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REVERSAL PROCESS OF PHOTOGRAPHY

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This invention relates to the processing of photographic materials. More particularly it relates to the processing of color reversal photographic materials. Still more particularly, it relates to an improvement in the first development step in color reversal processing.

It is known to use compounds having silver-halide solvent action as development accelerators in the first development step of color reversal processing. Without the use of such compounds, the development will be inefficient so that the reversal highlights are not cleared out and are heavy or dense in the final image. The development accelerator should clean out the highlights without excessive loss of image density and without producing a great deal of latent image growth. The accelerator should not cause fog in the unexposed portions of the film. On the other hand, for reasons not entirely understood, an accelerator may help to improve resolving power and definition of the image. In processing of a multilayer color element, the development accelerator may improve brightness, color saturation, penetration of developing agent and color balance among the various layers.

Both inorganic and organic compounds have been used as development accelerators, but in the more recent literature, it would appear that certain of the organic compounds, particularly the aliphatic amines, more nearly fulfill the desired requirements of a development accelerator as described above. Unfortunately many of these organic compounds are difficult to dissolve in the photographic developers, are volatile so that stabilization of concentration is difficult, and have objectionable odors.

An object of this invention is to provide improvement in the art of processing silver-halide emulsions, particularly in color reversal processing of silver-halide emulsions. Another object is to provide an improved first development step in color reversal processing using a novel class of development accelerators which overcomes the disadvantages of development accelerators known in the art. Specifically, the object of this invention is to provide a class of organic development accelerators for use in color reversal processing the members of which are very soluble, non-volatile, and free of objectionable odor. Other objects will be apparent from the following description of the invention.

The present invention provides an improvement in a reversal process of photography in which a photographic element, e.g., a photographic film, plate or paper having at least one light-sensitive silver halide emulsion layer, is first developed to form silver images, reexposed to light and given a second development to form silver images in the reverse areas, characterized in that the first development is carried out in a developer solution initially containing from about 0.005 to about 0.1 mole per liter of imidazole.

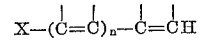
In a preferred aspect of the invention an improvement is provided in a reversal process of color photography wherein color component images are formed in each of a plurality of superimposed light-sensitive silver halide emulsion layers containing a non-diffusing color former and at least one light-filter layer, by a first development of exposed silver halide to form silver images only, followed by reexposure and a second development to form silver images and dye images in situ in the reverse image areas of the emulsion layers; characterized in that the first development is in an aqueous alkaline developer solution containing a compound encompassed by the above formula. Upon completion of the second or color reversal development, it will be found that the presence of the imidazole produces the equivalent of an increase in light sensitivity of the multicolor film used, together with excellent cleanout of reversal highlights and without significant loss in maximum density.

The aqueous alkaline developer solutions, except for the imidazole, contain the conventional ingredients, that is, the usual types of developing agents used for noncolorforming development, e.g., metol (N-methyl-p-aminophenol hydrosulfate or hydrochloride), hydroquinone, monochloro-, monobromo- or dichlorohydroquinone, toluquinone; the 3-pyrazolidones of Kendall U.S. Patent 2,289,367 and mixtures of two or more of these agents; sodium sulfite; sodium carbonate, sodium borate, borax; potassium bromide, and equivalents of these compounds.

In the case of the second development where a colored image is formed, the developer solution may contain any conventional primary aromatic amine color developing agent. Suitable such agents are described in the patents listed below describing useful color formers.

In general, the multilayer color films can have dispersed in the silver halide emulsion layers any non-diffusing color former. The color former or mixture of color formers selected for a particular layer will depend upon the specific spectral or absorption characteristics desired for said layer. Usually, three differently sensitized silver halide emulsion layers will be used which are primarily sensitive to the blue, green and red regions of the spectrum, and the color formers will be chosen to form yellow, magenta and cyan dyes which are complementary in color to the utilized sensitivity of the respective emulsion layers.

In the case of color formers, the color-forming nucleus has, as the active color-coupling group, a structure of the formula:



where *x* is HO—RHN—, where R is alkyl of 1–4 carbons, e.g., methyl, ethyl, propyl or butyl, and *n* is 0 or 1. Compounds of this type include phenolic or naphtholic compounds and aromatic primary or secondary amines with hydrogen or replaceable groups, e.g., halogen, carboxyl and sulfonic acid groups para to the hydroxyl and active methylene compounds such as acylacetarylides, cyanoacetyl compounds, pyrazolones and other heterocyclic active methylene-containing compounds. While these are the preferred color-formers, this invention works equally well with couplers and color developers that yield other types of dyes, for instance, the phenazonium and azine dyes as described in the following U.S. patents: Coles, 2,524,725; Schmidt et al., 2,536,010, 2,543,338; Tulagin et al., 2,524,741, 2,525,502, 2,525,503, 2,591,642, and the dyes described in Jennen, 2,673,801.

Preferred color formers are essentially colorless polymers which form coherent, smooth, water-permeable films. A practical class of such color formers is described in U.S. Patent 2,310,943 and in J. Am. Chem. Soc. 73, 4930 (1951). Others are described in U.S. Patents 2,758,029 and 2,828,205 and the patents listed therein.

