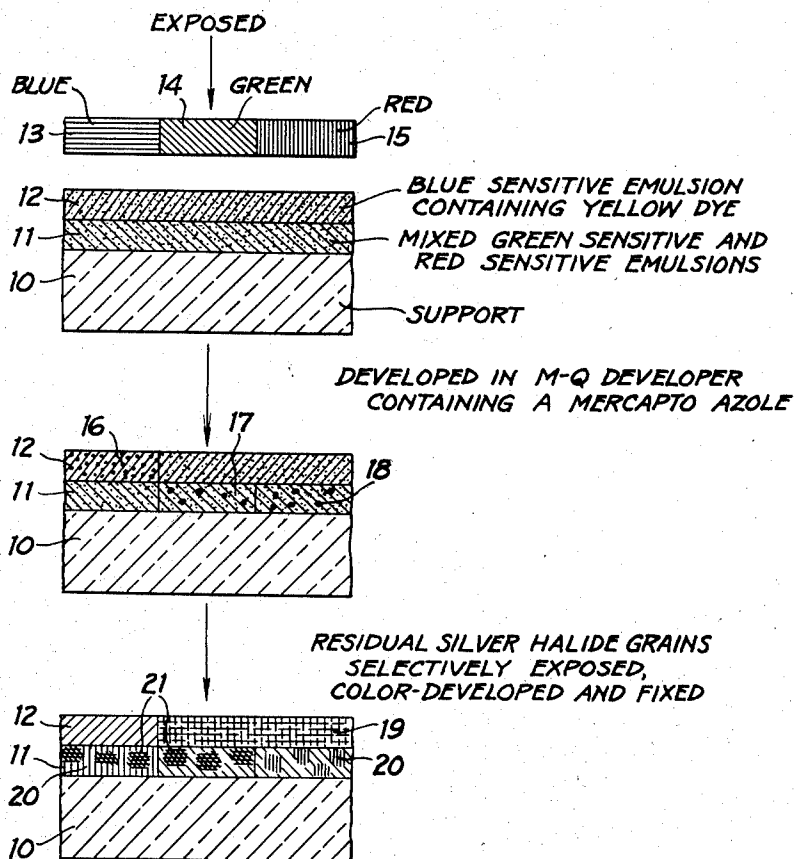


Oct. 21, 1952

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MERCAPTO AZOLES IN DEVELOPER FOR
MIXED GRAIN PHOTOGRAPHIC PROCESS
Filed Dec. 20, 1949

2,614,925



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UNITED STATES PATENT OFFICE

2,614,925

MERCAPTO AZOLES IN DEVELOPER FOR
MIXED GRAIN PHOTOGRAPHIC PROCESSBurt H. Carroll and Forrest A. Richey, Rochester,
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Application December 20, 1949, Serial No. 134,044

5 Claims. (Cl. 95-2)

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This invention relates to color photography and particularly to a mixed grain photographic process. In mixed grain processes, a mixture of sensitive silver halide grain sensitized to record different regions of the spectrum is used and a layer sensitized in this way may be combined on a single support with a layer sensitized to record only a single spectral region.

One of the defects encountered in color processes in which two or more of the component images are recorded in a single film is the occurrence of inter-image effects. By inter-image effects, we mean that the density of one of the component images is controlled not only by the exposure and development of the appropriate emulsion grains, but also by the development of other component images in adjacent layers or in adjacent areas of the same layer. These effects may be present in layer processes as well as in mixed grain processes. In mixed grain processes, for example those in which there is a negative development followed by selective exposure of the residual silver halide grains and color development of these grains to produce a reversal image, physical development may produce one of the more serious of these inter-image effects. Physical development brings about the exhaustion of the unexposed grains in the vicinity of exposed grains with consequent loss of density.

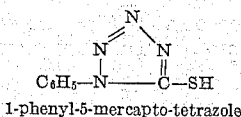
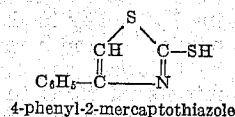
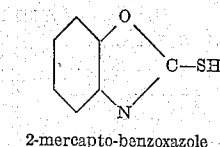
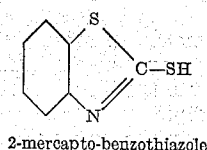
For example, in a mixed grain coating processed by selective re-exposure to produce reversal images, an area exposed to red light only will produce developable red-sensitive grains in proportion to the exposure, while green-sensitive and blue-sensitive grains should not be affected. The first development, for example, in an M-Q developer (a developer in which monomethyl-p-amino phenol and hydroquinone are the principal developing agents), would be followed by exposure to red light and development in a cyan coupler developer, exposure to green light and development in a magenta coupler developer and finally exposure to blue or white light and development in a yellow coupler developer. In the area exposed to red light, red-sensitive grains should become developable in the M-Q developer while the others should develop only in the appropriate coupler developers, giving an area of full strength of magenta and yellow and without cyan dye if there was full red light exposure in that area. If, however, there is physical development in the M-Q developer, some of the green-sensitive and blue-sensitive grains will be dissolved and deposited on the silver deposited from the red-sensitive grains and the magenta

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and yellow dyes will not have full intensity in the final image. Corresponding errors would be produced by physical development in the first or second color developers. A marked degree of physical development might be objectionable in any type of reversal processes including black and white, and in negative processes, either black and white or color, it introduces distortions of the reproduction scale which may be objectionable.

