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2,984,567

METHOD FOR ELIMINATION OF REVERSAL RE-EXPOSURE IN PROCESSING PHOTOGRAPHIC FILMS

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This invention relates to an improved method of photographic processing, and more particularly, to the reversal processing of photographic silver halide emulsions.

It is known that photographic silver halide emulsions for producing black-and-white images can be reversal processed by subjecting the exposed emulsions to conventional development, followed by bleaching, clearing, and reversal re-exposure, followed by a subsequent development step. Also, it is known that in the processing of the photographic silver halide emulsions of color films, the exposed emulsions can be subjected to conventional black-and-white development, followed by reversal exposure and subsequent color development. Both of these processes require that the exposed silver halide emulsions, after a first development, be given a subsequent reversal exposure before any further development can take place to produce the desired positive image.

Accordingly, it is an object of our invention to provide a method of eliminating the re-exposure required in black-and-white processing by reversal, as well as in certain color processing. Another object is to provide a method of color processing which not only eliminates reversal re-exposure, but also provides more accurate rendition of the colors in the original. Other objects will become apparent from a consideration of the following description and examples.

According to the method of our invention, the reversal re-exposure for the processing of black-and-white or color reproductions can be eliminated by treating the photographic silver halide emulsions after a first (negative) development with a solution containing an alkali metal (e.g., sodium, potassium, etc.) borohydride.

In the reversal processing of photographic silver halide emulsions for producing black-and-white images, the emulsions are exposed in the customary manner and given a first development in an ordinary photographic silver halide developer. The developed films are then washed and given a bleaching treatment in an ordinary photographic bleach bath containing an oxidizing agent, such as permanganate, dichromate, etc. After bleaching, the film is again washed and treated in a clearing bath, after which the film is again rinsed. Treatment of the film with an alkali metal borohydride aqueous solution produces a positive image, free from stain, without any exposure to light. If desired, the concentration of the alkali metal borohydride solution can be controlled so that no image is produced directly. Then, the treated emulsion can be given a conventional development which rapidly produces the desired positive image. The concentration of the alkali metal borohydride in the treating solution can vary depending upon whether it is desired to produce an image directly without any subsequent development, or whether it is desired to use a second development in a conventional photographic developer. In general, the concentration of the alkali metal borohydride can vary from about 0.1 g./liter to concentrations as high as 30 g./liter. While more concentrated solutions

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can be employed to produce an image directly without any subsequent development, there is generally no advantage in doing so.

For the processing of color films by reversal, it is apparent that no bleaching or clearing baths should be used after the first development, since color formation is accomplished by reversal re-exposure of the residual silver halide and subsequent treatment with a color developer which undergoes a coupling reaction with color-forming components or couplers, which can be present either in the developer itself or most advantageously, in the photographic silver halide emulsion layers. In those cases where the color-forming components or couplers are present in the photographic developers, it is apparent that the alkali metal borohydride treatment should not be used until immediately prior to the last color development step, inasmuch as the alkali metal borohydride will nucleate all silver halide which has not been exposed and developed previously. For example, in processing color films of the Kodachrome type, it is possible to use the alkali metal borohydride treatment immediately prior to the last color development step and to thus eliminate the re-exposure preceding that step. This treatment has been found to be far more effective than reversal re-exposure with intensive light sources, which have an insufficient effect on the remaining silver halide to provide accurate color development for the last step of the processing. Since the silver halide emulsion layers have already undergone extensive treatment and development in strongly alkaline solutions, the remaining silver halide has either been inadequately exposed during the last reversal re-exposure, or the sensitizing dyes and other emulsion addenda have been diminished in effectiveness by the extensive processing. Our treatment with alkali metal borohydrides causes the silver halides to become nucleated almost instantaneously so that color development can then be completed by developing in a conventional color developer without any intensive re-exposure.

Particularly useful color films for reversal processing according to the method of our invention are films comprising a conventional support, such as cellulose esters, glass, polyester film, polyvinyl acetal film, polycarbonate film, etc., having coated thereon at least two silver halide layers which have been sensitized to particular regions of the spectrum. These emulsions have incorporated therein the color-forming components or couplers, which combine with the oxidation products of the photographic color developers, to produce the desired color images. For example, a typical color film, useful in practicing our invention comprises a support having coated thereon a red-sensitized photographic silver halide emulsion having incorporated therein a coupler for the cyan image (e.g., a phenolic coupler), a green-sensitized photographic silver halide emulsion having incorporated therein a coupler for the magenta image (e.g., pyrazolone coupler), and a blue-sensitized photographic silver halide emulsion containing a coupler for the yellow image (e.g., a coupler containing an open-chain ketomethylene group). The photographic element can also contain conventional interlayers and filter layers, such as a yellow filter layer beneath the blue-sensitized emulsion to prevent exposure by blue light to either the red- or green-sensitized emulsion. Photographic color films of the above-described type can be processed by a technique requiring fewer steps than the processing of color films of the Kodachrome type mentioned above. For the processing of the emulsions having coupler compounds incorporated therein, it is only necessary to treat the exposed color film with the usual type of black-and-white developer for producing a negative silver image, followed by treatment with the alkali metal borohydride solutions herein de-

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scribed to nucleate the residual silver halide, which can then be developed with one of the conventional color developers.

