United States Patent Office 2,875,048
Patented Feb. 24, 1959

2,875,048

COMBINED PHOTOGRAPHIC DEVELOPING AND STABILIZING SOLUTION

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No Drawing. Application September 30, 1957
Serial No. 686,898

12 Claims. (Cl. 96—61)

This invention relates to processes for the development of silver images in photographic silver halide emulsion layers which processes dispense with the usual fixing and washing steps.

It is well known that developed silver halide emulsion layers containing silver images require the removal or inactivation of the residual silver halide for the picture to be stable under adverse conditions of light, heat and humidity. For this reason, fixing and washing steps are ordinarily employed after development to convert the silver halide to a soluble salt which is then washed out of the emulsion layer.

A number of processes have been proposed to dispense with the laborious fixing and washing steps. For example, Russell U. S. Patent 2,453,346, granted November 9, 1948, discloses the use of various sulfur compounds in conjunction with metal salts for stabilizing silver prints. Acidic solutions containing the sulfur compounds and metal salts are applied to silver halide emulsion layers following development of the silver image. In Dreywood U. S. Patent 2,525,532, granted October 10, 1950, emulsion layers are developed with a Metol-hydroquinone developer containing various sulfur compounds. Following development, the emulsions are treated with acid solutions prior to drying. In the Broughton et al. U. S. Patent 2,614,927, granted October 21, 1952, emulsions containing certain developing agents are developed with alkaline solutions followed by inactivation of the residual silver halide with solutions of sulfur compounds such as thioglycolic acid, thiourea or thiosulfates.

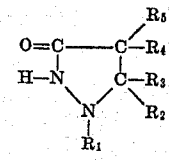
We have discovered that when combinations of certain silver halide developing agents and sufficient quantities of certain organic sulfur compounds are used in alkaline photographic developer compositions and these compositions are used for combined developing and stabilizing silver halide emulsion layers, stable silver images are obtained having low density and good resistance to print-out of the residual silver halide in the non-image background areas and having good resistance to fading or toning in the image areas which do not require fixing and washing.

One object of our invention is therefore to provide combined developing and stabilizing solutions for producing stable silver images. Another object is to provide methods for using the combined developing and stabilizing compositions in producing stable silver images. Other objects of our invention will appear from the following description.

These objects are accomplished by using as combined developing and stabilizing solutions for silver halide emulsion layers, alkaline compositions comprising particular silver halide developing agents and organic sulfur compounds.

The silver halide developing agents used in our combined developer and stabilizing compositions are either hydroxylamine or 3-pyrazolidone silver halide developing agents.

The 3-pyrazolidone silver halide developing agents have the general structure



in which the R groups each represent various substituents such as hydrogen, alkyl or aryl groups, for example, R_1 can be hydrogen or a group such as alkyl preferably containing from 1 to 4 carbon atoms, or an aryl group of the benzene or naphthalene series substituted or not, and R_2, R_3, R_4 and R_5 can be hydrogen atoms, or groups such as an alkyl group preferably of 1 to 4 carbon atoms or aryl such as phenyl.

The following compounds are representative of 3-pyrazolidone silver halide developing agents which are useful in the developer compositions of the invention:

