

Feb. 7, 1950

W. T. HANSON, JR., ET AL
MIXED GRAIN PHOTOGRAPHIC PROCESS

2,496,940

Filed Oct. 21, 1948

2 Sheets-Sheet 1

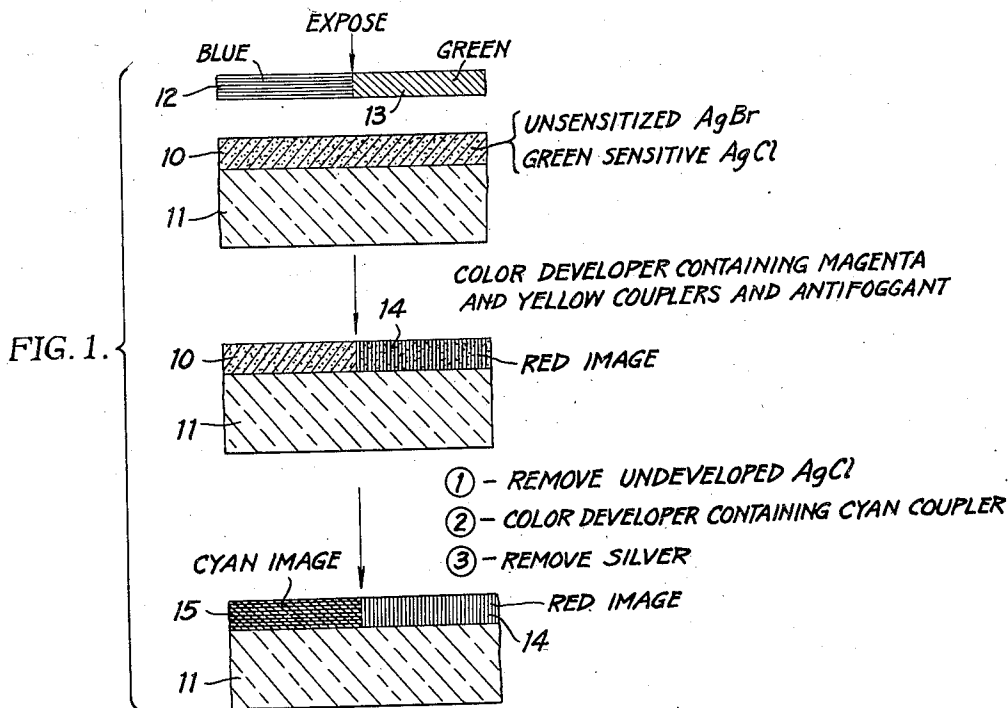


FIG. 3.

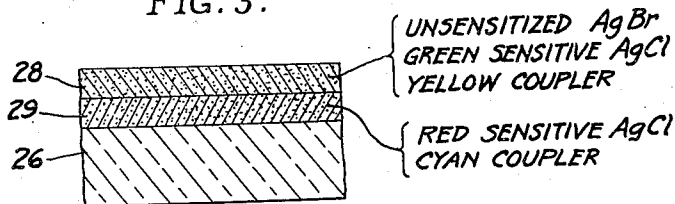


FIG. 4.

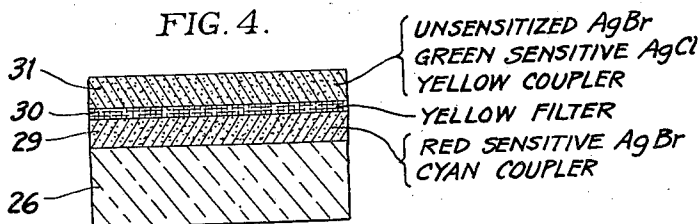
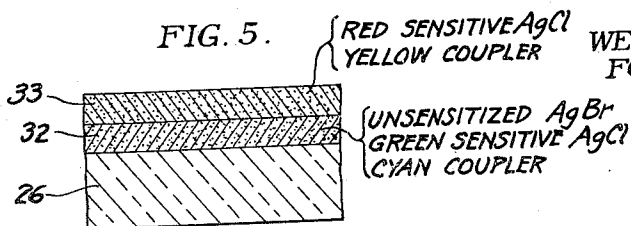


FIG. 5.



