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ANTISTAIN BATHS FOR SENSITIVE COLOR
PHOTOGRAPHIC MATERIAL

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1 Claim. (Cl. 95—88)

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This invention relates to photographic anti-stain baths, to anti-stain baths employed in multi-color photography, and especially to non-staining baths for the washing of multi-color photographic material following the bleaching and fixing treatment.

It is known that in the processing of multi-color reversible film and multi-color reversible film coated upon a white opaque support, the exposed film or exposed white opaque, is first developed with a normal black and white developer to produce a negative image. After development, the black and white negative material, without being fixed, is exposed to general illumination, followed by a second development with a color-forming developer. During the first and second development, the silver-halides in all the layers are reduced to metallic silver. After the second development, the material is cleared in running water, hardened in an aqueous solution consisting of either alum or potassium chrome, and then washed in running water. After the latter treatment, the silver present in all the layers formed during the first and second development is converted into a salt by any of the known silver-salt formers, commonly known as bleaching baths, and the silver salt thus formed is then removed by dissolving it in a silver-salt solvent such as, for example, hypo. The material is then washed for a long period of time and then dried.

Prior to the final washing operation it is essential that the residual second or color developer and bleach solutions be removed, otherwise stains will be formed during the drying operation, which are particularly noticeable in the white area. In order to prevent this staining, an extended washing time in running water of from fifteen minutes to two hours, has been proposed. Even if this proposal be adopted, stains are nevertheless formed after the drying operation. It is believed that the staining results from the oxidation of traces of the color developer retained in the layers of the material following color-forming development, which then react with the unused color-former.

An object of the present invention is to eliminate excessive washing times of color developed multi-color photographic material while preventing the formation of stain.

A further object of the invention is a final rinse bath which clears undesirable matter from a multi-color photographic material in a short time while avoiding staining.

Other objects and features of the invention will

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become more apparent as the description proceeds.

We have found that the above objects are accomplished by employing, as a final rinse bath, an aqueous solution containing a small quantity of boric acid. The concentration of the boric acid may vary from as little as 0.01% to 1%. Amounts higher than 1% give little improvement in stain prevention from a practical standpoint and, accordingly, concentrations ranging from between 0.05% to 0.5% are most desirable.

The photographic multi-layer materials, which may be processed with the anti-stain bath of the present invention, are color reversible film, color negative film, color reversible printing material coated on a white opaque base, and color paper, irrespective of whether the dyestuff images are produced with color-formers present in the emulsion or by a selective second exposure followed by color development. The color reversible film consists of an integral tripack emulsion coated on the usual clear cellulose acetate or nitrate film base. Each of the emulsions are sensitized to one of the primary colors of light; namely, blue, green, and red. The top layer is blue sensitive. A filter layer, yellow in color and blue absorbing, lies under the top layer. Below this filter layer, lies a green sensitive emulsion layer, and below this is a red sensitive emulsion layer. Each of the three silver-halide emulsion layers contain dye-forming compounds which unite during the development of silver image in an aromatic amine developing agent to form a dye with the oxidation product of the developing agent, or may be free from color-formers, in which case the film is processed with the color-formers in the color developers by the selective 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 color negative film is made up in the same manner as the color reversible film, with the exception that it may contain a layer of clear gelatin between the red sensitive layer and the green sensitive layer. The color reversible white opaque material is prepared in the same manner as color reversible film and the color negative film, with the exception that the base consists of an opaque white film. The color paper is also constructed in the same manner as the color reversible film and the color negative film, with the exception that the emulsion is coated on a baryta coated paper base.

As silver is formed during development, it must be removed after color development by treatment in a bleach, followed by treatment in a bath of

sodium thiosulfate according to usual practice. A yellow dye is formed in the blue sensitive emulsion; a magenta dye is formed in the green sensitive emulsion; and a cyan dye is formed in the red sensitive emulsion. Combinations of these three printing primaries will produce all of the other colors in the finished film or print. Suitable methods for the preparation of photographic multi-layer materials have been described in the literature relating to color photography, and are, therefore, not described here.

The following examples describe in detail methods for accomplishing the above objects, but it is to be understood that they are inserted merely for purposes of illustration and are not to be construed as limiting the scope of the invention.

Example I

A 4" x 5" full color transparency sheet of color film was printed by contact on two 4" x 5" sheets of color reversible white opaque film.

