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3,832,174

PHOTOGRAPHIC PROCESSES AND ELEMENTS
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No Drawing. Filed June 7, 1972, Ser. No. 260,617
Int. Cl. G03c 7/16, 7/32, 7/40
U.S. Cl. 96—22 10 Claims

ABSTRACT OF THE DISCLOSURE

Processes for providing photographic reproductions wherein silver negative images are developed in imagewise exposed photographic elements having at least two superposed hydrophilic colloid emulsion image recording layers containing silver halide and color forming couplers wherein at least one of the silver halide emulsion image recording layers contains from about 0.5 to 10 mole percent iodide, based on the total amount of halide in the emulsion layer. Development of the imagewise exposed negative photographic elements in a photographic color developer containing a silver halide solvent and removal of silver and silver halide from said negative elements result in color negatives having improved interimage characteristics.

The present invention relates to photographic processes, and more particularly to photographic processes for providing multicolor negative reproductions having improved interlayer interimage effects.

The dyes obtained in multicolor photographic reproductions are not always "true colors." For example, magenta dyes often have small amounts of blue light absorption and red light absorption. Likewise, yellow dyes and cyan dyes absorb small amounts of light other than blue and red light, respectively. The effects of such unwanted absorptions is the production of dark and desaturated colors or color hue errors.

Such deficiencies in dyes obtained in multicolor photographic processes can be compensated, at least in part, by creating certain interimage effects. Interimage effects can have significant influences on the color reproduction by giving partial or complete correction for the unwanted light absorptions by dyes used in photographic materials.

Interimage effects are well known in photographic multicolor processes. See, for example, Hanson and Horton, *Journal of the Optical Society of America*, vol. 42, No. 9 pages 663-669, September 1952 and Pinney "Interimage Effects and Color Reproduction," the SPSE Reporter, November 1960. It is well known that under certain development conditions the degree of development in one layer may be influenced by an adjacent developing layer. When this occurs in a multilayer negative element, the final dye content of the adjacent layer is a function of the development occurring in both layers. Such effects have been referred to as interlayer interimage effects.

Although interlayer interimage effects may be present in many developed, multilayer negative images they generally are too small to be of practical importance. This is especially true of many negative elements which receive direct color development.

In accordance with this invention novel means are provided for inducing interlayer interimage effects in elements for providing multicolor negative photographic reproductions.

It is, therefore, one object of this invention to provide a novel method for correcting for unwanted light absorptions by dye images formed in photographic multicolor negative processes.

It is another object of this invention to provide a novel method for providing interlayer interimage effects in photographic multicolor reproductions.

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These and other objects of this invention are accomplished by processing a silver halide negative multilayer color photographic element, wherein at least one of the silver halide emulsion image forming layers contains from about 0.5-10 mole percent iodide as mixed silver halide and at least one of the silver halide emulsion image forming layers is essentially iodide free, in a color developer solution containing a silver halide solvent followed by removal of residual silver and silver halide.

The interlayer interimage effects manifest themselves in such improved properties as brighter and more saturated colors prepared from such photographic elements.

Best results are obtained according to this invention when the silver haloiodide is silver chloroiodide, or preferably silver bromoiodide or silver bromochloroiodide. Advantageously, the silver haloiodide emulsion layer or layers contains from 0.5 to 10 mole percent, and preferably 1 to 6 mole percent iodide.

An especially useful emulsion arrangement consists of silver haloiodide in the red and green sensitive layers and an essentially iodide-free silver halide, such as silver chloride or bromide, in the blue sensitive layer. By "essentially iodide-free" we mean that small amounts, e.g. up to about 0.5 mole percent, of iodide may be present in the silver halide grains.

The emulsions can contain various chemical sensitizers, optical sensitizers, stabilizers, speed increasing compounds, plasticizers, hardeners and coating aids, such as are described and referred to in *Product Licensing Index*, Vol. 92, December 1971, publication 9232, at paragraphs III, V, VII, XI, XII, XV pp. 107-110. Any suitable support material can be used, such as those described in the *Product Licensing Index* reference at paragraph X.

The color forming developer solutions which can be used to produce the interlayer interimage effects according to this invention contain a silver halide solvent. The most useful of such color forming developer solutions employ phenylenediamine and substituted derivative developing agents, such as those disclosed in Weissberger et al., U.S. Pat. 2,548,574 issued Apr. 10, 1951; Weissberger et al., U.S. Pat. 2,552,240-2 issued May 8, 1951; and Weissberger et al., U.S. Pat. 2,566,271, issued Aug. 28, 1951. Typical phenylenediamine developing agents include diethyl-p-phenylenediamine hydrochloride, 2-amino-5-diethylaminotoluene monohydrochloride, 2-amino-5-(N-ethyl-N-laurylamino)-toluene, N-ethyl-N-(beta-methane sulfonamidoethyl)-4-aminoaniline, etc. The p-aminophenols and their substitution products where the amino group is unsubstituted can also be used. Various other materials may be included in the developer solutions depending upon the particular requirements, for example, an alkali metal sulfite, carbonate, bisulfite, bromide, iodide, etc., and the thickening agents used in viscous developer solutions such as carboxymethyl cellulose, gelatin, etc. The following is a typical developer solution given to illustrate but not limit the invention.

