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ANTISTAIN AGENTS FOR SILVER BLEACH SOLUTIONS

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This invention relates to photographic bleaching baths, particularly to bleaching baths employed in multicolor photography, and especially to non-staining baths for the bleaching of the silver image in a multicolor film following color coupling development.

It is known that in the processing of multicolor reversal film, the exposed film is first developed with a normal black and white developer to produce a negative. After development the black and white negative film, without being fixed, is then 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 film is cleared in running water for a period of from 15 seconds to 2 minutes, hardened in an aqueous solution consisting of either alum or potassium chrome alum for 5 minutes and then washed in running water from 10 to 20 minutes. 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 solution in a silver-salt solvent such as, for example, hypo.

Prior to the bleaching operation it is essential that all traces of residual second or color developer be removed, otherwise stains will be formed during the bleaching operation by the oxidation of the residual developing agent and subsequent coupling with unreacted color former, particularly noticeable in the highlight areas. In order to convert the difficultly soluble color developing agent to its salt and to wash it from the film so as to prevent staining, rinses in acid hardening solutions such as, for example:

(1) 5% potassium chrome alum
(2) 3% potassium alum+1% acetic acid
(3) 3% potassium alum+3% sodium acetate+1½% sodium bisulfate
(4) 2% potassium chrome alum+2½% sodium acetate+2% sodium citrate

and short stop baths such as, for example:

(1) 1% acetic acid
(2) 1% sodium bisulfite
(3) 3% sodium acetate+1% sodium bisulfate
(4) 5% potassium acid phthalate

together with extended washing times in running water from 15 minutes to 120 minutes have been proposed. Despite these proposals and the time consuming washing step, stains are nevertheless formed during the bleaching operation. It is believed that the staining results from the oxidation of traces of the color developing compounds retained in the layers of the film following color forming development which then react with the usused color former.

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The principal object of the present invention is to eliminate excessive washing times of a color developed multicolor film and to provide an improved bleaching bath which prevents the formation of stain.

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

We have found that the above objects are accomplished by incorporating into a bleach solution commonly known and used in color photography one of the aliphatic aldehydes, such as formaldehyde, paraformaldehyde (trioxymethylene), acetaldehyde (paraldehyde), aldol, crotonaldehyde, propionaldehyde and the like. This discovery makes it possible to considerably reduce the washing time between color development and the bleaching operation. The concentration of the aliphatic aldehyde required may vary considerably. For instance, as little as 5 cc. of an aliphatic aldehyde per liter of bleach solution has been found to eliminate stain, and as much as 80 cc. per liter can be used without interference with the properties of the bleaching solution. Amounts higher than 80 cc. per liter can be employed, but there seems to be little improvement in stain prevention above a concentration of 40 cc. per liter. For practical purposes, however, concentrations ranging between 10 cc. and 40 cc. per liter are most desirable. Inorganic hardeners such as alum and potassium chrome alum can also be employed instead of the organic gelatin hardeners. The stain reduction obtained, however, with the former is considerably less than that obtained with the latter.

As is well-known, all bleach solutions contain an oxidizing agent dissolved in a suitable solvent, such as, for example, water, with or without the presence of other adjuvants. A typical bleach solution consists of 100 grams of an oxidizing agent per liter of solution, and may contain one or more of the following ingredients:

Potassium bromide	10 grams (Converting agent)
Disodium phosphate	40 grams (Buffering salt)
Sodium bisulfate	5 grams (Buffering salt)
Sodium tetra phosphate	20 grams (Corrosion preventives)
Water to make up	1 liter (Solvent)

By an oxidizing agent we mean an inorganic chemical compound that will oxidize a metallic

silver image to form a silver-salt. Most commonly used oxidizing agents are alkali metal ferricyanides, such as sodium, potassium, ammonium ferricyanides, the alkali metal persulfates, i. e., the sodium and potassium persulfates, or mixtures of these salts.

By a converting agent we mean a chemical compound such as potassium bromide or sodium thiocyanate which by reason of a difference in solubility will replace the silver ferrocyanide formed in the bleaching reaction (when ferricyanide is used as the oxidizing agent) to form silver bromide or silver thiocyanate and thus impel the bleaching reaction to completion. Converting agents are sometimes called halogenizing agents.

By buffering agents we mean any substance that is added to bring the bleach solution to a specified pH and to maintain this pH even though small amounts of acids or alkali may be carried into the bleach by the film. The pH's used in bleaching color films are generally maintained between 3 and 9.

By corrosion preventives we refer to those compounds which retard the corrosive effect of the bleach solution on developing tanks, trays, etc. Large quantities (20–80 grams per liter) of alkali metal phosphates such as disodium phosphate, sodium tetraphosphate and the like, as well as the dialkylamino alcohols described in United States Patent 2,327,813, have been found to prevent corrosion effectively.

By solvent we refer to the liquid in which the above materials are dissolved which is usually water.

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

Two exposed 4'' x 5'' multilayer color film sheets of the reversal type were developed for 10 minutes at 68° F. in a developer of the following composition:

Metol	grams	2
Sodium sulfite	do	20
Hydroquinone	do	4
Sodium carbonate	do	80
Sodium thiocyanate	do	5
Potassium bromide	do	4
Water to make up	liters	1

The developed films were short stopped for 3 minutes in a 3% aqueous solution of acetic acid or other acid ester.

The films were washed for 2 minutes in running water, and then given a second exposure for 3 minutes to light of a No. 1 photo-flood lamp 30 inches away from the film.