Any of the known water-permeable colloid binding agents can be used in the emulsions. They may be of the natural or synthetic type, and suitable ones are described in the patents referred to above and in Huot U.S. Patent 2,920,962.

The invention will be further illustrated by, but is not intended to be limited to, the following examples.

Example I

A first-developer solution was made up having the following composition:

H_2O	ml	800
Monomethyl-p-aminophenol sulfate	g	1.0
Na_2SO_3, anhydrous	g	60.0
Hydroquinone	g	10.0
$Na_2CO_3 \cdot H_2O$	g	50.0
KBr	g	5.0

H_2O to 1.0 liter.

This developer solution was divided into five separate portions and imidazole was added to four of the portions to give the following concentrations:

Developer solution:	Imidazole concentration
A (control)	0.
B	0.5 g. per liter=.0075 molar.
C	1.0 g. per liter=.015 molar.
D	2.0 g. per liter=.03 molar.
E	4.0 g. per liter=.06 molar.

A multilayer material comprising:

(*a*) A dimensionally stable vinylidene chloride/methyl acrylate/itaconic acid copolymer coated polyethylene terephthalate film base support as described in Example IV of Alles U.S. Patent 2,779,684;

(*b*) A gelatino-silver bromo-iodide emulsion layer sensitive to blue and red light containing 6.8 mole percent silver iodide and 93.2 mole percent silver bromide and containing a non-migratory cyan color-former (containing a naphthol nucleus);

(*c*) A gelatino-silver bromo-iodide emulsion layer sensitive to blue and green light containing 6.8 mole percent silver iodide and 93.2 mole percent silver bromide and containing a non-migratory pyrazolone magenta color-former;

(*d*) A colloidal silver intermediate layer for absorbing blue light;

(*e*) A gelatino-silver bromo-iodide emulsion layer sensitive to blue light containing 1.7 mole percent silver iodide and 98.3 mole percent silver bromide and containing a non-migratory benzoyl acetanilide yellow color-former

is cut into a number of 10 inch by 35 mm. strips which are exposed in a conventional manner to a white light tungsten source (filtered to simulate daylight) through a square-root-of-two neutral density step-wedge. One of these exposed film strips was then placed in each of the developer solutions described above (labeled A–E) for 12 minutes at 75° F.

After the first development, all 5 films strips were

treated identically beginning with a 1 minute immersion in a chrome alum-acetic acid short stop bath, washing for 3 minutes in tap water, followed by a white-light, flash-exposure of 15 seconds to each side of the film strips. The second exposure was followed by color development for 15 minutes in an aqueous solution comprising, as the color developing agent, 10 grams per liter of solution of 4-amino-N-(β-methanesulfoneamidoethyl) - m - toluidine sesquisulfate monohydrate. The film strips were next rinsed in tap water for 10 seconds, treated again in the acid short stop bath for 1 minute 50 seconds, washed in tap water for 4 minutes, and bleached for 8 minutes in a solution of the following composition:

Potassium ferricyanide	g	60
KBr	g	20
Borax	g	20
Glacial acetic acid	ml	10
Potassium alum	g	25
pH		4.0

H_2O to 1 liter.

The film strips were then washed for 3 minutes in tap water, fixed for 3 minues in a solution containing 127 g. of anhydrous sodium thiosulfate per liter of solution, washed 8 minutes in tap water, and dried.

Image densities of the dried film strips to blue, green, and red lights were read on a precision integrating sphere densitometer (Frayne, J. G. with Crane, G. R., J. Soc. Motion Picture Television Engrs. 35, No. 2, Aug. 1950, p. 184) modified as described by A. C. Lapsley and J. P. Weiss (J. Soc. Motion Picture Television Engrs., 56, Jan. 1951, p. 23).

Calculations based on these density readings gave the following results:

First-developer	Relative Speed of Record			Gamma			Maximum Den.		
	Blue	Green	Red	Blue	Green	Red	Blue	Green	Red
A (control)	100	100	100	1.58	2.36	1.72	2.15	3.72	2.53
B	125	156	125	1.54	2.16	1.71	2.07	3.32	2.56
C	160	200	160	1.60	2.00	1.62	2.20	2.85	2.28
D	200	250	200	1.60	1.61	1.62	2.10	2.38	2.10
E	250	312	250	1.63	1.08	1.27	1.93	1.49	1.59

In this example and in the following ones, the temperature of the tap water was about 65° F.

