

UNITED STATES PATENT OFFICE

2,428,208

DICHROMATE BLEACH BATH CONTAINING
A WETTING AGENT AND METHOD OF
BLEACHING THEREWITHRichard O. Edgerton, Rochester, N. Y., assignor
to Eastman Kodak Company, Rochester, N. Y.,
a corporation of New JerseyNo Drawing. Application June 20, 1945,
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9 Claims. (Cl. 95—88)

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This invention relates to photography and particularly to dichromate bleaching baths for color photography.

Acid potassium dichromate bleach baths have been used in photography where it is desired to remove a silver image from a photographic layer without destroying or removing residual silver halide in the layer. Such baths have also been used in color photography where the photographic layer contains dye images such as color developed dye images as well as silver and silver halide. The silver can be removed from such layers without destroying either the dye images or the silver halide, by the use of acid dichromate bleach baths. A process in which the silver is to be removed from layers containing dye images is described in Mannes, Godowsky and Wilder U. S. Patent 2,258,187, granted October 7, 1941.

Acid dichromate bleach baths are generally used at a pH of 2.5 or lower. It has been found that when an acid dichromate bleach bath is used at a pH of less than 2.5 for about 10 minutes, for the treatment of photographic layers containing silver and color developed dye images, an appreciable amount of the dye is removed from the layer. This is especially true of the yellow dye images. If the pH of the bleach bath is increased to 2.5 or higher, silver bleaching is incomplete in the usual bleaching time of 10 minutes. This incomplete silver bleaching can be partly remedied by bleaching for a longer time but this also increases the loss of dye. Inorganic salts such as sodium or ammonium sulfate when present in the bleach solution also decrease the loss of dye to a slight extent; however, if the concentration of these inorganic salts is increased beyond a certain limit, silver bleaching is again inhibited and this must be compensated by lower pH, longer time or higher dichromate concentration, all of which result in further loss of dye.

It is therefore an object of the present invention to provide a dichromate bleach bath which can be used in the presence of a dye image and which will not remove an appreciable amount of the dye image during normal bleaching time. A further object is to provide a novel dichromate bleach bath in photography. Other objects will appear from the following description of my invention.

These objects are accomplished by incorporating in the dichromate bleach bath a wetting or dispersing agent.

The dichromate bleach baths used in photography usually consists of potassium dichromate

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or other alkali metal dichromate such as sodium or ammonium dichromate in an aqueous solution of sulfuric acid. Such baths may be used in either black and white or color photography to remove silver images from photographic layers without removing silver halide images in the layers. The dichromate bleach baths are useful in color photography, especially multi-color photography, where it is desired to remove a silver image without destroying a dye image in the photographic layer.

I have found that certain wetting or dispersing agents may be added to dichromate bleach baths of these types, and that the loss of color-developed dye images normally noticed when such bleach baths are used, can be reduced or almost eliminated. This effect of the wetting agents is unusual since it would be expected that wetting or dispersing agents would render the dyes more easily removable by the bleach bath. While I do not know the reasons for this action of the wetting or dispersing agents in the case of dichromate bleach baths, I have found that the loss of dye images, generally yellow dye images, is invariably reduced when the various types of wetting agents described herein are added to the bleach bath.

Among the wetting or dispersing agents which I have found suitable for addition to the bleach bath, there may be mentioned (1) alkyl naphthalene sulfonic acids and their water-soluble salts, such as iso-propyl naphthalene sodium sulfonate, the sodium alkyl naphthalene sulfonates, and diisopropyl naphthalene sulfonate, (2) the alkyl aryl sulfonates, (3) the higher fatty alcohol sulfates. These products are formed by reacting sulfuric acid with fatty alcohols such as those produced by esterifying higher fatty acids with lower aliphatic alcohols and reducing the mixture of esters to alcohols. These sulfates of the higher fatty alcohols are described, for example, in U. S. Patent 1,968,793, 1,968,794, 1,968,795, 1,968,796, and 1,968,797. These consist for the most part of the sulfates of oleyl, lauryl, stearyl, cetyl and octadecyl alcohols.

The use of these wetting agents in the dichromate bleach bath inhibits dye bleaching without inhibiting silver bleaching. The bleach bath can therefore be used to treat layers containing silver and dye images at normal treatment times of 8-10 minutes and at a pH of 1.9 to 2.2. The concentration of the wetting agent is limited by its solubility in an acid salt solution but the most satisfactory amount appears to be about 2 grams per liter of bleach bath. The amount of wetting

agent should not be above about 10 grams per liter of bleach bath or silver bleaching may be incomplete.