(1) 1-phenyl-3-pyrazolidone
(2) 1-p-tolyl-3-pyrazolidone
(3) 5-phenyl-3-pyrazolidone
(4) 5-methyl-3-pyrazolidone
(5) 1-p-chlorophenyl-3-pyrazolidone
(6) 1-phenyl-5-phenyl-3-pyrazolidone
(7) 1-m-tolyl-3-pyrazolidone
(8) 1-phenyl-5-methyl-3-pyrazolidone
(9) 1-p-tolyl-5-phenyl-3-pyrazolidone
(10) 1-m-tolyl-3-pyrazolidone
(11) 1-p-methoxyphenyl-3-pyrazolidone
(12) 1-acetamidophenyl-3-pyrazolidone
(13) 1-phenyl-2-acetyl-4,4-dimethyl-3-pyrazolidone
(14) 1-phenyl-4,4-dimethyl-3-pyrazolidone
(15) 1-m-aminophenyl-4-methyl-4-propyl-3-pyrazolidone
(16) 1-o-chlorophenyl-4-methyl-4-ethyl-3-pyrazolidone
(17) 1-m-acetamidophenyl-4,4-diethyl-3-pyrazolidone
(18) 1-p(β-hydroxyethylphenyl)-4,4-dimethyl-3-pyrazolidone
(19) 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidone
(20) 1-p-methoxyphenyl-4,4-diethyl-3-pyrazolidone
(21) 1-p-tolyl-4,4-dimethyl-3-pyrazolidone
(22) 1-(7-hydroxy-2-naphthyl)-4-methyl-4-n-propyl-3-pyrazolidone
(23) 1-p-diphenyl-4,4-dimethyl-3-pyrazolidone
(24) 1-p-(β-hydroxyethylphenyl)-3-pyrazolidone
(25) 1-o-tolyl-3-pyrazolidone
(26) 1-o-tolyl-4,4-dimethyl-3-pyrazolidone

When used in the combined developing and stabilizing composition in the presence of the sulfur compounds discussed below, these developing agents produce colorless oxidation products and so do not contribute to stain in the resulting print which has not been washed.

The sulfur compounds which are used in the developer compositions are the following: monothioglycerol

$$HOCH_2CH_2(OH)CH_2SH$$

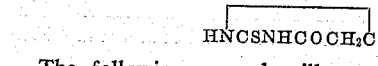
thioglycol $HOCH_2CH_2SH$, β-mercaptoethylamine

$$H_2NCH_2CH_2SH$$

N,N-diethyl-β-mercaptoethylamine

$$(C_2H_5)_2NCH_2CH_2SH$$

and 2-thiobarbituric acid



The following examples illustrate the combined developing and stabilizing solutions and their use for obtaining stable silver images.

EXAMPLE 1

1-phenyl-3-pyrazolidone	grams	3.0
Sodium sulfite, desiccated	do	50.0
Sodium carbonate, monohydrate	do	40.0
l-ascorbic acid	do	10.0
Sodium hydroxide	do	10.0
Monothioglycerol (98.7%)	ml	30.0

Water to make 1.0 liter.

The solution had a pH of 10.24.

This formula is generally useful for producing stable silver images in emulsion layers of all kinds but has been found to be particularly useful for processing direct reversal papers such as Kodagraph Autopositive Paper where other stabilizing techniques have not been satisfactory. That is, when the emulsion was treated with a solution of titanous chloride and mercaptosuccinic acid, prints were obtained which turned yellow on exposure to ultraviolet radiation whereas the above formula gave prints which were substantially unaffected on exposure to ultraviolet radiation. In the above formula, the sulfite content may be reduced appreciably if desired, for example, to 2.0 grams per liter and stable prints will still be obtained. Minimum processing times of the order of 30 to 90 seconds at room temperature are satisfactory for the above formula with most emulsions. At elevated temperatures such as 100° F. the processing time may be reduced appreciably to about 10–30 seconds.

EXAMPLE 2

Hydroxylamine hydrochloride	grams	10.0
Monothioglycerol (50%)	ml	30.0
Sodium hydroxide	grams	21.0
5-methyl benzotriazole (1%)	ml	10.0

Water to 1.0 liter.

pH=12.9.

Silver halide sensitized materials may be processed in this formula for varying lengths of time and dried immediately thereafter to yield stable silver images. For example, Kodagraph Autopositive Extra Thin Paper processed in this composition for 30 seconds gave prints highly stable to ultraviolet radiation. Stable prints have also been obtained using this formula by treating an unexposed emulsion layer with the composition for a few seconds immediately before exposure without subsequent treatment.

EXAMPLE 3

	Grams
Hydroxylamine sulfate (95%)	10.0
Sodium sulfite, desiccated	50.0
2-thiobarbituric acid	32.0
Sodium hydroxide	30.0

Water to make 1.0 liter.

pH=12.5.