Example II

Example I was essentially repeated, using a multi-layer film of the same structure as described but coated from somewhat more sensitive emulsions having larger silver halide grain size in the case of the layers containing cyan and magenta color formers. These latter emulsions contained silver halide which was 3.4 mole per cent in silver iodide and 96.6 mole percent in silver bromide while the emulsion layer containing the yellow color former was as previously described. The same general qualitative effects can be observed but they are quantitatively smaller because, it is presumed, the imidazole has less solvent action on the larger silver halide grains. With duplication of processing and density reading as described in Example I it was possible to obtain the following data:

First-developer	Relative Speed of Record			Gamma			Maximum Den.		
	Blue	Green	Red	Blue	Green	Red	Blue	Green	Red
A (control)	100	100	100	1.54	2.40	2.14	2.63	3.05	3.13
B	100	125	100	1.50	2.72	1.90	2.33	2.88	2.86
C	128	125	100	1.40	2.18	1.90	2.17	2.58	2.73
D	160	156	125	1.60	1.88	1.80	2.19	2.16	2.52
E	200	156	160	1.52	.86	1.86	1.85	1.10	2.25

Example III

A first developer solution was made up having the following composition:

Water	ml	800
Monomethyl-p-aminophenol	g	1.0
Na_2SO_3, anhydrous	g	60
Hydroquinone	g	10
$Na_2CO_3 \cdot H_2O$	g	50
KBr	g	5.0

H_2O to 1.0 liter.

This developer solution was divided into two portions identified as follows:

Portion A—control..... No addition.
Portion B—imidazole..... 1.4 g./liter (0.021 molar).

A multilayer color film had a structure similar to that described in Example 1 except that all three of the light-sensitive emulsion layers contained a silver halide which was 1.7 mole percent in silver iodide and 98.3 mole percent in silver bromide. From this film there were cut two 10-inch by 35-mm. strips which were exposed as in Example I.

One of the exposed strips was treated in "portion A" and the other in "portion B" of the first development solution described above at 68° F. for 15 min. After first development, the strips were treated identically for 1 minute in a chrome alum-acetic acid short stop bath and then for three minutes in a tap water wash. There followed a white light flash exposure of 15 seconds to each side of the film strips which, in turn, was followed by simultaneous color development of the 3 film strips in a solution of the following composition:

H_2O	ml	800
p-Aminodiethylaniline, hydrochloride	g	2.5
Na_2SO_3, anhydrous	g	10
$Na_2CO_3 \cdot H_2O$	g	47
KBr	g	2.0

H_2O added to make 1 liter.

Color development was followed by a 10-second rinse in tap water; a 2-minute soaking in the chrome alum-acetic acid bath mentioned earlier in this example; a 4-minute wash period in tap water; a bleaching treatment for 8 minutes in a solution comprising, per liter of solution, 10 g. of potassium dichromate and 20 grams of KBr; a 3 minute wash; a fixing bath for 3 minutes; and a 10 minute wash period. The processing solutions were maintained at 68° F. The film strips were dried in a conventional manner and then densities were read as in Example I.

Calculations based on these readings gave the following results:

Accelerator in First Developer	Relative Speed of Record			Maximum Density of Record		
	Blue	Green	Red	Blue	Green	Red
Control	100	100	100	4.00	3.83	3.22
Imidazole	283	399	303	3.70	3.57	3.03

In the examples above the speed values indicate the relative speed of the developer which has arbitrarily been set at 100 for each of the three records as developed in the "control" solutions. If one developer gives a "relative speed" twice that of another, this means that the photographic film will require about half the degree of exposure to give an image of a given density when treated similarly in the two developers. The term "gamma" is used as defined in Neblette, Photography (published by D. Van Nostrand Company, 1942), page 412.

In the processing of color reversal photographic films an advantageous increase in speed can be obtained by the use of first-developer solutions as described herein.

The increase in speed through use of such development accelerators is achieved without sacrifice, to the extent that occurs with use of many of the known development accelerators, in other properties, e.g. maximum density, graininess and fogging tendency. The practice of this invention results in developed images having cleaner reversal highlights and improved definition. The excellent water-solubility of the imidazole used in accordance with this invention makes them compatible with other ingredients in a wide variety of developer solutions. This water-solubility also assures thorough and even distribution of the development accelerator throughout the emulsion and, in the case of a multilayer color element, this is important in achieving good color balance. A further and very significant advantage of use of imidazole is that it is free of the objectionable odors of many of the known organic-type developer accelerators. Also, being non-volatile compounds, there is no danger of change of concentration of accelerator as a function of age of the developer solution. Although primarily of use as developer accelerators in color reversal processing, the compounds of this invention are also useful as development accelerators in other types of photographic developer solutions, particularly in black-and-white reversal processing. In general, this invention is a method of accelerating development without promoting fog, solution of unexposed grains or latent image growth.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

I claim:

1. A reversal process of photography in which an exposed photographic element having at least one light-sensitive silver halide emulsion layer containing a non-diffusing color former
   (*a*) is given a first development in an aqueous alkaline developer solution containing a developing agent to form silver images only,
   (*b*) re-exposed to light
   (*c*) given a second development in an aqueous developer solution containing a primary aromatic amino color developing agent to form both silver and dye images in the reverse areas of said emulsion layer; said process being characterized in that the first development is carried out in a developer solution containing about 0.005 to about 0.1 mole of imidazole per liter of solution.

2. A process as defined in claim 1 wherein said photographic element contains a plurality of superposed light-sensitive silver halide emulsion layers each containing a non-diffusing color former.

3. A process as defined in claim 1 wherein the developer solution for the first developer contains hydroquinone.

4. A process as defined in claim 1 wherein the developer solution for the first developer contains a mixture of N-methyl-p-aminophenol and hydroquinone.

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