Developer Solution:

Water	-----ml	1000.00
Sodium hexametaphosphate	-----g--	2.00
Sodium sulfite	-----g--	4.00
Sodium carbonate H ₂ O	-----g--	20.00
Potassium bromide	-----g--	2.00
2-amino - 5 - diethylaminotoluene monohydrochloride	-----g--	3.00
Sodium thiocyanate	-----g--	1.00

In addition to those developing agents referred to above, any of the other well known color forming developing agents can be employed to advantage in the process of this invention.

Developer solutions containing these conventional color forming developing agents are modified, according to this

invention, by the addition of a silver halide solvent to the developer formulation in order to achieve the production of the interlayer interimage effects.

The useful silver halide solvents according to this invention include the following: ammonium hydroxide, ethylenediamine, dithiooctanediol, ethanolamine, isopropylamine, n-butylamine, 1,8-dihydroxy-3,6-dithiaoctane, as well as others well known in the art. The silver halide solvents especially useful according to this invention are the thiocyanate salts such as guanidine thiocyanate, sodium thiocyanate, potassium thiocyanate, etc.

The silver halide solvents may be used in concentrations of from about 0.1 to 5.0 grams/liter with a preferred range of from about 0.5 to 2.5 grams/liter especially useful.

The interlayer interimage producing, iodide-containing emulsions of this invention can be used in a process for providing a multicolor photographic reproduction which includes (1) developing silver images in an exposed photographic element having at least two superposed hydrophilic colloid layers containing silver halide and (2) forming differentially colored dye images in proportion to said silver images. For example, the iodide emulsions are highly useful in complete photographic negative processes wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion image recording layers wherein the element is given a first imagewise exposure, followed by a development in a color developing solution containing a silver halide solvent for reducing the silver and then removing the residual silver and silver halide whereby dye images having brighter and more saturated colors are produced.

As is known, a highly useful arrangement of light sensitive silver halide layers for the production of negative multicolor photographic records comprises a support having a coated thereon, superposed light sensitive silver halide image recording colloid layers which are sensitive, respectively, to red, green and blue radiation. Silver images can be developed in such layers, and dyes formed image-wise in proportion to the developed silver image. Advantageously, cyan, magenta and yellow dyes are formed in proportion to the red, green and blue layers respectively. Such dyes can be formed in any convenient manner, such as in the conventional color processes wherein a dye image is formed having a complementary relationship to the region of the spectrum to which the silver halide emulsion is sensitized. The dyes that are formed according to this invention can be produced from any of the color formers known to the art. By "color formers" we mean compounds that react with oxidized color developing agents to form dyes. Suitable color formers are the color couplers known to the art. Examples of typical color forming couplers are listed in the aforementioned *Product Licensing Index* reference at paragraph XXII.

For example, a typical multilayer negative color film may comprise three units coated on a support the first unit on a support containing a silver halide emulsion image recording layer sensitized to red radiation and adapted to produce a cyan dye; a second unit comprising at least one silver halide emulsion image recording layer sensitized to green radiation and adapted to produce magenta colored dye; and a third unit comprising at least one silver halide emulsion image recording layer sensitive to blue radiation and adapted to produce a yellow colored dye. Any one of such units or any two of such units, can contain the iodide containing silver halide emulsions of this invention. In a preferred embodiment the red and green sensitive units contain the iodide content silver halide. The interlayer interimage effect is achieved whether the combination of emulsion layers provided by this invention is employed in a yellow, magenta, cyan or other colored dye producing color forming unit so long as the exposed element is developed in a color developer containing a silver halide solvent.