It is therefore an object of the present invention to provide a method for controlling inter-image effects in a mixed grain photographic layer. A further object is to provide a method for decreasing color degradation in a mixed grain emulsion layer. A still further object is to provide a means of controlling and reducing physical development during development of a mixed grain photographic emulsion. Other objects will be apparent from the following description of our invention.

These objects are accomplished by performing the first or negative development of a mixed grain photographic layer in a developer containing an azole having a mercapto substituent. Specific compounds which we have found useful for this purpose are the following, the first two being preferred.



The accompanying drawing illustrates in sectional views a mixed grain film at successive stages in our process.

According to our invention, a mixed grain photographic coating is used which may have three differently sensitized silver halide particles coated as a single layer as described, for example, in Mannes and Godowsky U. S. Patent 2,388,856, or the red-sensitive and green-sensitive silver halide grains may be incorporated in a single layer, with the blue-sensitive silver halide grains in a separate layer, either containing a yellow filter dye or separated from the mixed grain layer by an inter-layer containing a yellow coloring material. After exposure of the mixed

grain element, it is developed in a black-and-white developer, preferably an M-Q developer, containing one of the mercapto azoles referred to above. This produces negative silver images in the region of the emulsion layer or layers which were exposed to blue, green or red light. Colored images are then produced in the layer by selective re-exposure and color development. For example, the element is exposed to red light and developed in a developing solution containing a primary aromatic amino coloring developing agent and a cyan coupler, that is, a coupler capable of producing a cyan image upon development. The residual green-sensitive silver halide grains are next exposed with green light and the element developed in a color developer containing a magenta coupler. The only remaining sensitive grains are the blue-sensitive grains, and the element may therefore be exposed to either blue light or white light followed by development in a coupler developer containing a yellow-forming coupler. After conversion of the developed silver to a silver salt and fixing, the element contains colored images corresponding to the original subject photographed.

The following example illustrates a film processed according to our invention.

A mixed grain emulsion was made by sensitizing a silver chlorobromide emulsion to red light with an 8-alkyl or 8-phenyl-3,4,3',4'-dibenzothiocarbocyanine dye as described in Brooker U. S. Patents 1,969,444 and 1,969,447 and mixing it with an equal quantity of a silver bromide emulsion sensitized to green light with a 3,4-benzothia-2'-cyanine dye as described in Brooker U. S. Patent 1,935,696. This emulsion was coated on a suitably subbed cellulose organic acid ester film support and when dry, was coated with an unsensitized silver bromide emulsion containing tartrazine as a filter dye to limit the action of blue light to the unsensitized emulsion.

The film prior to exposure is illustrated in the first stage of the accompanying drawing where 10 is the film support coated with emulsion layer 11 of mixed green-sensitive and red-sensitive emulsions and the blue-sensitive emulsion layer 12 containing a yellow dye.

The film prepared in this way was exposed to an object or image represented in the drawing by a filter having a blue portion 13, a green portion 14 and a red portion 15. This exposure is followed by negative development for 10 minutes at 20° C. in a developer which may have the following composition:

	Grams
N-methyl-p-amino phenol sulfate.....	6
Hydroquinone.....	10
Sodium sulfite.....	50
Sodium carbonate.....	30
Potassium bromide.....	5
1-phenyl-5-mercapto tetrazole.....	0.01
Water to 1 liter.	

The film after negative development is shown in the second stage of the drawing where 16 indicates the negative silver produced by the blue exposure, 17 indicates the negative silver produced by green exposure and 18 indicates the negative silver produced by red exposure. The negative silver images 17 and 18 are shown as being less dense than the negative image 16; this is merely by way of illustration to indicate that in the portion of layer 11 exposed to green light there are unexposed and undeveloped red-sensitive grains and in the portion of layer 11 exposed

red light there are unexposed and undeveloped green-sensitive grains.

After washing the film for about 5 minutes, it was exposed through the base for about 20 seconds to 100-foot candles of light through a red filter transmitting light of longer wave length than 640 millimicrons, to expose the residual red-sensitive grains and was then developed for 12 minutes in a color-forming developer which may have the following composition:

A.	Grams
p-Amino diethyl aniline HCl.....	2
Sodium sulfite.....	6
Sodium carbonate.....	50
Potassium bromide.....	5
Potassium thiocyanate.....	1
Water to 950 cc.	

B.	Grams
o-Hydroxy diphenyl.....	3
Sodium hydroxide.....	5
Water.	

(For use, Solution B is added to Solution A.)

The film was then exposed from the support side to green light of an intensity of from 2,000 to 13,000-foot candles for about 20 seconds to expose the residual green-sensitive grains and the film was then developed for about 10 minutes in a developer which may have the following composition:

A.	Grams
p-Amino diethyl aniline HCl.....	1½
Sodium sulfite.....	1
Potassium bromide.....	2
Water to 950 cc.	

B.	Grams
1 - (p - nitrophenyl) - 3 - methyl - 5 - pyrazolone.....	3
Water.....	50

(For use, Solution B is added to Solution A.)