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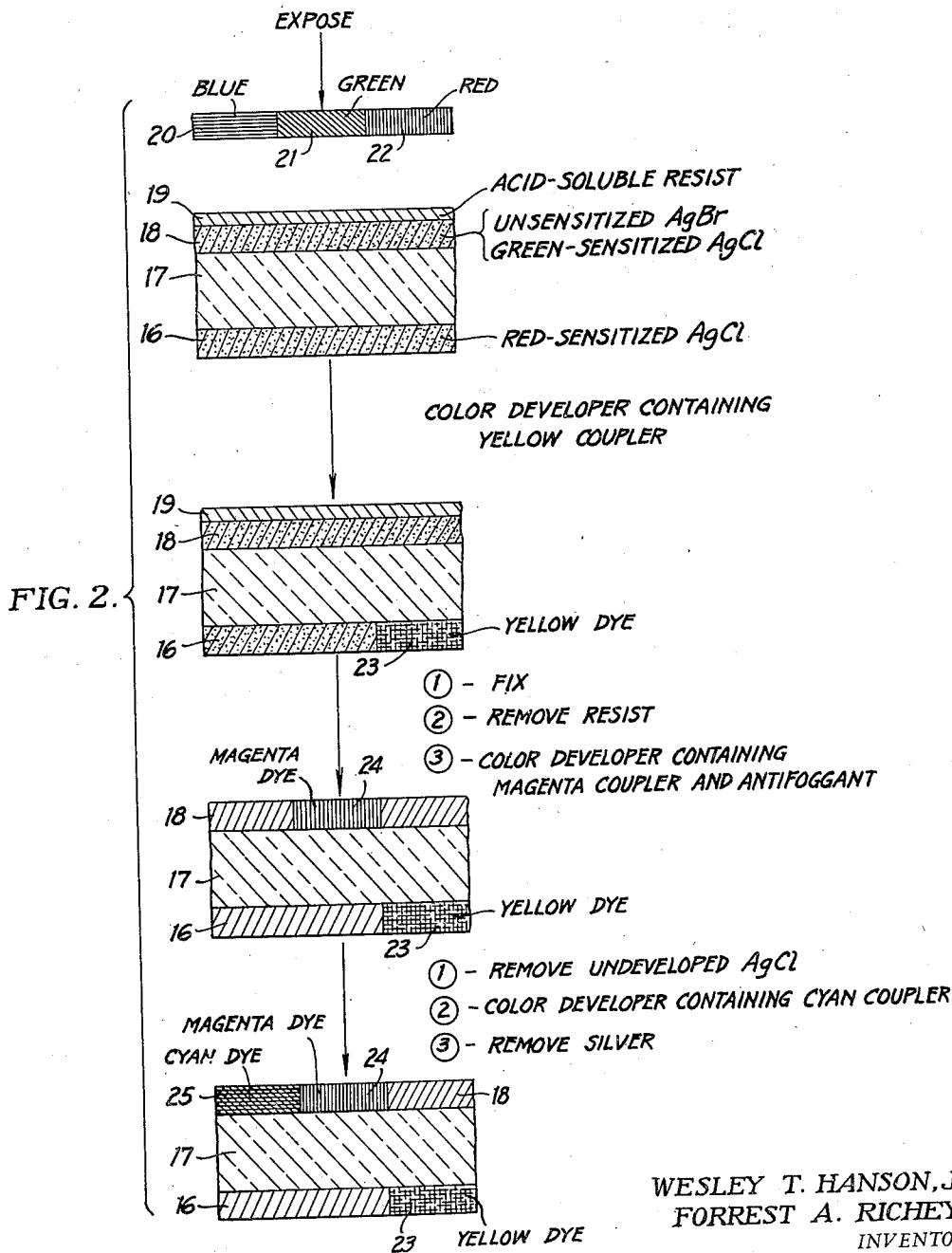
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2 Sheets-Sheet 2



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2,496,940

MIXED GRAIN PHOTOGRAPHIC PROCESS

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Application October 21, 1948, Serial No. 55,686

4 Claims. (Cl. 95—2)

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This invention relates to photography, and particularly to a mixed grain process of color photography.

Mixed grain processes of color photography have been suggested many times in photographic literature. One of the great difficulties with these processes is that of keeping the differently sensitized silver halide particles separate in the emulsion layer and processing them to obtain differently colored images. The present invention relates to processing the mixed grain emulsion layer to form the desired dye in the region of the separate silver halide grains.

It is known that silver chloride and silver bromide emulsions develop at different rates and it has frequently been reported that the differential rate of development of such emulsions can be made use of as a basis of a mixed grain color process. The differential rate of development of chloride and bromide emulsions is not sufficiently great, however, that the exposed grains can be separated upon development in this way, and mixed grain processes have not been made to operate successfully upon this principle.

