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Kane et al.

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[54] RAPID DEVELOPMENT PROCESS

[75] Inventors: **John R. Kane,** Piffard; **Harry G. Morse,** Rochester, both of N.Y.

[73] Assignee: **Itek Corporation,** Lexington, Mass.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 771,325, Oct. 28, 1968, Pat. No. 3,582,341.

[52] **U.S. Cl.** .....**96/66 HD,** 96/61, 96/66.3, 96/66.4

[51] **Int. Cl.** **G03c 5/30**

[58] **Field of Search**.....96/66, 66 HD, 66 T

[56] **References Cited**

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Primary Examiner—J. Travis Brown

Assistant Examiner—Judson R. Hightower

Attorney—Homer O. Blair, Robert L. Nathans and W. Gary Goodson

[57] **ABSTRACT**

A process and compositions for rapidly developing and fixing a high contrast, low speed photographic film such as microfilm. The first step in the process comprises contact of an exposed photographic film with an alkaline developer composition comprising (*a*) a mixture of hydroquinone and 1-phenyl-3-pyrazolidone in a weight ratio of from 15:1 to 6:1 as the developing agent, the mixture contained in the developer composition in an amount of from 15 to 40 grams per liter; and (*b*) potassium sulfite as preservative in an amount from 60 to 120 grams per liter. Preferably, the developer composition has a pH from about 10 to 11 and contains a restrainer such as potassium bromide in an amount of from 2 to 10 grams per liter.

Following contact with the developer composition, the developed film is preferably contacted with a fixer such as one comprising from 200 to 400 grams per liter sodium thiosulfate crystals, 50 to 100 grams per liter of potassium sulfite and 100 to 200 grams per liter of ammonium thiocyanate.

The process of the invention provides rapid development of high contrast, low speed films and has, for example, a capability of developing microfilm in about 10 seconds or less. The high speed is believed to be attributable, at least in part, to the use of the above-noted combination of developing agents. Moreover, the process results in a developed negative free of a uniform red coloration or stain characteristic of films of this nature. Finally, the developer composition is highly resistant to the detrimental effects of aeration, has excellent keeping qualities and can be stored for long periods of time without noticeable deterioration.

18 Claims, No Drawings

RAPID DEVELOPMENT PROCESS

This is a continuation-in-part of U. S. application Ser. No. 771,325, now U.S. Pat. No. 3,582,341, filed October 28, 1968.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to photographic chemistry and more particularly, to a process for developing high contrast, low speed photographic film such as microfilm.

2. Description of the Prior Art

As is well known in the art, microfilming is the technique of copying documents to reduced size on film, usually 16- and 35- mm. film. The negatives made therefrom can be read in enlarging readers, or enlargements onto paper may be made to provide copies. Special miniature cameras are used, typically having variable magnification, automatic focusing and high-definition lenses. Many cameras are mounted in automated microfilm processors into which the documents are fed rapidly, photographed, moved through the machine and developed automatically. Reductions in size may range from 8 to as much as 40. Special projection equipment made for reading the films may give an enlargement onto a table or a diffusing rear-projection screen, with provision for rapidly winding the film and framing any desired page.

Because of the substantial reduction in size of the copied documents, films must be provided that are capable of yielding developed images of exceptional definition and contrast. It is known in the art that photographic emulsions of low speed having a fine grain structure provide desired contrast and definition. Moreover, film used for microfilming is typically provided with a dye layer disposed between the base and emulsion layers. The dye absorbs light during exposure, thereby proventing the light from passing through the film base and reflecting back into the emulsion. In the absence of the dye layer, reflected light would expose areas adjacent to the image areas resulting in a loss of image clarity.

There are special problems associated with the processing of microfilm, especially where automated microfilm processor equipment is involved. For example, using conventional developers, development time for the low speed, high contrast films will typically exceed 2 minutes. This would be an intolerable length of time for an automated piece of equipment. Furthermore, the pumping of processing chemicals results in substantial aeration thereof and the processing chemicals must be exceptionally stable to oxidation. Finally, the intermediate layer of dye disposed between the base and emulsion layers usually takes on a red coloration upon exposure to conventional developing agents resulting in a uniform red staining of the film.