The following examples will serve to illustrate more fully the manner of practicing our invention.

Example 1

An ordinary photographic silver halide emulsion, such as Kodak Plus-X 16 mm. Reversal Film was exposed to a step wedge in an Eastman Type Ib sensitometer and then developed for 3 minutes in a developer having the following composition:

	G.
N-methyl-p-aminophenol sulfate -----	2.0
Sodium sulfite, anhydrous -----	90.0
Hydroquinone -----	8.0
Sodium carbonate monohydrate -----	52.5
Potassium bromide -----	5.0
Water to make 1 liter.	

The developed film was then rinsed thoroughly with water and bleached for 2 minutes in a composition having the following formula:

Potassium bichromate -----g--	9.4
Sulfuric acid -----cc--	12.0
Water to make 1 liter.	

The bleached emulsion was then rinsed thoroughly with water and treated for 1 minute in an aqueous solution containing 3% sodium sulfite. The emulsion was again rinsed thoroughly with water and treated for 1 minute in a solution containing 5 g. of potassium borohydride and 50 g. of anhydrous sodium sulfate (to prevent swelling) in 500 cc. of water. A strong positive image, free from stain and neutral black in color, was immediately obtained.

The particular silver halide emulsion processed in the above example was a silver bromide emulsion.

Example 2

A photographic multi-layer color element containing three differentially sensitized photographic silver halide emulsion layers, having color-forming agents or couplers incorporated therein, was exposed in the usual manner to a subject. The exposed color film was then developed in a developer having the following composition:

Sodium hexametaphosphate -----g--	2.0
N-methyl-p-aminophenol sulfate -----g--	6.0
Sodium sulfite, anhydrous -----g--	50.0
Hydroquinone -----g--	6.0
Sodium carbonate monohydrate -----g--	35.0
Potassium bromide -----g--	2.0
Sodium thiocyanate -----g--	1.5
0.5% solution of 6-nitrobenzimidazole nitrate -----cc--	12.0
0.1% solution of potassium iodide -----cc--	10.0
Water to make 1 liter.	

The element was then thoroughly washed with water and treated in a hardening bath having the following composition:

Potassium chrome alum crystals -----g--	30.0
Water to make 1 liter.	

The element was then thoroughly washed with water and treated for 30 seconds in a solution having the following composition:

	G.
Sodium borohydride -----	0.25
Sodium hydroxide -----	4.0
Water to make 1 liter.	

The element was then treated in a color developer having the following composition:

Benzyl alcohol -----cc--	6.0
Sodium hexametaphosphate -----g--	2.0

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Sodium sulfite, anhydrous -----g--	5.0
Trisodium phosphate -----g--	40.0
Potassium bromide -----g--	0.25
0.1% solution of potassium iodide -----cc--	10.0
Sodium hydroxide -----g--	6.5
Color developer ¹ -----g--	11.33
Ethylenediamine sulfate -----g--	7.8
Citrazinic acid -----g--	1.5
Water to make 1 liter.	

¹ 4-amino-N-ethyl-N - (β - methanesulfonamidoethyl) - m - toluidine sesquisulfate monohydrate.

The element was then thoroughly washed with water and treated in a clearing and fixing bath having the following composition:

	G.
Sodium thiosulfate -----	150.0
Sodium bisulfite -----	20.0
Water to make 1 liter.	

The element was then treated in a bleach bath having the following composition:

	G.
Potassium dichromate -----	5.0
Potassium ferricyanide -----	70.0
Potassium bromide -----	20.0
Water to make 1 liter.	

The element was again washed and treated once again with the clearing and fixing bath identified above. The element was again washed and treated in a stabilizing bath having the following composition:

Formaldehyde (37% by weight) -----cc--	7.0
Dispersing agent ¹ -----g--	0.5
Water to make 1 liter.	

¹ Such as Triton-X 100, i.e., an alkylaryl polyether alcohol (octylphenoxy polyethoxy ethanol).