This formula may be used for simultaneous development and stabilization of Autopositive Paper for about 30 seconds at room temperature. Formulas of this type can also be used in stabilizing print-out images obtained by exposure of high speed print-out papers. For this purpose it may be advantageous to prepare the composition from the following stock solutions:

Solution A

	Grams
Hydroxylamine sulfate (95%)	20.0
Sodium sulfite, desiccated	100.0
Sodium hydroxide	13.0

Water to make 1.0 liter.

Solution B

2-thiobarbituric acid	60.0
Sodium hydroxide	39.0

Water to make 1.0 liter.

pH of each solution=12.4.

The two solutions can be mixed for use in the proportions of about 0.5 to 2 parts of A per part of B and development carried out for about 30 seconds to 2 minutes depending on the particular emulsion under consideration.

EXAMPLE 4

	Grams
Hydroxylamine sulfate	10.0
Sodium sulfite, desiccated	50.0
N,N-diethyl-β-mercaptoethylamine hydrochloride	23.0
Sodium hydroxide	30.0

Water to make 1.0 liter.

Emulsions can be processed in this composition for about 60 to 90 seconds at room temperature. When β-mercaptoethylamine hydrochloride is used in the formula in place of the diethyl derivative, the processing time may be reduced.

EXAMPLE 5

	Grams
Sodium sulfite, desiccated	4.0
1-phenyl-3-pyrazolidone	4.0
l-ascorbic acid	20.0
2-thiobarbituric acid	32.0
Sodium hydroxide	30.0

Water to make 1.0 liter.

pH=12.5.

This composition was found to be particularly useful for processing Kodak Autopositive 43 Paper for 15 seconds at room temperature yielding prints exhibiting no discoloration after 60 seconds' exposure at 1 foot from a 45-ampere arc lamp.

EXAMPLE 6

Samples of the formula of Example 3 were prepared in which the concentration of 2-thiobarbituric acid was varied from 2, 20, 25 and 32 grams per liter, the pH of each solution being 12.5 adjusted with dilute NaOH solution. Each formula was used for processing Kodak Autopositive 43 Paper for 15, 30 and 60 seconds and the solution then blotted off immediately thereafter. The prints obtained by using the solution containing 2 grams of 2-thiobarbituric acid per liter yielded prints unstable to ultraviolet radiations. At 20 grams per liter, slight print-out was obtained upon exposure of the prints to ultraviolet radiation. At 25 and 32 grams per liter, the prints were very stable. Accordingly, it is desirable to use at least about 15 grams per liter of 2-thiobarbituric acid to obtain reasonably well stabilized prints, the upper limit being dependent in part on the solubility of the compound and on matters of economy.

With the other sulfur compound of the invention the concentrations in the developing and stabilizing compositions can be of the order of at least about 5 to 10 grams per liter.

In the manner of the above examples other compositions may be compounded having hydroxylamine in combination with thioglycol, and the 3-pyrazolidone compounds in combination with thioglycol, the β-mercaptoethylamines and 2-thiobarbituric acid.

In the above examples, the combined developer-stabilizing solutions were compounded so as to be most effective with particular photographic elements such as Autopositive paper. Some adjustments in ratio of developing agent to sulfur compound and pH may be necessary when using the compositions for processing other emulsions. These compositions can be applied by any of the conventional methods of processing such as immersion, spray application, surface application and the like.

The following experiments were carried out to demonstrate the improved results obtainable with the compositions of the invention compared to similar formulas containing other silver halide developing agents and sulfur compounds as stabilizers.

EXAMPLE 7

Solution 1

The developer composition of Example 1.

Solution 2

Same as Solution 1 but containing the same amount of thiourea in place of thioglycerol.

Solution 3

Water	ml	100
Sodium sulfite, desiccated	grams	8
d-Iso-ascorbic acid	do	5
Hypo	do	3
Sodium hydroxide	do	2.5
Potassium bromide	do	0.2
1-phenyl-3-pyrazolidone	do	0.25
0.5% benzotriazole	ml	5.0

Solution 4

1-phenyl-3-pyrazolidone	grams	1.0
Hypo	do	50.0
Ascorbic acid	do	10.0
Potassium bromide	do	2.0
Sodium carbonate, monohydrate	do	20.0

Water to 1 liter.

