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FIRST DEVELOPER FOR MULTILAYER COLOR FILM OF THE REVERSAL TYPE

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This invention relates to photographic developers and particularly to an improved first developer for multi-layer color film of the reversal type.

It has been claimed by operators in this field that the addition of very small quantities of soluble iodides to photographic developing solutions increases the rate of development, while larger quantities decrease the rate. The function of the soluble idodides is to precipitate insoluble silver salts. When potassium iodide is added to a hydroquinone or a p-monomethylaminophenol sulfate developer in a concentration ranging from 16.6 mgs. to 3.3 grams per liter of developer, it produces an increase in density, which rises to a maximum with increasing concentration and thereafter falls progressively. When the developing solution contains a concentration of potassium iodide greater than that which shows the maximum effect, it produces relatively more active development in the depths of the emulsion than in the surface layers.

It is known that in order to develop out the latent image in an exposed multi-layer photographic film of the reversal type it is necessary to develop the film first with a black and white developer. In this first development, the exposed silver-halide grains are reduced to metallic silver. The developing agents heretofore employed contain, in addition to the organic reducing agent such as hydroquinone or p-monomethylaminophenol, a small quantity of potassium bromide and sodium thiocyanate. The potassium bromide lowers the degree of ionization of silver bromide and by reducing the concentration of silver cations restrains development, whereas the sodium thiocyanate dissolves the residual silver-halide, which otherwise would prevent the clearing out of the highlight portions of the image.

In the case of multi-layer color film of the reversal type, it is difficult to obtain this silver-halide dissolving effect uniformly in all three emulsion layers. There is a tendency for the sodium thiocyanate to attack the top layer, which is usually the yellow layer, more strongly because of the higher concentration of the silver-halides in this layer. As the developing solution, containing the silver-halide solvent, diffuses deeper into the layer, the active concentration of the sodium thiocyanate decreases.

It is an object of the present invention to provide an improved photographic developer, for multi-layer color film of the reversal type, in which action of the silver-halide solvent is effectively controlled.

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Another object is to provide an improved first developer for reversal multi-layer color film which restrains the development of the yellow top layer and produces a greater density in such layer.

I have found that the foregoing undesirable effect on the yellow layer of a multi-layer color film of the reversal type, can be counteracted and controlled by the addition of a small quantity of potassium iodide to any black and white developing agent employed in the first development of color film and containing potassium bromide and a silver solvent. The presence of potassium iodide in an amount ranging from 2 to 12 mgs. per liter of developing solution, counteracts the effect of the silver solvent in the top layer as follows: The iodide ion is absorbed on the silver bromide crystal, in some cases actually replacing the bromide ion in the lattice of the silver-halide. The absorbed iodide ion greatly reduces the solubility of the silver-halide crystal in the silver solvent such as sodium thiocyanate, etc. Since the largest concentration of iodide ion is present in the top layer, the addition of small quantities of potassium iodide to the developer insures a means of balancing out the effect of the silver solvent in its more vigorous action on the top layer. Surprisingly, potassium iodide in an amount greater than 12 mgs. per liter of developer does not show this balancing-out effect. As a matter of fact, the presence of potassium iodide in the developer in an amount greater than 12 mgs. per liter shows a tendency to restrain development in all layers, i. e., yellow, magenta, and cyan layers.

Photographic multi-layer color materials, which may be developed with the first developer in accordance with the present invention, include all color reversible film. Such color reversible film consists of an integral tripack emulsion coated on the usual clear cellulose acetate or nitrate film base. Each of the emulsions is sensitized to one of the primary colors, namely, blue, green, and red. The top layer is blue sensitive. The filter layer, yellow in color and blue absorbing, lies under the top layer. Below this filter layer, is a green sensitive layer, and below this is a red sensitive layer. Each of the three silver-halide emulsion layers may contain dye-forming compounds which unite during the development of the silver image in an aromatic primary amino developing agent to form a dye with the oxidation product of the developing agent. Or the emulsions may be free from color-formers, in which case the film is processed with the color-

formers in the color developers by the second exposure and color development method as described in United States Patents 1,897,866; 1,900,870; 1,928,709 and 1,980,941.