Photographic color elements which can be processed according to the method described in Example 2 above include the elements shown in Schinzel U.S. Patent 2,266,443, issued December 16, 1941, and Fierke U.S. Patent 2,272,191, issued February 10, 1942, for example. Photographic elements, wherein the silver halide emulsions contain the coupler or color-forming component in dispersed form, have been found particularly suitable for the process described in Example 2. It has been found that ordinary processing of such reversal-type films frequently causes a re-reversal effect, particularly in the magenta dye image and a density loss in the shoulder region of the reversal exposure scale. By shoulder reversal, we mean the occurrence of a dye maximum in the reversal scale at some point prior to the no-exposure step of the scale of densities developed in the black-and-white developer. This effect is believed to be due, at least in part, by inadequate reversal exposure and use of partially exhausted color developer. Use of the alkali metal borohydride solutions of our invention not only eliminates the necessity for a reversal exposure, but it also materially improves dye formation in the magenta layer.

Example 3

A photographic silver chlorobromide emulsion was exposed to a step wedge in the usual manner and then developed for about 2 minutes in a developer for high contrast emulsions, such as a developer having the following composition:

	G.
Sodium sulfite, anhydrous -----	30.0
Paraformaldehyde -----	7.5
Potassium metabisulfite -----	2.6
Boric acid crystals -----	7.5
Hydroquinone -----	22.5
Potassium bromide -----	1.6
Water to make 1 liter.	

The exposed film was then bleached for 1 minute in a

potassium permanganate bleach containing sodium chloride and hydrochloric acid as a stain remover. After washing, the film was treated for about 30 seconds in a 2% sodium bisulfite clearing bath and then treated with a 1% aqueous solution of potassium borohydride. An image rapidly appeared. It was free from stain and had a neutral black color.

Development of the exposed photographic silver halide emulsions to produce a black-and-white negative image as described in the foregoing examples can be accomplished using any of the conventional developers customarily employed in photographic art for producing black-and-white negative images. Such developers include compounds known as polyhydroxybenzenes (e.g., hydroquinone, catechol, pyrogallol, etc.) and N-substituted aminophenols (e.g., N-methylaminophenols, N-ethylaminophenols, etc.), or mixtures of such developers. Prominent among such developing agents for the rapid development of photographic images are those comprising hydroquinone and Elon developer (N-methyl-p-aminophenol). Instead of using polyhydroxybenzenes, it is also possible to use the well known class of developing agents referred to in the photographic art as 3-pyrazolidones, such as those described in Kendall et al. U.S. Patent 2,704,762, issued March 22, 1955.

Color development, as described in the above examples, can be carried out using any of the well known color-forming developers which are capable of coupling with the color-forming components or couplers. Particularly useful color-forming developers are the phenylenediamines and substituted derivatives thereof. Typical of such color-forming developers are the sulfonamido-substituted p-phenylenediamines disclosed in Weissberger U.S. Patent 2,548,574, issued April 10, 1951, the substituted p-phenylenediamines disclosed in Weissberger et al. U.S. Patents 2,552,240-2, issued May 8, 1951, and the substituted p-phenylenediamines disclosed in Weissberger et al. U.S. Patent 2,566,271, issued August 28, 1951. Other phenylenediamine color-forming developers can be employed to like advantage in the process of our invention.

The processes for producing direct positive images, as described in the foregoing specification, have been previously described in the prior art, and our invention is not to be limited to any particular method of processing photographic silver halide emulsions according to these well known techniques. Rather, our invention resides in the discovery that alkali metal borohydrides can be employed in the form of their aqueous solutions to either nucleate silver halides so that silver images can be obtained by known techniques of photographic development, or the silver halides can be treated for a period of time sufficient to fog substantially all of the residual silver halide so that no subsequent photographic development is required. The extent of treatment will obviously depend upon the type of film being treated and whether one desires to obtain merely a black-and-white image, or whether one desires to process a color film to produce subtractively-colored images. The pH of the alkali metal borohydride solutions can be varied to modify the activity of the alkali metal borohydrides. In general, we have found that the pH should advantageously not be allowed to drop below about 10, since these borohydrides become somewhat unstable at too low pH (i.e., toward acid side of neutrality) values.

Instead of using sodium bisulfite or sodium sulfite as reducing agents in the direct reversal process for producing black-and-white images, it is possible to use other alkali metal salts, such as those of potassium, etc.

The method of processing color films as herein described is particularly useful where the photographic silver halide emulsions are hardened prior to the treatment with the alkali metal borohydride solutions. Where color films are used which have emulsions which have not been previously hardened, it is desirable in many cases to

harden the emulsion before treatment with the alkali metal borohydride solutions.