The film was then exposed for about 20 seconds to approximately 2,000-foot candles of white light to expose the residual blue-sensitive silver halide grains and developed for about five minutes in a developer which may have the following composition:

A.	Grams
p-Amino diethyl aniline HCl.....	1
Sodium sulfite.....	1
Potassium thiocyanate.....	1
Water to 990 cc.	

B.	Grams
Aceto acet anilide.....	10
Sodium hydroxide.....	1
Water 10 cc.	

(For use, Solution B is added to Solution A.)

After development in the yellow color-forming developer, the film was washed for about five minutes, and bleached for about six minutes in a solution having the following composition:

Potassium ferricyanide.....	50
Ammonium hydroxide (28% solution).....	2½
Potassium bromide.....	5
Water to 1 liter.	

The film was then fixed for about five minutes in hypo, washed for several minutes and dried in warm air. It then appeared as shown in the final stage of the drawing in which 19 indicates the yellow image in layer 12, 20 indicates the magenta image in layer 11, and 21 indicates the cyan image in layer 11.

The photographic effects of the mercapto azoles used according to our invention are illustrated by the following data obtained with a two-layer coating of the type described in the specific example.

The film was developed in the M-Q developer described above and a control experiment was developed in the same developer without the 1-phenyl-5-mercapto tetrazole. The emulsion, after first development in the M-Q developer, was successively flashed with red light, developed in a cyan coupler developer, flashed with green light, developed in a magenta coupler developer, bleached, fixed, washed and dried as described in the specific example. The equivalent neutral densities were measured in a color densitometer (see Evans, Journal Society Motion Picture Engineers, 31, 194, 1938) for a definition of equivalent neutral density and a description of the densitometer in a neutral area and the green area with results shown in the following table.

Equivalent neutral densities

	Neutral			Green		
	Cyan	Ma-genta	Yel-low	Cyan	Ma-genta	Yel-low
Control.....	3.1	3.2	2.8	1.7	0.4	2.6
Experiment....	3.1	3.2	3.2	2.6	0.4	3.2

In the neutral area, both green-sensitive and red-sensitive grains were developed so that there was no selective physical development of one on the other and the cyan and magenta images were the same in both developers; there was, however, a loss of yellow density in the control which was corrected by the presence of the 5-phenyl-1-mercapto tetrazole. In the green area (made up of cyan and yellow dyes) green-sensitive grains were made developable in large numbers, and in the control development there was considerable physical development of red-sensitive grains onto the green-sensitive grains with loss of cyan density. This along with the yellow was corrected by the mercapto tetrazole as shown by the table.

It will be understood that the modifications, for example, included here are illustrative only, and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. The method of controlling the inter-image effects in the development of a silver halide emulsion layer containing at least two sets of silver halide grains, each set being sensitive to a different spectral region, which comprises exposing said layer to a colored object or image and developing it in a black-and-white developer containing an azole having a mercapto substituent, and then successively exposing the sets of residual silver halide grains to light to which each set is sensitive and successively developing said sets of silver halide grains to different colored images in said layer with different color-forming developer solutions.

2. The method of controlling the inter-image effects in the development of a silver halide emulsion layer containing at least two sets of silver halide grains, each set being sensitive to a different spectral region, which comprises exposing said layer to a colored object or image and developing it in a black-and-white developer containing 1-phenyl-5-mercaptotetrazole, and then successively exposing the sets of residual silver halide grains to light to which each set is sensitive and successively developing said sets of silver halide grains to different colored images in said layer with different color-forming developer solutions.

3. The method of controlling the inter-image effects in the development of a silver halide emulsion layer containing at least two sets of silver halide grains, each set being sensitive to a different spectral region, which comprises exposing said layer to a colored object or image and developing it in a black-and-white developer containing 4-phenyl-2-mercaptothiazole and then successively exposing the sets of residual silver halide grains to light to which each set is sensitive and successively developing said sets of silver halide grains to different colored images in said layer with different color-forming developer solutions.

4. The method of decreasing color degradation in a mixed grain photographic layer containing silver halide grains separately sensitive to the red and green spectral regions, which comprises exposing only a portion of the silver halide grains of said layer to a colored object or image and developing them in a black-and-white developer containing an azole having a mercapto substituent and then successively exposing residual red-sensitive grains of said layer to red light and developing them in a color developer, and exposing residual green-sensitive grains of said layer and developing them in a different color developer.

5. The method of decreasing color degradation in a mixed grain photographic layer containing silver halide grains separately sensitive to the red and green spectral regions, which comprises exposing only a portion of the silver halide grains of said layer to a colored object or image and developing them in a black-and-white developer containing 1-phenyl-5-mercaptotetrazole and then successively exposing residual red-sensitive grains of said layer to red light and developing them in a color developer, and exposing residual green-sensitive grains of said layer and developing them in a different color developer.

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The following references are of record in the file of this patent:

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