This invention will be further illustrated by the following examples:

EXAMPLE 1

A multilayer color negative print film element bearing in order on a transparent support, a gelatino silver halide red sensitive, cyan-forming unit, a gelatin interlayer, a gelatino silver halide green sensitive, magenta-forming unit, a yellow filter layer, a gelatino silver halide blue sensitive layer, yellow-forming unit and a gelatin overcoat layer is first prepared. The cyan and magenta forming layers contain a silver bromiodide emulsion of 6 mole percent iodide. The yellow-forming layer contains a conventional silver chlorobromide emulsion. A control is prepared as described above, except that the emulsions contain only silver chloride or silver bromide. Separate samples of these elements are then exposed to red, green or blue light through a step tablet on a sensitometer. Separate samples of each of these elements are then given overall flash exposure with each of the two primary colors not used for the stepwise exposure and processed at a temperature of from 20–28° C. as follows:

Baths

- | | |
|------------------|--------------|
| 1. Color develop | 5. Wash |
| 2. Stop-fix | 6. Fix |
| 3. Wash | 7. Wash |
| 4. Bleach | 8. Stabilize |

The chemical composition of the above processing baths is as follows:

Developer:

Water	ml.	1000.00
Sodium hexametaphosphate	g.	2.00
Sodium sulfite	g.	4.00
Sodium carbonate H ₂ O	g.	20.00
Potassium Bromide	g.	2.00
2-amino - 5 - diethylaminotoluene monohydrochloride	g.	3.00
Sodium thiocyanate	g.	1.00

Stop-Fix Bath:

Water	ml.	600
Sodium thiosulfate	g.	240.0
Sodium sulfite, desiccated	g.	15.0
Acetic acid, (28%)	ml.	48.0
Boric acid	g.	7.5
Potassium alum	g.	15.0
Water to	ml.	1000.00

Bleach:

Water	ml.	1000.00
Potassium dichromate	g.	5.0
Potassium bromide	g.	20.0
Potassium alum	g.	40.0

Fix:

Water	ml.	600
Sodium thiosulfate	g.	240.0
Sodium sulfite, desiccated	g.	15.0
Acetic acid, (28%)	ml.	48.0
Boric acid	g.	7.5
Potassium alum	g.	15.0
Water to	ml.	1000.00

Stabilizer:

Formaldehyde 37% solution	ml.	15
Kodak Photo-Flo concentrate	ml.	2.0
Water	liter	1

The processed film is then analyzed for interimage effects. Curves are plotted for magenta interimage as a function of cyan, yellow interimage as a function of cyan, cyan interimage as a function of magenta and yellow interimage as a function of magenta for a flash density level of 2.5. The greater the density (ΔD) difference, the greater the interlayer interimage effects. The negative figures in Table I indicate the restraint in development of the various layers which is a measure of correction for the unwanted absorptions of these layers.

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TABLE I

Silver halide in emulsions	Interlayer interimage effect (ΔD)
Control:	
Magenta interimage as a function of cyan	-0.02
Yellow interimage as a function of cyan	-0.04
Cyan interimage as a function of magenta	0.00
Yellow interimage as a function of magenta	-0.04
Element 1:	
Magenta interimage as a function of cyan	-0.37
Yellow interimage as a function of cyan	-0.22
Cyan interimage as a function of magenta	-0.40
Yellow interimage as a function of magenta	-0.40

The procedure of Example 1 is performed at about room temperature but higher temperature of up to 55° C. may be used with a resultant decrease in processing time.

EXAMPLES 2-6

Several elements and a control element are prepared as in Example 1, except that the emulsions have silver halide contents as set forth in Table II.

TABLE II

Example	Cyan	Mole percent halide (Br/I)	Ma-genta	Mole percent halide (Br/I)	Yellow	Mole percent halide (Br/I or Cl/Br)
2	AgBrI	97.5/2.5	AgBrI	97.5/2.5	AgBrI	99.5/0.5
3	AgBrI	97.5/2.5	AgBrI	97.5/2.5	AgClBr	2/98
4	AgBrI	94/6	AgBrI	97.5/2.5	AgClBr	2/98
5	AgBrI	94/6	AgBrI	99/1	AgClBr	2/98
6	AgBrI	99/1	AgBrI	99/1	AgClBr	2/98

These elements are processed as in Example 1 with the color developer used therein, containing 1.0 g. of the silver halide solvent sodium thiocyanate per liter of color developer. The greater the density (ΔD) difference the greater the interimage effect. The interimage effect is reported in Table III as the difference in density for a flash density of approximately 2.5.

TABLE III

	Magenta interimage	Yellow interimage	Cyan interimage	Yellow interimage
	Function of cyan (ΔD)	Function of cyan (ΔD)	Function of magenta (ΔD)	Function of magenta (ΔD)
Control	-0.02	-0.04	0.00	-0.04
Example:				
2		-0.16		-0.11
3	-0.14	-0.16	-0.48	0.00
4	-0.31		-0.22	
5	-0.24		-0.00	
6	-0.07	-0.11	-0.23	+0.07

EXAMPLES 7-12

Elements of Examples 2-6 are processed according to the procedure of Example 1 except that 2.0 g./liter of sodium thiocyanate is employed in the color developer formulation of Example 1. The resulting interimage effects are listed in Table IV. Where interimage values are not obtainable for a flash density of 2.5, values are taken at the next highest and next lowest flash density, so that in some instances two values are listed.

