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Hara et al.

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[54] **PHOTOGRAPHIC MATERIAL DEVELOPMENT METHOD**

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Related U.S. Application Data

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **96/66.3,** 96/50 PT, 96/59, 96/22

[51] **Int. Cl.** **G03c 5/30,** G03c 5/26, G03c 5/50

[58] **Field of Search** 96/50, 66, 66.3, 109

[56] **References Cited**

UNITED STATES PATENTS

2,453,346	11/1948	Russell	96/109
3,086,863	4/1963	Hunt et al.	96/114
3,126,282	3/1964	Hunt	96/59
3,353,956	11/1967	Rogers et al.	96/29
3,377,166	4/1968	Weyerts et al.	96/66.3
3,576,633	4/1971	Henn et al.	96/66.5
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3,708,299	1/1973	Shimamura et al.	96/50 R

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[57] **ABSTRACT**

A method of processing photographic materials wherein an imidazole compound is present during development to improve development characteristics, for example the speed of development, is disclosed.

7 Claims, No Drawings

PHOTOGRAPHIC MATERIAL DEVELOPMENT METHOD

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation application of our earlier copending application Ser. No. 5,957, filed on Jan. 26, 1970, and claiming priority from Jan. 24, 1969 based on Japanese Patent application Ser. No. 5126/69, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a silver halide photographic material and more particularly, it is concerned with a method of processing a silver halide photographic light-sensitive material.

2. Prior Art

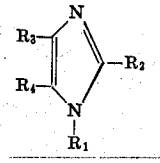
In the development of a silver halide photographic material, it is desirable to promote the rate of development or to increase the speed of the photographic material. For these purposes, it is known to use amine compounds as development accelerators. Typical examples are alkylamines (as disclosed in U.S. Pat. No. 2,196,037), aralkylamines (as disclosed in U.S. Pat. Nos. 2,496,903; 2,515,147 and 2,541,889), phenoxyalkylamines (as disclosed in U.S. Pat. No. 2,482,546), heterocyclic alkylamines (as disclosed in U.S. Pat. No. 2,605,183), morpholine, piperidine, and the like (as disclosed in U.S. Pat. No. 2,304,025) and xylilenediamine (as disclosed in British Patent No. 1,086,618).

However, these amines generally have a bad odor. Furthermore, their concentrations in the processing solutions often cannot be held constant because of their volatility. Although the rate of development is accelerated by amines, the film speed does not increase correspondingly and rather an increase in fog and deterioration in the granularity of the developed silver are observed.

It is the principal object of this invention to provide a development accelerator capable of being used easily, of accelerating the rate of development and of increasing the effective speed with no fog increase nor deterioration of the silver image.

DESCRIPTION OF THE INVENTION

For this object, the present invention provides a method of treating a photographic light-sensitive material which comprises developing a silver halide photographic light-sensitive material in the presence of an alkyl-substituted or hydroxyalkyl-substituted imidazole derivative represented by the following general formula,



wherein R_1, R_2, R_3 and R_4 each is selected from the group consisting of a hydrogen atom, an alkyl group, a hydroxyalkyl group and an alkenyl group and wherein

at least one of R_1, R_2, R_3 and R_4 is selected from the group consisting of an alkyl group, a hydroxyalkyl group and an alkenyl group.

DETAILED DESCRIPTION OF THE INVENTION

Illustrative compounds within the scope of the above formula and which can be used in the invention, are:

2-methylimidazole
4-methylimidazole
2,4-dimethylimidazole
2-ethyl-4-methylimidazole
2-amyl-imidazole
1-isoamyl-2-methylimidazole
4,5-dimethylimidazole
2-ethylimidazole
1-methylimidazole
2,4,5-trimethylimidazole
4-hydroxymethyl-5-methylimidazole
4-(2-hydroxyethyl)-5-methylimidazole
1-allyl-2-methylimidazole
1-vinyl-2-methylimidazole

The above compounds are known. Methods for their preparation are described in *The Chemistry of Heterocyclic Compounds, Imidazole and Derivatives*, Interscience Publishers, Inc., New York (1953). As is described in U.S. Pat. No. 3,126,282, imidazole can be added to the first step (black and white development) of a color reversal processing for the films in which couplers are incorporated, but this compound is less effective in development acceleration than the alkylimidazole derivatives of the present invention.