Conventional developers for processing photographic film, and heretofore used for processing microfilm, comprise developers such as organic reducing compounds as exemplified by hydroquinone, monomethylparaminophenol sulphate (Elon, Metol) pyrogallol (1,2,3-hydroxybenzene), Amidol (2,4-diaminophenol) and p-phenylenediamine; an alkali such as sodium hydroxide or sodium carbonate to give desire pH; a preservative such as sodium sulfite to prevent degradation of the developer composition by oxygen; and an antifoggant such as potassium bromide

to prevent the development of unexposed silver halide crystals. It is known in the art that a developer composition composed of known materials such as those exemplified above may be formulated so as to provide specific desired results such as high speed development, fine grained images, high density images and the like by careful selection of composition components and the proportions thereof. In this respect, developers have been formulated to provide rapid development of high contrast, low speed films from materials using conventional materials. Such compositions are disclosed in numerous patents including U. S. Pat. Nos. 2,448,857; 2,614,927; 2;710,257; 2,757,091; 3,088,824; 3,132,943; and 3,356,502.

A typical formulation for high speed development is illustrated in U. S. Pat. No. 2,710,257 above noted, and is composed of a major portion of hydroquinone and a minor portion of the surfate of p-methylaminophenol (Metol) as developing agent, sodium hydroxide as alkali, sodium sulfite as preservative, potassium bromide as restrainer and various other additives as antifoggants, for toning and the like. Though this formulation and others as represented in the prior art do provide rapid development of photographic film, they are not fully suitable for development of microfilm. For example, contact of exposed microfilm having an intermediate dye layer with prior art developers results in a uniform red staining of the microfilm. Furthermore, the prior art developers are not sufficiently stable to withstand the extreme aeration resulting from the pumping operations in the automated microfilm processing equipment.

STATEMENT OF THE INVENTION

The present invention provides a process and compositions for rapid development of low speed, high contrast film and is especially suitable for the processing of microfilm minimizing the above-noted problems associated therewith. The process involves a first step of contacting an exposed photographic film with an alkaline developer composition comprising (*a*) a mixture of hydroquinone and 1-phenyl-3-pyrazolidone in a weight ratio of from about 15:1 to 6:1 as the developing agents, the mixture of agents contained in the developer composition in an amount of from 15 to 40 grams per liter; and (*b*) potassium sulfite as preservative in an amount of from 60 to 120 grams per liter. Preferably the developer composition has a pH of about 10 to 11 and contains a restrainer such as potassium bromide in an amount of from about 2 to 10 grams per liter.

The second step in the process preferably involves contact of the developed film with a fixer composition such as one comprising from 200 to 400 grams per liter of sodium thiosulfate crystals, 50 to 100 grams of potassium sulfite and 100 to 200 grams per liter of ammonium thiocyanate.

Using the process of this invention, low speed, high contrast film is developed in a period of about 10 seconds with the processed film being substantially free of a red coloration or staining. Moreover, the processing chemicals are highly resistant to the detrimental effects of aeration, have excellent keeping qualities and can be stored or used for extended periods of time without noticeable deterioration. Rapid

development is believed to be due in part to a synergism resulting from the combination hydroquinone with 1-phenyl-3-pyrazolidone in the above specified proportions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred developer composition in accordance with the invention is set forth in the following table:

	Minimum	Maximum
1-Phenyl-3-pyrazolidone, gr	1.0	2.5
Hydroquinone, gr	15.0	30.0
Potassium sulfite, gr	60.0	120.0
Potassium bromide, gr	2.0	10.0
Sodium hydroxide, gr	4.0	15.0
Benzotriazole, gr	0	0.5
Water	to 1 liter	to 1 liter

In the above formulation, the hydroquinone and the 1-phenyl-3-pyrazolidone are each developing agents and used in a weight ratio to each other of from 15:1 to 6:1. It is necessary that the combination of developing agents be used as they co-react with each other to provide a synergism resulting in substantially decreased development time and increased image quality. If the 1-phenyl-3-pyrazolidone is used alone in an amount equal to as much as 5 times its specified amount in the above formulation, the development time is short, but the developed image is of low contrast, poor density, and otherwise unacceptable quality. If hydroquinone is used alone in an amount equal to the total amount of to developing agents in the above formulation, the development time is excessive and the developed image is of poor density in the low exposure region. The combination of developing agents in the amount and proportions above specified provides a developed image in 10 seconds or less of excellent contrast, density and quality.

Potassium sulfite is used in the above formulation for two purposes. First, it acts as a preservative and prevents degradation of the developer composition due to excessive aeration. In addition, it acts to decolorize the intermediate dye layer so that the developed film has a low level of uniform red discoloration. Preferably, it is present in an amount of at least about 80 grams per liter of developer solution. It should be noted that sodium sulfite, in lesser concentrations, is a conventional additive to prior art developer compositions. However, it has been found that sodium sulfite substituted for potassium sulfite in the above formulation is substantially less effective in performing the function of decolorizing the dye layer.