It is, therefore, an object of the present invention to provide a novel mixed grain photographic process. A further object is to provide a method for differentiating between silver chloride and silver bromide grains upon development. Other objects will appear from the following description of our invention.

These objects are accomplished according to our invention by developing an exposed emulsion layer containing a mixture of silver bromide and silver chloride grains, with a primary aromatic amino developing agent containing one or more of certain compounds hitherto used as antifoggants. The antifoggants which we have found useful for the purpose of giving effective differential development of silver chloride and silver bromide emulsions are 6-nitrobenzimidazole, 5-nitroindazole, benzotriazole and 2-amino-5-methyl benzotriazole.

In the accompanying drawing are shown sectional views of films processed according to our invention.

The mixed grain emulsions used according to our invention are made by mixing an ordinary silver bromide or bromiodide emulsion with a silver chloride emulsion which will ordinarily be sensitized to red or green light. In place of the silver chloride emulsion a chlorobromide emulsion may be used in certain cases, the distinction between silver bromide and silver chlo-

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robromide being made by the developers used according to our method.

The mixed grain emulsion may be used in conjunction with another emulsion either of silver bromide or silver chloride to form a three-color process and the mixed grain emulsion may be coated on the same side of the support as the single emulsion either above or beneath it, or on the opposite side of the support. Either or both emulsion layers may contain a color coupler of the non-diffusing type or a coupler incorporated so as to reduce its diffusion tendency.

The developing agents used with the emulsion of our invention are primary aromatic amino developing agents such as diethylaminoaniline, 2-amino-5-diethylaminotoluene, N-ethyl-N-methylsulfonamidoethyl-p-phenylenediamine or 2,6-di-iodo-4-aminophenol. These developing agents may be used in solutions containing soluble couplers in those cases where there is no coupler present in the emulsion layer.

In developing the mixed grain layers according to our invention, the exposed layer is first developed in a color developing solution such as that described above containing one or more of the antifoggants 6-nitrobenzimidazole, 5-nitroindazole, benzotriazole and 2-amino-5-methyl benzotriazole. These antifoggants are used in an amount of from 0.4 to 1 gram per liter of developing solution. Since this developing solution containing the antifoggant does not develop the exposed silver bromide to any appreciable extent, the exposed silver chloride only is developed. Any undeveloped silver chloride in the emulsion layer is then removed by fixing with a solution of sodium sulfite which removes the silver chloride but does not affect the silver bromide. The exposed silver bromide is then developed in a normal color developer, that is, a developer not containing the antifoggant. This developer may or may not contain a color coupler depending upon whether a coupler has been incorporated in the emulsion layer.

Example 1

A two-color mixed grain process may be carried out according to our invention as follows.

As shown in the first stage of Figure 1 of the drawing, a mixed emulsion layer of unsensitized silver bromide and green sensitized silver chloride emulsion 10 was coated on a support 11 of any suitable material such as cellulose ester, synthetic resin or paper. The silver chloride grains of emulsion layer 10 were green sensitized

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with a sensitizing dye having little or no tendency to wander, for example, 5-(2-ethyl-1 (2)-benzoxazolylidene)-ethylidene-3-n-primary heptyl-1-phenyl-2-thiohydantoin. After exposure of this emulsion through a filter having a blue portion 12 and a green portion 13, it was treated in a prebath of 10.0 grams of 6-nitrobenzimidazole nitrate per liter of water for one minute and was then developed in a developer of the following composition:

	Grams
p-Diethylaminoaniline	3
Sodium sulfite	5
Sodium carbonate	20
Potassium chloride	2
1-phenyl-3-(p-nitrobenzoylamino)-5-pyrazolone	3
ω -Benzoylacetanilide	0.6
Sodium hydroxide	1.3
6-nitrobenzimidazole nitrate	0.5
Water to 1 liter.	

After development for 14 minutes and washing for 4 minutes, the film appeared as shown in the second stage of Figure 1 of the drawing with a red image 14 in the portion of the layer exposed to green light. The red image was formed by the mixture of magenta and yellow couplers in the developing solution.

