United States Patent Office 3,761,260
Patented Sept. 25, 1973

3,761,260

PHOTOGRAPHIC BLEACH COMPOSITION

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No Drawing. Filed Aug. 9, 1971, Ser. No. 170,277
Claims priority, application Great Britain, Sept. 21, 1970, 44,875/70
Int. Cl. G03c 7/16, 5/32
U.S. Cl. 96—60 R 9 Claims

ABSTRACT OF THE DISCLOSURE

A method of bleaching photographic silver images by means of a solution containing an alkali metal or ammonium dichromate and a water-soluble iodide in a weight ratio of 50:1 and 1:1, is described. By the presence of the iodide, bleaching is accelerated.

The present invention relates to photographic bleach compositions containing a dichromate as the oxidizing agent, and more particularly to the improvement of the silver bleaching action of said compositions.

In the production of photographic dye images and black-and-white reversal images the metallic silver formed during development should be bleached, i.e. converted by means of bleach solutions containing oxidizing agents into water-soluble silver salts or silver salts that are soluble in silver halide solvents such as sodium thiosulphate. Typically, such bleaching solutions contain in addition to the oxidizing agent an agent, preferably an alkali metal chloride or an alkali metal bromide, which converts the silver salt initially formed in the bleaching reaction into the less soluble silver chloride or silver bromide and thus impels the bleach reaction to completion.

Whereas it is generally easy to completely remove metallic silver images formed in photographic materials not containing colour couplers or dyestuffs, difficulties are often encountered with photographic multilayer colour materials. Thus in areas where metallic silver should be removed, residual images remain which may consist of silver sulphide or silver encapsulated by the dyestuff formed. For instance when using dichromate bleaching solutions it is often difficult to bleach or to bleach at an acceptable rate the metallic silver image formed upon colour development in the blue-sensitive silver halide emulsion layer, which comprises a yellow forming coulour coupler. This manifests itself in high unwanted side-absorptions of the yellow dyestuff image formed upon colour development and thus leads to incorrect colour reproduction.

It has now been found that silver bleaching by means of an alkali metal or ammonium dichromate as oxidizing agent can be accelerated by addition to the dichromate bleaching solution of a water-soluble iodide for example an alkali metal iodide such as sodium and potassium iodide or ammonium iodide.

The favourable action of the iodides on dichromate bleaching is not considered to be due to any action of iodide ions. It is possible that the accelerated bleaching is due to the formation of free iodine which itself bleaches the silver.

Thus, in accordance with the present invention there is provided a method of accelerating the bleaching of a metallic silver containing photographic element by treatment of the said metallic silver with a bleaching solution comprising in addition to the dichromate oxidizing agent a water-soluble iodide.

The invention further provides a solution for the bleaching of a metallic silver containing photographic element which comprises a dichromate oxidizing agent and a water-soluble iodide.

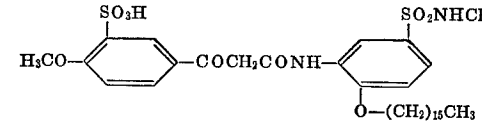
The ratio of dichromate oxidizing agent to iodide used in the bleaching solutions according to the invention may be between very wide limits but it should not outweigh the dichromate. Generally the weight-ratio of dichromate to iodide is comprised between 50:1 and 1:1, preferably between 10:1 and 2:1.

The bleaching solutions according to the present invention may comprise in addition to the dichromate oxidizing agent and the iodide any of the common ingredients used in such solutions for instance alkali metal chlorides or bromides such as potassium bromide as rehalogenizing agent, sodium sulphate, water-softeners, thickening agents, hardeners, optical brightening agents, etc. Any of the materials used in bleach baths can be used to obtained the desired pH-value, e.g. sulphuric acid, hydrochloric acid, phosphoric acid, acetic acid, boric acid, citric acid, sodium citrate, monosodium phosphate, sodium bisulphate, etc. The pH of the bleach solutions generally falls between a range of from 2 to 4, a pH of about 3 being generally preferred.

The following examples illustrate the present invention.

EXAMPLE 1

A positive multilayer tricolour film-material comprising in the blue-sensitive silver halide emulsion layer the yellow-forming colour coupler of the formula:



was exposed through a blue filter and processed in the conventional way by the steps of treatment in a prebath, rinsing, colour development, fixing, rinsing, bleaching, rinsing, fixing and rinsing thus forming a yellow dye-image. Bleaching took place for 2 min. in a bath of the following composition A:

water: 800 ml.
potassium bromide: 20 g.
potassium dichromate: 5 g.
potassium alum (crystalline): 40 g.
sodium bisulphate: 0.6 g.
water to make: 1000 ml.

The pH-value of this bleaching solution was 3.10±0.10 which was kept constant by addition of sodium hydroxide (+) or sodium bisulphate (—).

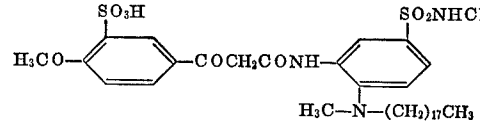
Density of the image formed was then measured behind a blue, a green and a red filter and compared with the density of images formed under identical circumstances with the only difference that to the bleaching bath 1 g. of potassium iodide was added. The addition of iodide gives lower densities, due to better bleaching, as can be taken from the table.

TABLE

Bleaching solution used	Density measured behind— Blue filter	Green filter	Red filter
Composition A	2.30	0.60	0.43
Composition A plus 1 g. of potassium iodide	2.14	0.50	0.32

EXAMPLE 2

Example 1 was repeated with the difference that the material now contained the yellow-forming colour coupler of the formula:



The results obtained are listed in the following table.

TABLE

Bleaching solution used	Density measured behind— Blue filter	Green filter	Red filter
Composition A	1.90	0.54	0.38
Composition A plus 1 g. of potassium iodide	1.88	0.48	0.30

What is claimed is:

1. Method of bleaching a metallic silver containing photographic multi-layer color material by treatment of the said material with a solution containing an alkali metal or ammonium dichromate as oxidizing agent wherein the said solution also contains a water-soluble iodide, the weight ratio of dichromate to iodide being between about 50:1 and 1:1.

2. Method according to claim 1, wherein said iodide is potassium iodide.

3. Method according to claim 1, wherein the ratio of dichromate to iodide is between about 10:1 and 2:1.

4. Method according to claim 1, the said solution also containing an alkali metal chloride or bromide.

5. A photographic bleach solution containing an alkali metal dichromate or ammonium dichromate and a water-soluble iodide in a weight ratio of dichromate to iodide from between about 50:1 and 1:1.

6. A photographic bleach solution according to claim 5, wherein said iodide is potassium iodide.

7. A photographic bleach solution according to claim 5, wherein the ratio of dichromate to iodide is between 10:1 and 2:1.

8. A photographic bleach solution according to claim 5, the said solution also containing an alkali metal chloride or bromide.

9. A photographic bleach solution according to claim 8, wherein the ratio of dichromate to iodide is between 10:1 and 2:1.

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U.S. Cl. X.R.

96—22, 53 UX