The films were color developed for 15 minutes in a developer of the following composition:

Sodium sulfite	grams	5
p-Amino diethyl aniline HCl	do	4
Sodium carbonate	do	40
Potassium bromide	do	1
Water to make up	liters	1

The color developed films were rinsed for 1 minute in running water, and hardened for 5 minutes in a 3% aqueous solution of chrome alum.

The hardened films were washed for 5 minutes in running water.

The first washed film was treated in solution No. 1 and the second washed film was treated in solution No. 2 of the following compositions:

		No. 1	No. 2
Disodium mono potassium ferricyanide	grams	100	100
Potassium bromide	do	10	10
Sodium tetra phosphate	do	20	20
Disodium phosphate	do	40	40
Sodium bisulfate	do	25	25
Formalin (35–40% solution of formaldehyde in water)	cc	---	20
Water to make up	liters	1	1

The two bleached film sheets were then washed in water for 5 minutes, fixed for 5 minutes in a 20% aqueous hypo solution, washed for an additional 5 minutes and then dried. The film bleached in solution No. 1 showed objectionable bluish stains, whereas the film bleached in solution No. 2 containing formalin was clear and unstained.

Example II

Two exposed 4'' x 5'' multilayer color film sheets of the negative type were developed for 10 minutes at 68° F. in a developer of the following composition:

Sodium sulfite	grams	0.5
2-amino-5-diethylamino toluene hydrochloride	grams	2.5
Hydroxylamine HCl	do	1
Sodium carbonate	do	65
Potassium bromide	do	2.5
Water to make up	liters	1

The developed films were short stopped for 5 minutes in a solution of the following composition:

Mono potassium phosphate	grams	80
Disodium phosphate	do	20
Water to make up	liters	1

The films were hardened for 3 minutes in a 3% chrome alum solution, and washed for 5 minutes in running water.

The first washed film was treated in solution No. 1 and the second washed film was treated in solution No. 2 of the following compositions:

		No. 1	No. 2
Potassium ferricyanide	grams	100	100
Disodium phosphate	do	4.3	4.3
Mono potassium phosphate	do	5.8	5.8
Potassium bromide	do	10	10
Sodium sulfite	do	---	0.5
Paraformaldehyde	do	---	16
Water to make up	liters	1	1

The paraformaldehyde in the above formula is relatively difficult to dissolve unless a small amount of alkali or sodium sulfite is first added to the water. We have found that 16 grams of paraformaldehyde dissolved with the aid of 0.5 grams of sodium sulfite to be the equivalent of 40–50 cc. of formalin.

The two bleached sheet films were then washed for 5 minutes, fixed for 5 minutes in a 20% aqueous solution of hypo, washed an additional 15 minutes and then dried. As in Example I, the film bleached in solution No. 1, containing no paraformaldehyde, showed bluish stains, whereas the film bleached in solution No. 2 was clear and unstained.

Example III

Example I was repeated with the exception that the bleach bath No. 2 contained 20 cc. of acetaldehyde instead of formalin. The film bleached in the solution containing no acetaldehyde showed objectionable bluish stains, while the film bleached with the solution containing acetaldehyde was clear and unstained.

Example IV

Example II was repeated with the exception that bleach bath No. 2 contained 20 cc. of crotonaldehyde instead of paraformaldehyde. The film bleached in the solution containing no crotonaldehyde showed objectionable bluish stains, while the film bleached with the solution containing crotonaldehyde was clear and unstained.

In place of aliphatic aldehydes referred to above, organic hardening agents such as the hydroxy aldehydes described in Sheppard and Houch, United States Patent 2,059,817, and the dialkyl diketones described in Staud and Briggs, United States Patent 2,063,351, may also be employed.

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 materials and varying the proportions of materials used are within the spirit and scope of the invention as defined in the appended claims.

We claim:

1. The method of preventing the staining action of a bleaching bath during the bleaching of silver in an exposed and color-developed photographic emulsion containing a residual color coupler and a residual aromatic primary amino developing agent which comprises treating the said emulsion with a silver bleaching bath containing as the only oxidizing agent a water-soluble inorganic oxidizing agent, selected from the class consisting of alkali metal ferricyanides and persulfates, and a carbonyl compound selected from the class consisting of aliphatic aldehydes and dialkyl di-ketones.

2. The method of preventing the staining action of a bleaching bath during the bleaching of silver in an exposed and color-developed photographic emulsion containing a residual color coupler and a residual aromatic primary amino developing agent which comprises treating the said emulsion with a silver bleaching bath containing as the only oxidizing agent a water-soluble inorganic oxidizing agent selected from the class consisting of alkali metal ferricyanides and persulfates, and formaldehyde.

3. The method of preventing the staining action of a bleaching bath during the bleaching of silver in an exposed and color-developed photographic emulsion containing a residual color coupler and a residual aromatic primary amino developing agent which comprises treating the said emulsion with a silver bleaching bath containing as the only oxidizing agent a water-soluble inorganic oxidizing agent selected from the class consisting of alkali metal ferricyanides and persulfates, and acetaldehyde.

4. The method of preventing the staining action of a bleaching bath during the bleaching of silver in an exposed and color-developed photographic emulsion containing a residual color coupler and a residual aromatic primary amino developing agent which comprises treating the said emulsion with a silver bleaching bath containing as the only oxidizing agent a water-soluble inorganic oxidizing agent selected from the class consisting of alkali metal ferricyanides and persulfates, and crotonaldehyde.

5. The method according to claim 1 wherein the concentration of the aliphatic aldehyde and dialkyl di-ketone ranges from 5 to 80 parts per liter of bleach.

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