TABLE IV

Example	Element of example	Magenta interimage	Yellow interimage	Cyan interimage	Yellow interimage
		Function of cyan (ΔD)	Function of cyan (ΔD)	Function of magenta (ΔD)	Function of magenta (ΔD)
	Control	0.0	0.0	0.0	0.0
7	1	-0.48/-0.50	-0.54	-0.77/-0.66	-0.98/-1.21
8	2		+0.29		-0.58/-0.67
9	3	0.16	-0.29	-0.45/-0.72	-0.62/-0.72
10	4	-0.20/-0.45		-0.50/-0.43	
11	5	-0.19/-0.35		-0.26/-0.21	
12	6	-0.07/-0.10	-0.24	-0.48/-0.28	-0.27/-0.23

EXAMPLES 13-21

Several multilayer color negative elements are prepared. To a transparent polyethylene terephthalate support is applied, in order, a gelatino silver bromoiodide emulsion of

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6 mole percent iodide that is sensitive to the red region of the spectrum, a cyan forming unit, a gelatin interlayer, a gelatino silver bromoiodide emulsion of 6 mole percent iodide, a magenta-forming unit, a yellow filter layer, a gelatino silver bromochloride blue sensitive layer and a yellow-forming unit with a gelatin overcoat. A control is prepared as described above, except that all three emulsions contain silver bromide. These elements are then exposed to red, green or blue light through a step tablet on a sensitometer. Separate samples of each of these elements are then given overall flash exposure with each of the two primary colors not used for the stepwise exposure and processed as in Example 1, except that the silver halide solvent sodium thiocyanate is substituted with the following silver halide solvents:

TABLE V

Example:	Solvent
13	Guanidine thiocyanate
14	Potassium thiocyanate
15	Ammonium hydroxide
16	Ethylene-diamine
17	Dithiooctanediol
18	Isopropylamine
19	n-Butylamine
20	Ethanolamine
21	1,8-dihydroxy-3,6-dithiaoctane.

In all these examples the elements containing the silver bromoiodide emulsions yield brighter and more saturated dye images with the resulting negative image being of fine quality for use as a color negative.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In a process for providing interlayer interimage effects in multilayer silver halide emulsion containing color photographic elements which process comprises

(a) utilizing an imagewise-exposed element containing from 0.5-10 mole percent iodide as mixed silver halide in at least one of the silver halide emulsion image recording layers and at least one silver halide emulsion image recording layer being essentially iodide free,

(b) developing said image-wise exposed element in a color developer, and

(c) removing residual silver and silver halide from said element;

the improvement which comprises in step (b) using a color developer which contains silver halide solvent, whereby a color negative is obtained having improved interimage characteristics.

2. The process for providing improved photographic interimage effects as defined in claim 1 wherein the element contains a first emulsion image recording layer

sensitive to blue radiation said layer also containing a color former that forms a yellow colored dye upon color development and a second emulsion image recording layer spectrally sensitized to red radiation and which con-

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tains a color former that forms a cyan colored dye upon color development.

3. The process for providing improved photographic interimage effects as defined in claim 11 wherein the element contains a first emulsion image recording layer sensitive to blue radiation; said layer also containing a color former that forms a yellow colored dye upon color development and a second emulsion image recording layer spectrally sensitized to green radiation and which contains a color former that forms a magenta colored dye upon color development.

4. The process for providing improved photographic interimage effects as defined in claim 1 wherein the element contains a first emulsion image recording layer spectrally sensitized to red radiation said layer also containing a color former that forms a cyan colored dye upon color development and a second emulsion image recording layer spectrally sensitized to green radiation and which contains a color former that forms a magenta colored dye upon color development and a third emulsion image recording layer sensitive to blue radiation and which contains a color former that forms a yellow colored dye upon color development.

5. The process according to claim 4 wherein the red sensitive emulsion layer contains 0.5-10 mole percent iodide as mixed silver halide.

6. The process according to claim 4 wherein the green sensitive emulsion layer contains 0.5-10 mole percent iodide as mixed silver halide.

7. The process according to claim 4 wherein both the green and red sensitive emulsion layers contain 0.5-10 mole percent iodide as mixed silver halide.

8. The process according to claim 1 wherein the color developer solution contains a phenylenediamine developing agent.

9. The process of claim 1 wherein the silver halide solvent is a thiocyanate salt.

10. The process of claim 1 wherein the silver halide solvent content of the color developer solution is from about 0.5 to 2.5 grams per liter of color developer solution.

References Cited

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U.S. Cl. X.R.

96—66 R, 74

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,832,174 Dated August 27, 1974

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 4, "claim 11" should read --claim 1--.

Signed and sealed this 10th day of December 1974.

(SEAL)
Attest:

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