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PROCESS FOR PREVENTING STAINS ON PHOTOGRAPHIC COLOR MATERIAL DURING DRYING FOLLOWING EXPOSURE, BLEACHING, AND FIXING TREATMENT

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8 Claims. (Cl. 95—88)

1

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 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 alum, 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.

During the 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 final 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 during and after the drying operation, which makes it imperative to keep the washing time as short as possible. 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.

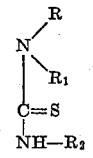
An object of the present invention is to eliminate excessive washing time of color developer multi-color photographic material while preventing the formation of stain.

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

2

Other objects and features of the invention will become more apparent as the description proceeds.

I have found that the above objects are accomplished by employing, as a final rinse bath, an aqueous solution containing a small quantity of a substituted or unsubstituted thiourea which corresponds to the following general formula:



wherein R is either hydrogen, methyl or ethyl group, and R_1 and R_2 which may be alike or different represent hydrogen or an aliphatic hydrocarbon radical of not more than 4 carbon atoms, e. g., methyl, ethyl, propyl, isopropyl, propenyl, butyl, and the like.

The following are examples of suitable substituted and unsubstituted thioureas which may be employed for the purpose herein set forth.

Thiourea
Methylthiourea
Ethylthiourea
Propylthiourea
2-propenylthiourea
Butylthiourea
Trimethylthiourea
Sym-dimethylthiourea
Sym-diethylthiourea
Sym-dipropylthiourea
Sym-dibutylthiourea
As-dimethylthiourea
As-diethylthiourea

This discovery makes it possible to reduce the final washing time considerably. The concentration of the substituted thiourea may vary somewhat. For instance, as little as a 0.1% solution in water has been found to eliminate stain for the most part, but as much as a 3% solution may be used if one wishes to take the greatest precaution to ensure freedom from stain. As for the unsubstituted thiourea, i. e., thiourea, the concentration may vary from 0.1% to 9%, best results being obtainable, however, at a concentration ranging from 0.1% to 5%.

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 white opaque film, and color paper irrespective of whether the dye-

stuff images are produced with the color-formers incorporated in the emulsion or by a selective second exposure and color development wherein the color-formers are added to the developing solution. 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 while 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 multilayer 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 the purpose 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-Methylaminophenol 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	5
Hydroxylamine HCl	do	2
Sodium carbonate	do	40
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 (40%)	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 up	liter	1

After fixing, the material was washed for 10–15 minutes in running water at 68° F.

After the final wash, one print was allowed to dry while the other was rinsed in a 0.5% aqueous solution of thiourea and then allowed to dry. At this point the prints appeared identical. After normal drying, the print rinsed in the thiourea 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 the thiourea solution did not change.

Example II

Example I was repeated with the exception that the colored material employed was a color paper and the final rinse was a 1% solution of methylthiourea instead of a 0.5% solution of thiourea. The color print washed in water showed objectionable stains after drying while the print treated with the solution containing methylthiourea was clear and unstained.

Example III

Example I was repeated with the exception that the final rinse bath was a 1% solution of ethylthiourea instead of a 0.5% solution of thiourea. After fixing and washing, the color print rinsed in plain water showed objectionable stains while the color print treated by a rinsing solution containing ethylthiourea was clear and unstained.

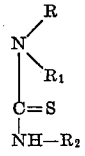
From the above examples it is manifest that the multilayer photographic material rinsed in plain water shows marked staining upon drying

of said material. This staining occurs especially under slow drying conditions and is probably due to the slow coupling of the oxidation product of the color developer with the 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. It will be obvious to anyone skilled in the art that many modifications such as substituting equivalent material and varying the proportions of materials used are within the spirit and scope of the invention as defined in the appended claims.

I claim:

1. In a process of color photography, the method of preventing stains on color images selected from the class consisting of indophenol and azomethine dyes produced in a multilayer color film by color-forming development, which comprises rinsing said film after exposure, color-forming development, bleaching, and fixing, with an aqueous solution consisting of water and a compound of the following general formula:



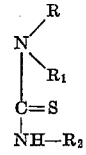
wherein R is a member selected from the class consisting of hydrogen, methyl and ethyl groups, and R_1 and R_2 are members selected from the class consisting of hydrogen and an aliphatic hydrocarbon radical of not more than 4 carbon atoms.

2. In a process of color photography, the method of preventing stains on color images selected from the class consisting of indophenol and azomethine dyes produced in a multilayer color film by color-forming development which comprises rinsing said film after exposure, color-forming development, bleaching, and fixing, with an aqueous solution consisting of water and thiourea.

3. In a process of color photography, the method of preventing stains on color images selected from the class consisting of indophenol and azomethine dyes produced in a multilayer color film by color-forming development which comprises rinsing said film after exposure, color-forming development, bleaching, and fixing, with an aqueous solution consisting of water and methylthiourea.

4. In a process of color photography, the method of preventing stains on color images selected from the class consisting of indophenol and azomethine dyes produced in a multilayer color film by color-forming development which comprises rinsing said film after exposure, color-forming development, bleaching, and fixing, with an aqueous solution consisting of water and ethylthiourea.

5. In a process of producing color photographic images selected from the class consisting of indophenol and azomethine dyes in a multilayer color film by exposing the film, color-forming developing the same, bleaching, fixing and washing, the improvement which comprises avoiding the formation of stain, after the aforesaid exposure, color-forming development, bleaching, fixing and washing operation, by rinsing the film with an aqueous solution consisting of water and a compound of the following general formula:



wherein R is a member selected from the class consisting of hydrogen, methyl and ethyl groups, and R_1 and R_2 are members selected from the class consisting of hydrogen and an aliphatic hydrocarbon radical of not more than 4 carbon atoms.

6. In a process of producing color photographic images selected from the class consisting of indophenol and azomethine dyes in a multilayer color film by exposing the film, color-forming developing the same, bleaching, fixing and washing, the improvement which comprises avoiding the formation of stain, after the aforesaid exposure, color-forming development, bleaching, fixing and washing operation, by rinsing the film with an aqueous solution consisting of water and thiourea.

7. In a process of producing color photographic images selected from the class consisting of indophenol and azomethine dyes in a multilayer color film by exposing the film, color-forming developing the same, bleaching, fixing and washing, the improvement which comprises avoiding the formation of stain, after the aforesaid exposure, color-forming development, bleaching, fixing and washing operation, by rinsing the film with an aqueous solution consisting of water and methylthiourea.

8. In a process of producing color photographic images selected from the class consisting of indophenol and azomethine dyes in a multilayer color film by exposing the film, color-forming developing the same, bleaching, fixing and washing, the improvement which comprises avoiding the formation of stain, after the aforesaid exposure, color-forming development, bleaching, fixing and washing operation, by rinsing the film with an aqueous solution consisting of water and ethylthiourea.

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