United States Patent Office 3,042,520 Patented July 3, 1962

3,042,520

BLEACHING BATH FOR PROCESSING COLOR FILM

Carl E. Johnson, Binghamton, N.Y., assignor to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Apr. 23, 1959, Ser. No. 808,306
9 Claims. (Cl. 96—60)

This invention relates to photographic bleaching baths. More particularly, this invention relates to solutions used in bleaching the silver image in a multicolor film following color forming development.

It is known that in the processing of multicolor photographic film, the silver formed in all the layers during development is converted into a silver salt by any of the well known bleach solutions which commonly contain an alkali metal ferricyanide as the oxidizing agent, a buffer mixture and in most instances, an alkali metal halide such as sodium chloride or potassium bromide. The silver salt thus formed is then removed by dissolving it in a silver-salt solvent such as hypo.

It has been observed that with certain color film emulsions, especially those which contain dispersions of lipophilic color formers, the silver formed during the development step was not readily converted by the bleach bath into hypo soluble salts. Prolonged bleaching reduced the amount of silver, but did not completely remove it. In these lipophilic color former systems, the color emulsions contain an organic solvent for the color former and these solvents have a tendency to occlude the metallic silver following development thereby preventing the oxidizing agent or salt former in the bleach bath from coming in contact with the silver to convert the silver into a silver salt by the customary bleaching bath.

It has already been proposed to incorporate into the bleach solution certain water-soluble organic compounds which are supposed to accelerate the bleaching rate. Among such compounds are monohydroxy alcohols, aliphatic ketones and phenoxy alcohols. However, these compounds work best with hydrophilic color formers fast to diffusion, but are less effective when used for the bleaching of solvent dispersed lipophilic color formers.

It is an object of this invention to provide a bleach bath containing a novel bleach accelerator which permits the rapid and complete removal of residual, occluded silver from the developed film.

Other objects and advantages of this invention will be apparent from the following description.

I have found that ethylene glycol mono n-hexyl ether (n-hexoxyethanol) is an excellent accelerator for photographic solutions which are used in converting the metallic silver in a developed photographic color film into a hypo-soluble silver salt. This compound is also known as n-hexyl Cellosolve and has the following formula:

$$C_6H_{13}—OCH_2CH_2—OH$$

My experiments have shown that n-hexoxyethanol is a more effective bleach accelerator than the monohydroxy alcohols, ketones and phenoxy alcohols of the prior art, especially when used for the bleaching of color materials which contain lipophilic color formers dispersed by the use of high boiling solvents. In addition, it is much cheaper than the prior art accelerators.

Photographic bleach solutions which are used for the processing of color film contain in aqueous solution, an alkali metal ferricyanide such as lithium, potassium or sodium ferricyanide as the oxidizing agent which converts

the metallic silver formed during development into a silver salt which is soluble in silver halide solvents such ts hypo (sodium thiosulfate). Typically, such a bleach solution contains, in addition to the ferricyanide, a halogenizing agent preferably an alkali metal chloride or an alkali metal bromide which converts the silver ferricyanide initially formed in the bleaching reaction into the less soluble silver chloride or silver bromide and thus impels the bleach reaction to completion.

The bleach reaction should be carried out at a preselected pH and consequently, the ferricyanide bleach solutions contain a buffering agent which maintains the desired pH even though small amounts of acids or alkali may be carried into the bleach by the film. The pH of the bleach solutions falls between a range of from 3 to 9, a pH between 4 and 6 being generally preferred. Among the more frequently used ingredients of such buffer mixtures are alkali metal phosphates such as disodium and monosodium phosphate, sodium citrate, sodium metaborate, borax, sodium bisulfate, boric acid, citric acid or phthalic acid. Some of the ingredients of the buffer mixture act also as corrosion inhibitors and retard the corrosive action of the ferricyanide bleach on metallic developing tanks, trays and the like.

In many instances, an alkali metal ferrocyanide is included which gives a tempering action to a freshly mixed bleach solution in order to simulate the performance of a partially used bleach. The rate of bleaching depends on the oxidation-reduction potential which in turn is a function of pH and the relative ferrocyanide-ferricyanide concentration. No such oxidation reduction-potential can be established so long as ferricyanide only is in the fresh solution, and no ferrocyanide has been formed as a result of the bleaching action. The desired tempering action is achieved by adding to a fresh bleach solution specified amounts of ferrocyanide thus establishing an oxidation reduction-potential which otherwise would be set up only after part of the ferricyanide had been reduced to ferrocyanide. On the other hand, the oxidation-reduction potential of the bleach solution can be increased and the effective life time of the solution can be extended by the addition of an alkali persulfate such as sodium persulfate.

Consequently, the photographic bleach solutions which are contemplated herein contain as their essential ingredients an alkali metal ferricyanide and n-hexoxyethanol together with other bleach adjuvants including buffer mixtures, alkali metal halides, particularly alkali metal bromides and alkali metal ferrocyanides and/or alkali metal persulfates. Photographic bleach solutions which we have found to be effective may be compounded in the following proportions.

Alkali metal ferricyanide	grams	30 to 120
Alkali metal halide	do	2 to 20
Buffer mixture	do	5 to 30
Alkali metal ferrocyanide	do	2 to 12
or		
Alkali metal persulfate	do	2 to 12
n-Hexoxyethanol	milliliters	2 to 20
Water to make 1 liter.		