The film was then treated for 4 minutes in a differential fixing bath of 100 grams of sodium sulfite per liter of water to remove undeveloped silver chloride without affecting the silver bromide. After a further 4 minute wash, the film was developed for eight minutes in a second color developer of the following composition:

	Grams
2-amino-5-diethylaminotoluene	2
Sodium sulfite	5
Sodium carbonate	15
Potassium bromide	5
2,4-dichloro-1-naphthol	1.5
Sodium hydroxide	1.3
Water to 1 liter.	

After a 10 minute wash and bleaching in the following solution:

	Grams
Potassium ferricyanide	80
Potassium bromide	20
Water to 1 liter.	

and a further rinse and treatment in the following hypo solution to remove all silver and undeveloped silver halide:

	Grams
Sodium sulfite	10
Sodium thiosulfate	200
Water to 1 liter.	

and a further 10 minute wash, the film appeared as shown in the last stage of Figure 1 of the drawing with a red image 14 and a cyan image 15 in the emulsion layer.

Example 2

A three-color mixed grain process using a film having emulsion layer coated on both sides of the support may be carried out according to our invention as follows:

As shown in the first stage of Fig. 2 of the drawing, a silver chloride emulsion 16 sensitized to red light with 3,3'-dimethyl-4,5,4',5'-dibenzthiacarbocyanine iodide was coated on one side of a support 17 of any suitable transparent material such

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as cellulose ester, synthetic resin or paper. On the opposite side of support 17, there was coated a layer 18 of unsensitized silver bromide mixed with green-sensitized silver chloride, the emulsion layer 18 being similar to the emulsion layer 10 of the preceding example. Over emulsion layer 18 there was coated a layer 19 of an acid-soluble resist, for example, polyvinyl pyridine (French Patent 849,126).

After exposure of this film, through a filter having a blue portion 20, a green portion 21 and a red portion 22, it was developed for three minutes in a developer of the following composition:

	Grams
2-amino-5-diethylamino toluene	3
Sodium sulfite	2
Sodium carbonate	20
Potassium chloride	4
Potassium bromide	1
Sodium hydroxide	2
ω -Benzoylacetanilide	3
Water to 1 liter.	

This development formed a yellow image 23 in emulsion layer 16 as shown in the second stage of Fig. 2 of the drawing, without affecting the exposed grains of emulsion layer 18. The resist layer 19, being soluble only in acid solution, prevented penetration of the alkaline developer solution to the layer 18. The residual silver chloride was removed from the layer 16 and it was then fixed for two minutes in the following alkaline solution:

	Grams
Sodium sulfite	10
Sodium thiosulfate	200
Water to 1 liter.	

After washing in water for three minutes, the resist layer 19 was removed by treatment in the following solution:

Sodium sulfite	grams	15
Acetic acid (28% solution)	cc	47
Boric acid (crystals)	grams	7.5
Potassium alum	do	15
Water to 1 liter.		

After again washing for three minutes, the film was treated for three minutes in a solution of 10 grams of 6-nitrobenzimidazole nitrate per liter of water, rinsed and a magenta dye image formed in layer 18 by development for 4 minutes in the following developing solution:

	Grams
2-amino-5-diethylamino toluene	4
Sodium sulfite	2
Sodium carbonate	20
Potassium chloride	2
6-nitrobenzimidazole nitrate	1
Sodium hydroxide	2
1-phenyl-3-(p-nitrobenzoylamino)-5-pyrazolone	4
Water to 1 liter.	

This resulted in the formation of a magenta dye image 24 in the portions of emulsion layer 18 exposed to green light. Because of the presence of 6-nitrobenzimidazole in the developing solution, only the silver chloride of layer 18 was developed and the silver bromide was not affected.

After washing for three minutes and treatment for 4 minutes in a differential fixing bath of 100 grams of sodium sulfite per liter of water to remove undeveloped silver chloride without affect-

ing the silver bromide in layer 18, the film was washed for 3 minutes and developed for 3 minutes in a cyan color developer of the following composition:

	Grams
2-amino-5-diethylamino toluene-----	3
Sodium sulfite-----	5
Sodium carbonate-----	15
Potassium bromide-----	5
Sodium hydroxide-----	2
2,4-dichloro-1-naphthol-----	2.5
6-nitrobenzimidazole nitrate-----	0.05
Water to 1 liter.	

After washing in water for 10 minutes, the silver was bleached in the following solution:

	Grams
Potassium ferricyanide-----	80
Potassium bromide-----	20
Water to 1 liter.	

and the film was rinsed and fixed in the following bath:

	Grams
Sodium sulfite-----	10
Sodium thiosulfate-----	200
Water to 1 liter.	

