, wherein said silver halide solvent is sodium thiosulfate.

5. The developer of claim **1**, wherein said silver halide solvent is a combination of sodium thiosulfate and potassium thiocyanate.

6. The developer of claim **1**, wherein said alkali agent is a member selected from the group consisting of potassium hydroxide, soidum hydroxide, sodium thiphosphate, and triethanolamine.

7. The developer of claim **1**, which further contains an anti-fogging agent.

8. The developer of claim **7**, wherein said anti-fogging agent is a member selected from the group consisting of potassium bromide and 6-nitrobenzimidazole.

9. The developer of claim **1**, further containing an anti-oxidant.

10. The developer of claim **9**, wherein said antioxidant is a member sleected from the group consisting of potassium fulfite, sodium sulfite, sodium bisulfite, metapotassium metabisulfite, sodium benzenesulfonate, ascorbic acid, and diethylhydroxlamine.

11. The developer of claim **1**, wherein said toner is a member selected from the group consisting of 3-morpholinomethyl-1-phenyl-1,3,4-triazole, 5-methyl-3-morpholinomethyl-1-phenyl-1,3,4-triazole-4-in-2-thione, and 3-hydroxymethyl-5-methyl-1,3,4-triazole-4-in-2-thione.

12. A viscous developer for the diffusion transfer process, which contains:

a. a developing agent selected from the group consisting of ethylhydroquinone, isopropylhydroquinone, n-butylhydroquinone and t-butylhydroquinone,

b. a silver halide solvent selected from the group consisting of sodium thiosulfate and a mixture of sodium thiosulfate with potassium thiocyanate,

c. a cellulose thickening agent selected from the group consisting of methyl cellulose, hydroxyethyl cellulose and carboxymethyl cellulose, and

d. an alkali agent selected from the group consisting of potassium hydroxide, sodium hydroxide, sodium triphosphate and triethanolamine,

said developer having a viscosity ranging from 1,000 to 20,000 cp.

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