The compounds of the present invention can be applied to silver halide photographic materials in general, as development accelerators in particular, for relatively low speed fine grain materials. Addition of the known development accelerators into a developer results in deterioration of graininess and resolution, which is particularly undesirable in materials used for high resolution purposes. On the contrary, use of the compounds of this invention is not accompanied by a comparable deterioration of the photographic image. In color reversal processing, the presence of the compounds of this invention in the black and white developer also increases the film speed or shortens the processing time. They act more effectively in increasing the rate of development, increasing the speed and image sharpness of a photographic image than the commonly used thiocyanates and alkylamines. Moreover, the compounds of the present invention are not accompanied by any increase in developer fog. The light-development can also be accelerated without deterioration of dot quality. The compounds of the present invention can be rapidly processed without raising the developing temperature, although with a combination of the imidazoles of the present invention and a temperature increase, a further reduction of processing time is also possible.

The developers to which the compound of the present invention can be effectively applied is the commonly used silver halide photographic developer, that is, aqueous solution containing one or more of hydroquinone, 1-phenyl-3-pyrazolidone and N-methyl-p-aminophenol, to which antioxidants such as sodium sulfite or ascorbic acid, salts such as sodium sulfate, pH-adjusting compounds or pH-buffers such as boric acid, borax, sodium hydroxide, sodium carbonate or trisodium phosphate, development inhibitors such as potas-

sium iodide or potassium bromide, and organic fog retarders such as 6-nitrobenzoimidazole or benzotriazole can be added. In some cases, aldehydes such as formaldehyde or glutaraldehyde can be added thereto. Besides being added to a developer, the compound of this invention can also be added to a bath prior to development or can be incorporated into a silver halide emulsion. In the case of adding to a developer, the amount of the compound can generally range from 0.01 g. to 100 g. per 1000 ml. of the developer, preferably from 0.05 g. to 10 g./1. When the compound is added to a silver halide emulsion, a suitable amount can be from 0.01 g. to 50 g. per 1 mol. of silver halide and the addition can be carried out at any step in making the emulsion. Preferably, it is incorporated into the emulsion after the second ripening step and before the coating step. Furthermore, instead of incorporating the compounds of this invention directly into an emulsion layer, they can be added to an adjacent layer, such as a protective layer, after which it permeates through the emulsion layer. The compounds of the present invention can be applied to silver chloride, silver bromide, silver chlorobromide, silver iodide, silver iodobromide and silver chloroiodobromide emulsions. The emulsion can be sensitized chemically with an unstable sulfur compound, a gold compound or mixtures thereof. The emulsion can be spectrally sensitized with a cyanine dye or a merocyanine dye. The emulsion can be stabilized with a heterocyclic compound, such as 4-hydroxy-6-methyl-1,3,3a, 7-tetraxindene or 1-phenyl-5-mercaptotetrazole. Furthermore, the emulsion can be hardened with a hardener such as formalin or mucochloric acid or can contain a surface active agent to facilitate coating.

The following examples are given to illustrate the invention further in detail, but without limiting it.

EXAMPLE 1

A fine grain positive film for cinematic use, on which a fine grain silver chlorobromide-gelatin emulsion had been coated, was subjected to development with a developer having the following composition at 27°C.

Developer A	
Water	800 ml.
N-Methyl-p-aminophenol sulfate	20 g.
Sodium Sulfite	100 g.
Hydroquinone	5 g.
Borax	2 g.
Water to make 1000 ml.	

The standard development time for the developer of the above formula was 4 minutes, but, when a compound of this invention, 2-methyl-imidazole was added, the developing time was shortened as shown in Table 1 below. Development in 4 minutes with addition of a compound of this invention gave the high sensitivity as shown in Table 1 below.

EXAMPLE 2

A high speed film, comprising a support with a color sensitized silver iodobromide-gelatin emulsion coated thereon, was subjected to development at 20°C. with a developer having the following composition.

Developer B		
Water	800	ml.
1-Phenyl-3-pyrazolidone	0.2	g.
Sodium Sulfite	100	g.
Hydroquinone	5	g.
Borax	2	g.
Boric Acid	1	g.
Potassium Bromide	1	g.
Water to make 1000 ml.		

The standard development time for the developer of the above formula was 8 minutes, but, when a compound of this invention, 2-methylimidazole, was added, the developing time was shortened as shown in Table 2 below.

TABLE 2

Developer B	Amount Added g./l. (mol./l.)	Developing Time
Control	0	8 min.
with 2-Methylimidazole	0.82 (1×10^{-2})	6 min.
with 2-Methylimidazole	1.64 (2×10^{-2})	5 min.