Solution 5

	Grams
Sodium hydroxide	30
Sodium sulfite, desiccated	50
Hydroxylamine hydrochloride	15
Hypo	200

Water to 1 liter.

When the above formulas were used for developing an exposed emulsion layer at room temperature, only the first solution containing 1-phenyl-3-pyrazolidone and thioglycerol yielded prints having ultraviolet light stable silver images. In addition, formulas 3, 4 and 5, all containing hypo, were particularly objectionable since they readily precipitated silver from solution especially when used at elevated temperatures which condition was apparent after 10 minutes at 100° F. Solution 1 showed no tendency to precipitate silver at temperatures ranging from room temperature to 180° F. and pH ranges of from 8 to 13. Also, Solutions 3 and 4 produced mottled prints with a Kodagraph Autopositive Paper. Furthermore, Solution 5 produced prints which faded out completely upon storage under adverse conditions of heat and humidity.

EXAMPLE 8

	Grams
Hydroquinone	5.5
Sodium sulfite, desiccated	50.0
Sodium carbonate monohydrate	50.0

Water to 1 liter.

Upon addition of 32 grams per liter of thiobarbituric acid to this developer formula at pH 10.4 and use of the composition for developing samples of Autopositive Paper, it was found that development was completely repressed, no sign of image being obtained even after 5 minutes of treatment.

EXAMPLE 9

The effectiveness of thiobarbituric acid and potassium iodide as stabilizing agents was compared by adding 32 grams of each per liter of the developing composition of Example 3, the pH being adjusted to 12.5 in each case. Samples of a photographic paper were developed for 15, 30 and 60 seconds in each formula, then blotted and dried. The baths containing thiobarbituric acid gave black images on a white background and the other baths containing potassium iodide gave very weak images on a yellow background.

What we claim is:

1. A photographic developer composition comprising an aqueous alkaline solution of (1) a member of the class consisting of hydroxylamine and a 3-pyrazolidone silver halide developing agent and (2) a member of the class consisting of monothioglycerol, thioglycol, β-mercaptoethylamine, N,N-diethyl-β-mercaptoethylamine and 2-thiobarbituric acid.

2. A photographic developer composition comprising an aqeous alkaline solution of 1-phenyl-3-pyrazolidone and monothioglycerol.

3. A photographic developer composition comprising an aqueous alkaline solution of 1-phenyl-3-pyrazolidone and 2-thiobarbituric acid.

4. A photographic developer composition comprising an aqueous alkaline solution of hydroxylamine and 2-thiobarbituric acid.

5. A photographic developer composition comprising an aqueous alkaline solution of hydroxylamine and a β-mercaptoethylamine.

6. A photographic developer composition comprising an aqueous alkaline solution of hydroxylamine and monothioglycerol.

7. A process for producing a stable photographic silver image which comprises treating an exposed silver halide emulsion layer with an alkaline solution containing (1) a compound of the class consisting of hydroxylamine and a 3-pyrazolidone silver halide developing agent, and (2) a compound of the class consisting of monothioglycerol, thioglycol, β-mercaptoethylamine, N,N-diethyl-β-mercaptoethylamine and 2-thiobarbituric acid.

8. A process for producing a stable photographic silver image which comprises treating an exposed silver halide emulsion layer with an alkaline solution containing 1-phenyl-3-pyrazolidone and monothioglycerol.

9. A process for producing a stable photographic silver image which comprises treating an exposed silver halide emulsion layer with an alkaline solution containing 1-phenyl-3-pyrazolidone and 2-thiobarbituric acid.

10. A process for producing a stable photographic silver image which comprises treating an exposed silver halide emulsion layer with an alkaline solution containing hydroxylamine and 2-thiobarbituric acid.

11. A process for producing a stable photographic silver image which comprises treating an exposed silver halide emulsion layer with an alkaline solution containing hydroxylamine and monothioglycerol.

12. A process for producing a stable photographic silver image which comprises treating an exposed silver halide emulsion layer with an alkaline solution containing hydroxylamine and a β-mercaptoethylamine.

References Cited in the file of this patent

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