The following example illustrates a bleach bath according to my invention:

Potassium dichromate.....	grams..	2.5
Sulfuric acid (concentrated).....	c.c....	2.5
Sodium sulfate.....	grams..	100
Ammonium sulfate.....	do.....	100
Alkyl aryl sulfonate.....	do.....	2
Water to 1 liter		

My bleach bath is especially useful for the treatment of emulsion layers containing yellow dye images such as the dyes formed by coupling the development product of primary aromatic amino developing agent with couplers forming yellow dye images in the photographic layer such as the following couplers described in Weissberger U. S. Patent 2,298,443, granted October 13, 1942.

- (33) N-(p-benzoylacetyaminobenzenesulphonyl)-N-methyl-aniline
- (34) N-(p-benzoylacetyaminobenzenesulphonyl)-N-iso-amylaniline
- (39) N-(p-benzoylacetyaminobenzenesulphonyl)-N-n-amylaniline
- (36) N-methyl-p-(benzoylacetyamino)-benzenesulphon-p-nitroanilide
- (37) p-benzoylacetyamino-N-(p-toluenesulphonyl)-N-methyl-aniline
- (40) N-(p-benzoylacetyaminobenzenesulphonyl)-N-(γ-phenylpropyl)-aniline
- (41) N-(p-benzoylacetyaminobenzenesulphonyl)-N-benzyl-p-toluidine
- (42) N-(p-benzoylacetyaminobenzenesulphonyl)-N-(γ-phenylpropyl) p-tert.-amylaniline
- (46) N-(p-benzoylacetyaminobenzenesulphonyl)-N-(γ-phenylpropyl)-(o)-, (m)-, or (p)-toluidine

My invention is especially useful for treating photographic layers containing yellow dye images dispersed in the layer in particles of water-insoluble but water-permeable solvent for the dye, produced as described in Mannes and Godowsky U. S. Patent 2,304,940, granted December 15, 1942, or Jelley and Vittum 2,322,027, granted June 15, 1943. The Mannes and Godowsky patent describes the use of cellulose esters as the water-insoluble, water-permeable solvent for the dye.

It will be understood that the modifications included herein are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

What I claim is:

1. A bleach bath for removing only the silver from a photographic layer containing silver, and coupled dye images, comprising a sulfuric acid solution of an alkali metal dichromate and a wetting agent selected from the group consisting of alkyl naphthalene sulfonates, alkyl aryl sulfonates, and higher primary alkyl sulfates.

2. A bleach bath for removing only the silver from a photographic layer containing silver and coupled dye images, comprising an aqueous sulfuric acid solution of potassium dichromate and a water-soluble higher primary alkyl sulfate.

3. A bleach bath for removing only the silver from a photographic layer containing silver and coupled dye images dispersed in said layer in particles of water-insoluble solvent for said dye, comprising a sulfuric acid solution of an alkali metal dichromate and a wetting agent selected

from the group consisting of alkyl naphthalene sulfonates, alkyl aryl sulfonates, and higher primary alkyl sulfates.

4. The method of removing only the silver from a photographic layer containing silver and coupled dye images which comprises treating said layer with a sulfuric acid solution of alkali metal dichromate and a wetting agent selected from the group consisting of alkyl naphthalene sulfonates, alkyl aryl sulfonates and higher primary alkyl sulfates.

5. The method of removing only the silver from a photographic layer containing silver and coupled dye images dispersed in said layer in particles of water-insoluble solvent for said dye, comprising treating said layer with a sulfuric acid solution of alkali metal dichromate and a wetting agent selected from the group consisting of alkyl naphthalene sulfonates, alkyl aryl sulfonates and higher primary alkyl sulfates.

6. The method of removing only the silver from a photographic layer containing silver and coupled dye images dispersed in said layer in particles of water-insoluble but water-permeable cellulose ester which is a solvent for said dye, comprising treating said layer with a sulfuric acid solution of alkali metal dichromate and a wetting agent selected from the group consisting of alkyl naphthalene sulfonates, alkyl aryl sulfonates and higher primary alkyl sulfates.

7. The method of removing only the silver from a photographic layer containing silver and coupled dye images dispersed in said layer in particles of water-insoluble but water-permeable cellulose ester which is a solvent for said dye, comprising treating said layer with an aqueous sulfuric acid solution of potassium dichromate and a water-soluble higher primary alkyl sulfate.

8. The method of removing only the silver from a photographic layer containing silver and yellow coupled dye image dispersed in said layer in particles of a liquid, water-insoluble but water-permeable solvent for said dye, comprising treating said layer with a sulfuric acid solution of alkali metal dichromate and a wetting agent selected from the group consisting of alkyl naphthalene sulfonates, alkyl aryl sulfonates and higher primary alkyl sulfates.

9. The method of removing only the silver from a photographic layer containing silver and yellow coupled dye image dispersed in said layer in particles of a liquid, water-insoluble but water-permeable solvent for said dye, comprising treating said layer with an aqueous sulfuric acid solution of potassium dichromate and a water-soluble higher primary alkyl sulfate.

RICHARD O. EDGERTON.

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