EXAMPLE 3

A high resolution plate, comprising a support with an ultra-fine grain silver iodobromide gelatin emulsion coated thereon, was subjected to development at 20°C. with a developer having the following composition.

Developer C		
Water	800	ml.
1-Phenyl-3-pyrazolidone	0.5	g.
Sodium Sulfite	50	g.
Hydroquinone	12	g.
Sodium Carbonate Monohydrate	60	g.
Potassium Bromide	2.0	g.
Benzotriazole	0.2	g.
Water to make 1000 ml.		

The standard development time for the developer of the above formula was 6 minutes, but when a compound of this invention, 2-methylimidazole, was added, the developing time was shortened as shown in Table 3 below. Development in 6 minutes with addition of the compound of the invention gave the high speed as shown in Table 3 below.

TABLE 1

Developer A	Amount g./l.	Development in 4 Min. Relative Sensitivity	Fog	Gamma	Developing Time Required for Obtaining a Relative Sensitivity of 100
Control	0	100	0.04	1.35	4 min.
with 2-Methylimidazole	1	220	0.04	1.35	2 min.
with 2-Methylimidazole	4	430	0.05	1.40	1 min.

TABLE 3

Developer C	Amount g./l.	Development in 4 Min. Relative Sensitivity	Fog	Gamma	Developing Time Required for Obtaining a Relative Sensitivity of 100
Control	0	100	0.04	3.24	6 min.
with 2-Methylimidazole	1	180	0.04	3.80	3 min.

EXAMPLE 4

A fine grain positive film for cinematic use comprising a support with a fine grain silver chlorobromide-gelatin emulsion coated thereon, was subjected to development at 24°C. with a developer having the following composition.

Developer D		
Water	800	ml.
N-Methyl-p-aminophenol Sulfate	1.7	g.
Sodium Sulfate	50	g.
Hydroquinone	4.4	g.
Borax	10	g.
Boric Acid	5.0	g.
Potassium Bromide	0.5	g.
Water to make 1000 ml.		

The standard development time for the developer of the above formula was 5 minutes, but, when 1×10^{-2} mol./l. of a compound of the invention was added, the developing time was shortened as shown in Table 4 below.

TABLE 4

Developer D	Amount Added g./l.	Developing Time
Control	0	5 min.
with 2-Methylimidazole	0.82	3 min. 10 sec.
with 2,4-Dimethylimidazole	0.96	3 min.
with 2,4,5-Trimethylimidazole	1.10	3 min.
with 2-Ethylimidazole	0.96	3 min. 20 sec.
with 1-Methylimidazole	0.82	2 min. 50 sec.
with 4-Hydroxymethyl-5-methylimidazole	1.12	3 min. 20 sec.
with 2-Methyl-4-butylimidazole	1.38	3 min. 20 sec.
with 4-Allyl-2-methylimidazole	1.22	2 min. 40 sec.

EXAMPLE 5

A microfilm, comprising a support with a fine grain silver chlorobromide-gelatin emulsion coated thereon, was subjected to development at 20°C. with a developer having the following composition.

Developer E		
Water	800	ml.
N-Methyl-p-aminophenol Sulfate	1.0	g.
Sodium Sulfite	75	g.
Hydroquinone	9.0	g.
Sodium Carbonate Monohydrate	29	g.
Potassium Bromide	6.0	g.
Water to make 1000 ml.		

The standard development time for a developer of the above formula was 4 minutes, but, when a compound of this invention, 2-methylimidazole, was added, the developing time was shortened as shown in Table 5 below. Development in 4 minutes with the addition of a compound of this invention gave a high speed as shown in Table 5 below.

TABLE 5

Developer E	Amount g./l.	Development in 4 Min. Relative Sensitivity	Fog	Gamma	Developing Time Required for Obtaining a Relative Sensitivity of 100
Control	0	100	0.19	4.00	4 min.
with 2-Methylimidazole	1	160	0.19	4.10	2 min.
with 2-Methylimidazole	4	330	0.20	4.15	1 min.

EXAMPLE 6

A high speed direct X ray film, comprising a support with a silver iodobromide-gelatin emulsion coated thereon, was subjected to a high temperature rapid development at 35°C. with Developer C of Example 3. With Developer C, 100 seconds was ordinarily required for development, but, when a compound of this invention was added, the developing time was shortened as shown in Table 6 below.