The following examples will serve to illustrate my invention, but are not restricted thereto.

Example I

A three-foot strip of 35 mm. multilayer color film of the negative type, containing lipophilic color formers dispersed according to the method described in United States

Patents 2,269,158 and 2,322,027 was exposed and processed as follows:

The film was first color developed for 12 minutes at 68° F. in a developer of the following composition.

Sodium sulfite	grams	2
(4 - amino- N - ethyl - N - [β - methanesulfonamidoethyl]-m-toluidene sesquisulfate monohydrate)	grams	5
Sodium carbonate (monohydrate)	do	67.5
Potassium bromide	do	1
Benzyl alcohol	milliliters	5

Water to make 1 liter.

The developed film was short stopped for 2 minutes in a bath of the following composition.

	Grams
Acetic acid	10
Sodium acetate	20

Water to make 1 liter.

The material was then hardened for 5 minutes in a 3 percent aqueous solution of potassium chrome alum, and washed in water for 5 minutes.

The film was then bleached for 8 minutes in a solution having the following composition.

	Grams
Potassium ferricyanide	50.0
Potassium ferrocyanide	5.0
Sodium bromide	15.0
Disodium phosphate	11.0
Citric acid	8.0
Boric acid	10.0
n-Hexoxyethanol	5.0

Water to make 1 liter.

The bleached film was washed in water for 5 minutes, fixed for 5 minutes in a 20 percent aqueous hypo solution, washed in running water for an additional 5 minutes, and then dried.

This film strip was entirely free from residual stain, whereas a type sample which had been processed in an identical manner except for the fact that the bleach solution did not contain any n-hexoxyethanol, showed an overall gray stain which was especially noticeable in the highlight areas and which was identified analytically as being composed of metallic silver.

Example II

Example I was repeated with the exception that a bleach solution was used which had the following composition.

Potassium ferricyanide	grams	50.0
Potassium ferrocyanide	do	5.0
Sodium bromide	do	15.0
Monosodium phosphate	do	10.0
Phthalic acid	do	2.0
n-Hexoxyethanol	milliliters	8.0

Water to make 1 liter.

The film was free from residual silver stain after being bleached for only 5 minutes. A comparsion film which had been treated in a bleach solution which contained 8 milliliters of benzyl alcohol in place of n-hexoxyethanol, showed pronounced silver stain even after 5 minutes of bleaching.

Various modifications, such as substituting equivalent materials and varying the proportions of materials used, will be obvious to persons skilled in the art. Therefore, the scope of the invention is to be limited solely by the appended claims.

I claim:

1. In a process of color photography, the method of removing silver from the film after dyestuff image formation by the action of a bleaching bath which comprises treating said film with such a bath containing an alkali metal ferricyanide and n-hexoxyethanol.

2. In a process of color photography, the method of removing silver from a color film containing dyestuff images which are produced by color forming development of an emulsion containing a color former fast to diffusion, the improvement which comprises subjecting said film to the action of a bleaching bath containing an alkali metal ferricyanide as an oxidizing agent and n-hexoxyethanol as a bleach accelerator.

3. A photographic bleaching bath comprising an aqueous solution of an alkali metal ferricyanide and n-hexoxyethanol.

4. A photographic bleaching bath as recited in claim 3 wherein the alkali metal ferricyanide is sodium ferricyanide.

5. A photographic bleach solution having the following composition:

Alkali metal ferricyanide	grams	30 to 120
Alkali metal halide	do	2 to 20
Buffer mixture	do	5 to 30
Ethylene glycol monohexyl ether	milliliters	2 to 20

Water to make 1 liter.

6. A photographic bleach solution having the following composition:

Potassium ferricyanide	grams	50.0
Potassium ferrocyanide	do	5.0
Sodium bromide	do	15.0
Disodium phosphate	do	11.0
Citric acid	do	8.0
Boric acid	do	10.0
n-Hexoxyethanol	milliliters	5.0

Water to make 1 liter.

7. A photographic bleach solution having the following composition:

Potassium ferricyanide	grams	50.0
Potassium ferrocyanide	do	5.0
Sodium bromide	do	15.0
Monosodium phosphate	do	10.0
Phthalic acid	do	2.0
n-Hexoxyethanol	milliliters	8.0

Water to make 1 liter.

8. A photographic bleach solution having the following composition:

Alkali metal ferricyanide	grams	30 to 120
Alkali metal halide	do	2 to 20
Buffer mixture	do	5 to 30
Alkali metal ferrocyanide	do	2 to 12
n-Hexoxyethanol	milliliters	2 to 20

Water to make 1 liter.

9. A photographic bleach solution having the following composition:

Alkali metal ferricyanide	grams	30 to 120
Alkali metal halide	do	2 to 20
Buffer mixture	do	5 to 30
Alkali metal ferrocyanide	do	2 to 12
Alkali metal persulfate	do	2 to 12
n-Hexoxyethanol	milliliters	2 to 20

Water to make 1 liter.

References Cited in the file of this patent

UNITED STATES PATENTS

2,419,900 Kaszuba ..... Apr. 29, 1947