The two sheets of 4" x 5" color reversible white opaque film were first developed for twelve minutes at 68° F. in a developer of the following composition:

p-Monomethylamine-m-phenol sulfate	grams	3
Sodium sulfite	do	50
Hydroquinone	do	6
Sodium carbonate (monohydrate)	do	40
Sodium thiocyanate	do	2
Potassium bromide	do	2
Water to make up	liter	1

The developed film was short stopped for 3 minutes at 68° F., in a 5% aqueous solution of sodium bisulfite.

The film was washed for 2 minutes in running water at 68° F., and then color developed for 15 minutes at 68° F., in a developer of the following composition:

p-Aminodiethylaniline HCl	grams	4
Sodium sulfite	do	20
Hydroxylamine HCl	do	1
Sodium carbonate	do	80
Potassium bromide	do	1
Water to make up	liter	1

The color developed film was rinsed for 4 minutes in running water at 68° F., and hardened for 5 minutes in a 3% aqueous solution of potassium chrome alum.

The hardened film was washed for 5 minutes in running water at 68° F. The washed material was then treated with a bleach bath of the following composition:

Di-potassium mono-sodium ferricyanide	grams	100
Potassium bromide	do	15
Disodium phosphate	do	40
Sodium bisulfate	do	25
Formalin	cc	20
Water to make up	liter	1

The bleached film was washed for 5 minutes at 68° F., and then fixed for 5 minutes in a solution of the following composition:

Hypo	grams	200
Borax	do	10
Water to make	liter	1

After fixing, the material was washed for 10 minutes in running water at 68° F.

After the final wash, one print was allowed to

dry while the other was rinsed for 2 minutes in a 0.1% solution of boric acid and then allowed to dry. At this point, the prints appeared identical. After normal drying, the print rinsed in the boric acid solution showed brighter colors and more brilliant highlights than the print given only a water wash for 15-20 minutes.

When the drying was carried out under conditions of high humidity so that the drying time was extended for several hours, the water rinsed print showed even greater highlight stains while the print rinsed in boric acid solution did not change.

Example II

A 2 1/4" x 2 1/4" color negative film was printed by projection on two 4" x 5" sheets of multi-layer photographic color paper.

The two 4" x 5" sheets of color paper were developed for 8 minutes at 68° F. in a developer of the following composition:

p-Aminodiethylaniline HCl	grams	3.5
Sodium sulfite	do	20
Sodium carbonate	do	80
Potassium bromide	do	1
Hydroxylamine HCl	do	2
Water to make up	liter	1

The developed film was short stopped for 5 minutes at 68° F. in a bath of the following composition:

Oxalic acid	grams	15
Potassium metabisulfite	do	15
Potassium oxalate	do	60
Sodium sulfate	do	20
Water to make up	liter	1

and then bleached for 5 minutes in a bleach bath of the following composition:

Potassium ferricyanide	grams	30
Potassium bromide	do	10
Water to make up	liter	1

The film was washed for 5 minutes at 68° F. and then fixed for 5 minutes in a solution of the following composition:

Hypo	grams	200
Borax	do	5
Water to make up	liter	1

After fixing, the material was washed for 30 minutes in running water at 68° F.

After the final wash, one print was allowed to dry while the other was rinsed for 2 minutes in a 0.1% solution of boric acid and allowed to dry. At this point, the prints appeared identical. After normal drying, the print rinsed in the boric acid solution showed brighter colors and more brilliant highlights than the print given only a water wash for 30 minutes.

Example III

Example I was repeated with the exception that the final rinse bath was a .01% solution of boric acid instead of a 0.1% solution. After fixing and washing, the color print rinsed in plain water showed objectionable stains, while the print treated with the boric acid solution was clear and unstained.

From the above examples it is manifest that the multi-layer photographic material rinsed in plain water shows marked staining upon drying of said material. This staining occurs especially under slow drying conditions, and is probably due to

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the coupling of the slow oxidation product of the color developer with a residual color-coupler present in one or more layers.

The above specific examples are to be regarded as merely illustrative of the invention and not in any sense restrictive.

This application is a continuation-in-part of our co-pending application Serial No. 627,534, filed November 8, 1945.

We claim:

In a process of producing color photographic images selected from the class consisting of indo-phenol and azomethine dyes in a color film having a plurality of silver halide emulsion layers by exposing the film, color developing the same, bleaching, fixing and washing, the improvement which comprises avoiding the formation of stain,

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after the bleaching, fixing, and washing operations, by rinsing the film with an aqueous solution consisting of water and boric acid in a concentration ranging from 0.01% to 1%.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,930,140	Becker	Oct. 10, 1933
1,981,391	Russell	Nov. 20, 1934
2,367,516	Muehler et al.	Jan. 16, 1945
2,367,548	Vittum	Jan. 16, 1945