TABLE 6

Developer C containing	Amount Added g./l. (mol/l.)	Developing Time
Control	0	100 sec.
with 2-Methylimidazole	2.1 (2.5×10^{-2})	55 sec.
with 2-Methylimidazole	4.2 (5.0×10^{-2})	45 sec.
with 2-Methylimidazole	2.4 (2.5×10^{-2})	45 sec.
with 2,4-Dimethylimidazole	2.4 (2.5×10^{-2})	45 sec.
with 2,4-Dimethylimidazole	4.8 (5.0×10^{-2})	40 sec.

EXAMPLE 7

A lithographic film for photomechanical use, comprising a support and a silver chlorobromide-gelatin emulsion coated thereon, was subjected to development at 20°C. with a developer having the following composition.

Developer F		
Water	500	ml.
Sodium Sulfite	30	g.
Paraformaldehyde	7.5	g.
Potassium Bisulfite	2.6	g.
Boric Acid	7.5	g.
Hydroquinone	22.5	g.
Potassium Bromide	1.6	g.
Water to make 1000 ml.		

The standard development time for the developer of the above formula was 2 minutes, but when a compound of this invention, 2-methylimidazole, was added, the developing time was shortened as shown in Table 7 below, without lowering the net point quality.

TABLE 7

Developer F	Amount Added g./l.	Developing Time
Control	0	2 min.
with 2-Methylimidazole	1	1 min. 30 sec.
with 2-Methylimidazole	2	1 min.

EXAMPLE 8

A color photographic material, comprising substantially:

a. a blue-sensitive silver halide-gelatin emulsion layer containing a yellow color coupler forming a yellow dye by reaction with an oxidized developing agent;

b. a yellow filter layer;

c. a green-sensitive silver halide-gelatin emulsion layer containing a magenta color coupler forming a magenta dye;

d. a red-sensitive silver halide-gelatin emulsion layer containing a cyan color coupler forming a cyan dye; and

e. a film support;

was subjected to development at 20°C. for 15 minutes using the following developer.

Developer G		
Water	800	ml.
N-Methyl-p-aminophenol Sulfate	3.0	g.
Sodium Sulfite	50	g.
Hydroquinone	6.0	g.
Sodium Carbonate Monohydrate	42	g.
Potassium Bromide	3.0	g.
Water to make 1000 ml.		

The film was immersed in a solution of chrome alum for 3 minutes, then both sides were irradiated with white light and developed for 15 minutes with a color forming developer having the following composition:

Color Forming Developer		
Water	800	ml.
Benzyl Alcohol	6.0	ml.
Sodium Sulfite	5.0	g.
Trisodium Phosphate 12-Hydrate	35	g.
Potassium Bromide	1.0	g.
Sodium Hydroxide	2.5	g.
Citrazinic Acid	1.2	g.
4-Amino-N-ethyl-N-(beta.methanesulfonamide ethyl)-m-toluidine Sesquisulfate Monohydrate	10	g.
Water to make 1000 ml.		

Then, the film was washed with water for 5 minutes, immersed in a solution of acetic acid and sodium acetate for 5 minutes, washed with water for one minute, desilvered with a bleaching solution containing 50 g. of potassium ferricyanate and 15 g. of potassium bromide per 1 l. and fixed with sodium thiosulfate.

The standard development time for the above formula was 15 minutes, but, when a compound of this invention was added, the developing time was shortened as shown in Table 8 below. For comparison, a conventional agent, potassium thiocyanate, was also used.

TABLE 8

Color Forming Developer	Amount Added g./l. (1.0×10^{-2} mol./l.)	Developing Time
Control	0	15 min
with 2-Methylimidazole	0.82	9 min.
with 2,4-Dimethylimidazole	0.96	9 min.
with 1-Methylimidazole	0.82	8 min.
with 1-Allyl-2-Methylimidazole	1.22	7 min.
with Potassium Thiocyanate	0.97	12 min.

EXAMPLE 9

A reversal color film whose couplers are incorporated in the developers, comprising a support of cellulose acetate film and a red-sensitive silver iodobromide-gelatin emulsion, a green-sensitive silver iodobromide-gelatin emulsion, a blue light absorbing yellow filter layer consisting of colloidal silver and a blue-sensitive silver iodobromide-gelatin emulsion coated thereon in the order shown, was developed at 24°C. for five minutes with a black and white developer having the following composition.

Developer H

Water	800	ml.
N-Methyl-p-aminophenol Sulfate	2.0	g.
Sodium Sulfite	90	g.
Hydroquinone	8.0	g.
Sodium Carbonate Monohydrate	52.5	g.
Potassium Bromide	5.0	g.
Water to make 1000 ml.		