While other materials have been used in place of the alkali metal borohydrides of our invention, the nucleating effects are not nearly as useful as those described herein. For example, hydrazine compounds, such as phenylhydrazine, 1-naphthylhydrazine, p-bromophenylhydrazine, etc., can be used, though less advantageously than the alkali metal borohydrides of our invention. Other hydrazine compounds which can be used comprise those shown in Ives U.S. Patent 2,588,982, issued March 11, 1952. Again, the alkali metal borohydrides of our invention have distinct advantages over the hydrazine compounds shown in the United States patent.

What we claim as our invention and desire secured by Letters Patent of the United States is:

1. In a photographic reversal process comprising exposing a photographic silver halide emulsion to an image, developing said photographic silver halide emulsion to produce a black-and-white negative image by contacting said exposed photographic silver halide emulsion with a photographic developer, and subsequently obtaining a reversal positive image by contacting said photographic silver halide emulsion with a nucleating agent for a sufficient time only to nucleate previously unexposed silver halide substantially without the formation of a visible image, followed by contacting said photographic silver halide emulsion with a second photographic developer for a sufficient time to develop a visible image, the step of nucleating said photographic silver halide emulsion by contacting said photographic silver halide emulsion with an aqueous solution of an alkali metal borohydride having a pH of at least 10.0 and containing at least 0.1 g./liter of solution but not more than 30 g./liter of solution of an alkali metal borohydride selected from the class consisting of sodium borohydride and potassium borohydride for a sufficient time only to nucleate previously unexposed silver halide substantially without the formation of a visible image.

2. In a method of producing a photographic color reproduction comprising exposing to a colored image a photographic element containing at least two photographic silver halide emulsion layers which have been differentially sensitized to different spectral regions, developing said photographic element to a negative black-and-white image by treatment with a photographic black-and-white developer, contacting said photographic element with a nucleating agent for sufficient time only to nucleate previously unexposed silver halide substantially without the formation of a visible image, and developing said photographic element in a photographic color developer in the presence of a color-forming compound which couples with the oxidation products of said photographic color developer to produce a colored image, the step comprising nucleating said previously unexposed silver halide by contacting said photographic element with an aqueous solution of an alkali metal borohydride having a pH of at least 10.0 and containing at least 0.1 g./liter of solution but not more than 30 g./liter of solution of an alkali metal borohydride selected from the class consisting of sodium borohydride and potassium borohydride for a sufficient time only to nucleate said previously unexposed silver halide substantially without the formation of a visible image.

3. In a method of reproducing a photographic color reproduction comprising exposing to a colored image a photographic element comprising a support having coated thereon three photographic silver halide emulsion layers, one of said layers being sensitive to the red region of the spectrum and having dispersed therein a coupler for producing a cyan image, one of said layers being sensitive to the green region of the spectrum and containing a coupler for producing a magenta image, and the third one of said layers being sensitive to the blue region of the spectrum and containing a coupler for producing a

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yellow image, developing said photographic element in a photographic black-and-white developer to produce a negative image, contacting said photographic element with a nucleating agent for a sufficient time only to nucleate previously unexposed silver halide substantially without the formation of a visible image, developing said photographic element in a photographic phenylenediamine color developer to produce colored images bearing a complementary relationship to the color in the original being produced, contacting said photographic element with a photographic clearing and fixing solution, contacting said photographic element in an oxidizing bath to remove silver images, and contacting said photographic element with a clearing and fixing solution to remove residual silver salts from said photographic silver halide emulsion layers, the step of nucleating said previously unexposed silver halide by contacting said photographic element with an aqueous solution of an alkali metal borohydride having a pH of at least 10.0 and containing at least 0.1 g./liter of solution but not more than 30 g./liter of solution of an alkali metal borohydride selected from

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the class consisting of sodium borohydride and potassium borohydride for a sufficient time only to nucleate previously unexposed silver halide substantially without the formation of a visible image.

References Cited in the file of this patent

UNITED STATES PATENTS

1,628,445	Zelger	May 10, 1927
1,962,348	Jelley	June 12, 1934
2,122,599	Wilmanns et al.	July 5, 1938
2,159,466	Wilmanns et al.	May 23, 1939
2,295,013	Schinzel	Sept. 8, 1942
2,339,309	Weber et al.	Jan. 18, 1944
2,461,661	Schlessinger et al.	Feb. 15, 1949
2,766,760	Bogaty et al.	Oct. 16, 1956

OTHER REFERENCES

- Mees: "The Theory of the Photographic Process,"
 Revised Ed., p. 109, The MacMillan Co., N.Y., 1954.
 (Copy in Sci. Lib.)