Potassium bromide is used for its well-known function as a restrainer and antifoggant. The benzotriazole is an optional additive used in combination with the potassium bromide as an antifoggant.

The sodium hydroxide is used to provide the desired pH of from 10 to 11. In this respect, other known alkalis such as sodium carbonate, borax and the like may be substituted for sodium hydroxide provided that a pH of from 10 to 11 is achieved.

The developer composition of this invention is desirably used at slightly elevated temperatures and preferably within a temperature range of 85° to 95° F. with 90° F. being most preferred. Contact of the photographic film with the developer composition is dependent, to some extent, upon the film used. However, contact time of from 5 to 15 seconds is usually satisfactory.

Following development of the photographic film it is preferably contacted with a fixer composition as follows:

	Minimum	Maximum
Sodium thiosulfate crystals, gr	200	400
Ammonium thiocyanate, gr	100	200
Potassium sulfite, gr	50	100
Water	to 1 liter	to 1 liter

Crystalline sodium thiosulfate is a conventional fixing agent, however, its combination with ammonium thiocyanate produces a synergistic effect resulting in shorter fixation time. In addition, the ammonium thiocyanate is believed to solubilize to some extent an intermediate dye layer disposed between the base and emulsion layers of the photographic film. It is believed that this, in part, is responsible for the formation of black and white images with minimum red discoloration.

Potassium sulfite in the above formulation acts as a preservative and contributes to the decolorization of the dye layer. In this respect, the potassium sulfite performs the same function in the fixer composition as in the developer composition. An additional characteristic of the fixer composition is the absence of gelatin hardeners. Removal of hardeners ensures the rapid diffusion of wash water in and out of the emulsion making archival washing possible in the shortest possible time.

It should be understood that other conventional fixers may be substitued for those exemplified above, but the use of the above fixers provide the greatest decrease in red staining and constitute a preferred embodiment of the invention.

Contact of a developed photographic film with the fixer composition is short and typically is approximately equivalent to the contact time with the developer. The fixer composition is preferably used at a temperature of from 80° to 85°.

The following examples are set forth for purposes of illustration:

EXAMPLE 1

An exposed black and white negative film having an intermediate dye layer was developed in a developer maintained at 90° F. and having the following formulation:

1-Phenyl-3-pyrazolidone	2.1 gr
Hydroquinone	27.0 gr
Potassium sulfite	90.0 gr
Sodium hydroxide	6.0 gr
Potassium bromide	4.0 gr
Benzotriazole	0.1 gr
Water to	1 liter
pH	10.20

Contact of the exposed photographic film with the developer was for 10 seconds. The film was then immersed in a fixer composition having the following formulation:

Sodium thiosulfate crystals	280 gr
Ammonium thiocyanate	140 gr
Potassium sulfite	80 gr
Water to	1 liter

The temperature of the fixer composition was 80° F. and contact with the fixer was for a period of 10 seconds. The developed image was of high contrast, excellent resolution and free of red discoloration.

EXAMPLE 2

An exposed black and white negative film having an intermediate dye layer was developed in a developer maintained at 90° F. and having the following formulation:

1-Phenyl-3-pyrazolidone	1.6 gr
Hydroquinone	26.4 gr
Sodium sulfite	60.0 gr
Potassium bromide	4.0 gr
Sodium hydroxide	6.0 gr
Benzotriazole	0.1 gr
Water to	1 liter

Development time was approximately 10 seconds. Thereafter, the developed film was contacted for 10 seconds with the fixer of Example 1 at 80° F. The developed film was of high contrast, high resolution, but possessed a red discoloration.

EXAMPLE 3

The procedure of Example 1 was repeated with the substitution of 2.1 grams of mono-methyl-paraminolphenol sulfate for the 1-phenyl -3-pyrazolidone. The developed image was of poor contrast and quality.

EXAMPLE 4

The procedure of Example 1 was repeated with the substitution of about 30 grams of hydroquinone for the combination of the hydroquinone and 1-phenyl-3-pyrazolidone. After 10 seconds contact with the developer composition, no visual image was observable. After a full minute of contact with the developer, a visual image of poor speed and quality was observable.

EXAMPLE 5

The procedure of Example 1 was repeated with the substitution of approximately 10 grams of 1-phenyl-3-pyrazolidone for the combination of the hydroquinone and 1-phenyl-3-pyrazolidone of Example 1. After 10 seconds contact with the developer, the image was observable, but of poor density and low contrast.