This developer was divided into 4 parts with one to be used as a control and compounds of this invention were added to the remaining three.

A) Control	No Addition
B) 2-Methylimidazole	0.82 g./l. (0.01 mol./l.)
C) 1-Methylimidazole	0.82 g./l. (0.01 mol./l.)
D) 1-Allyl-2-methylimidazole	1.22 g./l. (0.01 mol./l.)

Then the film was washed with water for two minutes,
subjected to reversal exposure by red light from the back of the film and treated with a cyan color forming developer having the following composition at 24°C. for five minutes.

Cyan Color Forming Developer

Water	800	ml.
Sodium Sulfite	5.0	g.
2-Amino-5-diethylaminotoluene Hydrochloride	0.6	g.
Sodium Carbonate Monohydrate	15	g.
Potassium Bromide	0.5	g.
Potassium Iodide (0.1% aqueous solution)	5.0	ml.
1,5-Dihydroxy-2,6-dibromo-naphthalene)	1.2	g.
Sodium Hydroxide	2.0	g.
Monobenzyl-p-aminophenol Hydrochloride	0.2	g.
Water to make 1000 ml.		

The thus treated film was then washed with water for five minutes, desilvered for two minutes with a bleaching solution containing 100 g. of potassium ferricyanide and 10 g. of potassium bromide per 1 liter and fixed for 2 minutes with a solution of sodium thiosulfate. The characteristic values of the film subjected to cyan reversal development are shown in Table 9 below.

TABLE 9

Test No.		Amount Added g./l. (0.01 m./l.)	Characteristic Values: Relative Sensitivity Values	Characteristic Values: Maximum Density
A	Control	0	100	3.32
B	2-Methylimidazole	0.82	270	3.25
C	1-Methylimidazole	0.82	320	3.13
D	1-Allyl-2-methyl-imidazole	1.22	560	3.03

EXAMPLE 10

2-Methylimidazole of the invention in the form of aqueous solution was added to a silver iodobromide-gelatin emulsion containing 3.0 mol. percent of silver iodide and coated onto a film base, followed by drying. The test film was developed at 24°C. for 5 minutes with Developer D of Example 4. The resulting photographic characteristic values are shown in Table 10 below.

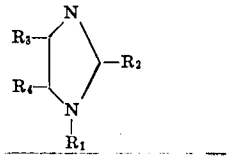
TABLE 10

Emulsion	Addition Amount g./l. mole silver halide	Characteristic Values: Relative Sensitivity	Fog	Gamma
Control	0	100	0.05	0.85
with 2-Methylimidazole	2	130	0.06	0.90
with 2-Methylimidazole	8	160	0.07	0.82

What is claimed is:

1. A process for accelerating the development of an exposed gelatino-silver halide photographic light-sensitive material, which comprises:
treating said photographic material with a member selected from the group consisting of a pre-bath for

development and a developer, said pre-bath comprising a conventional pre-bath for development and an imidazole derivative, and said developer comprising a conventional photographic developer and an imidazole derivative, said imidazole derivative represented by the following formula:



wherein R_1, R_2, R_3 and R_4 each represent a member selected from the group consisting of a hydrogen atom, an alkyl group, a hydroxyalkyl group, and an alkenyl group, and wherein at least one of said R_1, R_2, R_3 and R_4 is a member selected from the group consisting of an alkyl group, a hydroxyalkyl group, and an alkenyl group.

2. The process of claim **1,** wherein said compound is a member selected from the group consisting of 2,4-dimethylimidazole, 2-ethyl-4-methylimidazole, 2-ethylimidazole, and 1-allyl-2-methylimidazole.

3. The process of claim **1,** wherein said compound is 1-methylimidazole.

4. The process of claim **1,** wherein said compound is 2-methylimidazole.

5. The process of claim **1,** wherein said compound is a member selected from the group consisting of 4-methylimidazole, 2-amylimidazole, 1-isoamyl-2-methylimidazole, 4,5-dimethylimidazole, 2,4,5-trimethylimidazole, 4-hydroxymethyl-5-methylimidazole, 4-(2-hydroxyethyl)-5-methylimidazole, and 1-vinyl-2-methylimidazole.

6. The process of claim **1,** wherein said compound is present in an amount of from 0.01 to 100 grams per liter of developer.

7. The process of claim **6,** wherein said amount ranges from 0.05 to 10.0 grams per liter of developer.

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