After washing for 10 minutes in water, the film then appeared as shown in the last stage of Fig. 2 of the drawing with a yellow dye image 23 in layer 16 and magenta and cyan dye images 24 and 25, respectively, in layer 18.

Example 3

A three-color mixed grain process may be carried out alternatively using the film shown in Fig. 3 of the drawing in which a support 26 of any suitable material such as cellulose ester, synthetic resin or paper, was coated with superposed emulsion layers 27 and 28. Emulsion layer 27 was a silver chloride emulsion sensitized to red light as described in the preceding example and containing 7.5 grams per liter of emulsion of the cyan-producing coupler, 4,6-dichloro-5-methyl-2-(2',4'-di-tert.amylphenoxyacet-amino) phenol. Emulsion layer 28 consisted of a mixture of unsensitized silver bromide and green-sensitive silver chloride, the silver chloride grains being sensitized to green light as described in the preceding examples. Emulsion layer 28 also contained 7.5 grams per liter of emulsion of the yellow-forming coupler:

N-(4-benzoyl acetamino benzene sulfonyl)-N-benzyl-m-toluidine. Both the cyan and yellow couplers were incorporated in the emulsion layers in the manner described in Jelley and Vittum U. S. Patent 2,322,027.

After exposure of the film described in Fig. 3 of the drawing, the film was treated for 1 minute in a pre-bath of 6-nitrobenzimidazole nitrate, rinsed and developed for 14 minutes in the following solution:

	Grams
2-amino-5-diethylamino toluene-----	3
Sodium sulfite-----	2
Sodium carbonate-----	20
6-nitrobenzimidazole nitrate-----	0.5
Water to 1 liter.	

This developer forms a cyan dye image in emulsion layer 27 and a yellow dye image in emulsion layer 28, only the exposed silver chloride grains being affected.

After treating the film for three minutes in a stop bath of the same composition as the resist

removal bath used in the preceding example and treatment in the differential fixing bath previously described, the film was then treated for 10 minutes in a developer of the following composition:

	Grams
2,6-diiodo-4-amino phenol-----	7
Sodium sulfite-----	5
Sodium carbonate-----	20
Potassium bromide-----	2
Sodium hydroxide-----	2
1-phenyl-3-(p-nitrobenzoylamino)-5-pyrazolone-----	4
Water to 1 liter.	

This developer formed a magenta dye image in the region of the exposed silver bromide grains in layer 28. The developer does not couple with either of the incorporated couplers in layers 27 and 28 so that no dye image is formed by this solution in the regions of the exposed silver chloride grains in these layers. The film was then washed and the silver removed by bleaching and fixing as described in the preceding example. This is a "false color" process since a yellow image is formed in the region of the green-sensitive grains and a magenta image in the region of the blue-sensitive grains in layer 28.

Example 4

A different type of two-layer, three-color material is shown in Fig. 4 of the drawing. As shown therein, the support 26 was coated with an emulsion layer 29, a yellow filter layer 30 and an emulsion layer 31. The emulsion layer 29 was red-sensitive silver bromide sensitized as described in the preceding examples and containing a cyan-forming coupler as described in the preceding example. Emulsion layer 31 consisted of a mixture of unsensitized silver bromide grains and green-sensitive silver chloride grains and contained a yellow-forming coupler. It was similar in all respects to emulsion layer 28 shown in Fig. 3.

After exposure, the material shown in Fig. 4 of the drawing was processed by first developing it in a solution of the following composition:

	Grams
2,6-diiodo-4-amino phenol-----	7
Sodium sulfite-----	5
Sodium carbonate-----	20
Potassium bromide-----	2
Benzotriazole-----	0.4
Sodium hydroxide-----	2
1-phenyl-3-(p-nitrobenzoylamino)-5-pyrazolone-----	4
Water to 1 liter.	

This developer formed a magenta image in the green-sensitive silver chloride emulsion but did not affect the silver bromide grains because the oxidized developing agent does not react with the incorporated couplers and because the antifoggant in the solution prevents action of the developer on the exposed silver bromide grains.

After treatment in an acid stop bath and differential fixing as described in the preceding examples, the film was rinsed and developed in a developing solution of the following composition for 10 minutes:

	Grams
2-amino-5-diethylamino toluene-----	3
Sodium sulfite-----	2
Sodium carbonate-----	20
Water to 1 liter.	