EXAMPLE 6

The procedure of Example 1 was repeated with the following developer composition to obtain a developed image of high contrast, excellent resolution and free of red discoloration:

1-Phenyl-3-pyrazolidone	2.3 g.
Hydroquinone	32.4 g.
Potassium sulfite	104 g.
Sodium hydroxide	6.95 g.
Potassium bromide	3.65 g.
Benzotriazole	0.16 g.
Water to	1 liter
pH	10.30

It should be understood that the embodiments included in the specification are illustrative only and that the invention described is capable of modification without departing from the scope of the claims.

We claim:

1. A process for developing a silver halide photographic film comprising exposing the film, contacting with an alkaline developer composition comprising (*a*) a mixture of hydroquinone and 1-phenyl-3-pyrazolidone in a weight ratio of from about 15:1 to 6:1 as developing agents, the mixture of agents contained in the developer composition present in an amount of from 15 to 40 grams per liter of developer solution; and (*b*) potassium sulfite as a preservative in an amount of from 60 to 120 grams per liter of developer solution.

2. The process of claim 1 wherein the developer composition comprises an alkali present in quanities to produce a developer composition having a pH of from about 10 to 11.

3. The process of claim 2 wherein the potassium sulfite is present in an amount of at least about 80 grams per liter of developer composition.

4. The process of claim 2 wherein the photographic film has a layer of dye disposed between a base and a photosensitive emulsion.

5. The process of claim 2 where the developer composition is maintained at between 85° and 95° F. and contact time with the photographic film is about 10 seconds.

6. The process of claim 2 where the developed film is contacted with a photographic fixer.

7. The process of claim 2 where the developer composition has approximately the following formulation:

1-phenyl-3-pyrazolidone	2.0 gr
hydroquinone	27.0 gr
potassium sulfite	90.0 gr
alkali metal hydroxide	6.0 gr
potassium bromide	4.0 gr
benzatriazole	0.1 gr
water to	1 liter.

8. A process for developing an exposed low speed, high contrast photographic film including the steps of contacting the exposed film with a developer composition having the following formulation:

	Minimum	Maximum
1-phenyl-3-pyrazolidone, gr	1.0	2.5
hydroquinone, gr	15.0	40.0
potassium sulfite, gr	60.0	120.0
potassium bromide, gr	2.0	10.0
sodium hydroxide, gr	4.0	15.0
benzotriazole, gr	0	0.5
water	to 1 liter	to 1 liter

said hydroquinone and 1-phenyl-3-pyrazolidone being present in a weight ratio of from about 15:1 to 6:1, and contacting the developed film with a fixer having the following formulation:

	Minimum	Maximum
sodium thiosulfate crystals, gr	200	400
ammonium thiocyanate, gr	100	200
potassium sulfite, gr	50	100
water to	1 liter	1 liter.

9. The process of claim 8 where the ratio of hydroquinone to 1-phenyl-3-pyrazolidone ranges from 15:1 to 6:1.

10. The process of claim 8 where the developer composition has a pH of from 10 to 11.

11. An alkaline developer composition for developing a low speed, high contrast silver halide photographic film comprising: (*a*) a mixture of hydroquinone and 1-phenyl-3-pyrazolidone in a weight ratio of from

about 15:1 to 6:1 as developing agents, the mixture of agents contained in the developer composition being present in an amount of from about 15 to 40 grams per liter of developer composition and (*b*) potassium sulfite as a preservative in an amount of from about 60 to 120 grams per liter of developer composition.

12. The composition of claim **11** wherein the composition has a pH from about 10 to 11.

13. The composition of claim **11** wherein the potassium sulfite is present in an amount of from about 80 to about 120 grams per liter of developer composition.

14. A composition for developing a low speed, high contrast photographic film as follows:

	Minimum	Maximum
1-phenyl-3-pyrazolidone gr	1.0	2.5
hydroquinone gr	15.0	40.0
potassium sulfite gr	60.0	120.0
potassium bromide gr	2.0	10.0
sodium hydroxide gr	4.0	15.0
benzotriazole gr	0	0.5
water	to 1 liter	to 1 liter

said hydroquinone and 1-phenyl-3-pyrazolidone being present in a weight ratio of from about 15:1 to 6:1.

15. The composition of claim **14** having approximately a formulation as follows:

1-phenyl-3-pyrazolidone	2.3 gr
hydroquinone	32.4 gr
potassium sulfite	104 gr
sodium hydroxide	6.95 gr
potassium bromide	3.65 gr
benzotriazole	0.16 gr
water to	1 liter.

16. The composition of claim **14** where the ratio of hydroquinone to 1-phenyl-3-pyrazolidone ranges from 15:1 to 6:1.

17. The composition of claim **14** where the pH ranges from 10 to 11.

18. The composition of claim **14** where pH is about 10.2.

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