The following example will serve to specifically describe the invention as applied to multi-color positive film. This example should not, however, be construed as limiting or restricting the present invention, but should be considered merely as illustrative.

Example

A 4" x 5" multi-layer color film sheet of the reversal type, such as prepared according to United States Patents 2,179,228; 2,179,239; 2,186,-849 and 2,220,187, was exposed and developed for 10 minutes at 68° F. in a developer of the following composition:

p-Monomethylaminophenol sulfate	grams	3
Sodium sulfite	do	50
Hydroquinone	do	6
Sodium carbonate (monohydrate)	do	40
Potassium bromide	do	2
Sodium thiocyanate	do	2
Potassium iodide	mgs	3

Water to make 1 liter.

The developed film was short stopped for 3 minutes in a 3% aqueous solution of acetic acid, and washed for 2 minutes in running water.

The washed film was given a second exposure for 3 minutes to light of a No. 1 photoflood lamp 30 inches away from the film.

The reexposed film was color developed for 15 minutes in a developer of the following composition:

Sodium sulfite	grams	5
p-Diethylaminoaniline hydrochloride	do	4
Sodium carbonate	do	40
Potassium bromide	do	1

Water to make 1 liter.

The color developed film was rinsed for 1 minute in running water, and hardened for 5 minutes in a 3% aqueous solution of chrome alum.

The hardened film was washed for 5 minutes in running water, and bleached for 10 minutes in a bath of the following composition:

	Grams
Potassium ferricyanide	60
Potassium bromide	15
Disodium phosphate	13
Sodium bisulfate	6

Water to make 1 liter.

The bleached film was then washed in running water for 5 minutes, fixed in a 20% solution of hypo for 5 minutes, washed for another 5 minutes in running water and then dried.

The resulting transparency was of superior quality and showed a greater density in the top yellow layer with a pleasing color balance in all layers.

Instead of employing sodium thiocyanate as the silver-halide solvent, ethylenediamine or its salts such as the sulfate, chloride, etc. and ammonium chloride may be employed in a concentration ranging from 1 to 8 grams per liter of developer. Similarly, instead of employing p-monomethylaminophenol sulfate as the reducing agent in the first developer, any reducing agent which is normally employed in black and white developers may be used, provided it does not color or stain the mutilayer film as pyrogallol does.

I claim:

1. In the process of restraining the development of the yellow layer in a multi-layer color film of the reversal type which includes exposing said film, developing it with a first developing bath for silver halide, re-exposing to light, color developing and bleaching the same, the improvement comprising using as the first developing bath an aqueous developing solution comprising a developing agent for silver-halide, potassium bromide, a silver solvent, and potassium iodide in an amount ranging from 2 to 12 mgs. per liter of developer.

2. The process according to claim 1 wherein the silver solvent is a member selected from the class consisting of sodium thiocyanate, ammonium chloride, and ethylenediamine and its salts.

3. In the process of restraining the development of the yellow layer in a multi-layer color film of the reversal type which includes exposing said film, developing it with a first developing bath for silver halide, re-exposing to light, color developing and bleaching the same, the improvement comprising using as the first developing bath an aqueous developing solution comprising a developing agent for silver-halide, potassium bromide, sodium thiocyanate, and potassium iodide in an amount ranging from 2 to 12 mgs. per liter of developer.

4. In the process of restraining the development of the yellow layer in a multi-layer color film of the reversal type which includes exposing said film, developing it with a first developing bath for silver halide, re-exposing to light, color developing and bleaching the same, the improvement comprising using as the first developing bath solution of the following composition:

p-Monomethylaminophenol sulfate	grams	3
Sodium sulfite	do	50
Hydroquinone	do	6
Sodium carbonate (monohydrate)	do	40
Potassium bromide	do	2
Sodium thiocyanate	do	2
Potassium iodide	mgs	3

Water to make 1 liter.

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