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(54) Title: PHOTOGRAPHIC BLEACH COMPOSITIONS

(57) Abstract

A method of processing an imagewise exposed photographic silver halide material which includes a redox amplification dye image-forming step and a bleach step using an aqueous solution of hydrogen peroxide or a compound capable of releasing hydrogen peroxide.

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PHOTOGRAPHIC BLEACH COMPOSITIONS

This invention relates to photographic bleach compositions for use in redox amplification processes.

There are a number of proposals in the art to use peroxy compounds, eg hydrogen peroxide or a compound capable of releasing hydrogen peroxide, in bleach compositions in conventional colour processes. In US specification 4 277 556 there are described bleach solutions consisting of some 50 ml/l 30% hydrogen peroxide solution and 30 ml/l concentrated acetic acid. Such solutions however do not bleach the entire amount of silver present. US specification 4 454 224 describes an improvement on the above in which the bleach solution further contains a polyacetic acid and is alkaline having a pH of 7 or more. Other peroxide bleach solutions must contain an organic metal complex salt, eg US specification 4 301 236, while others must employ a bleach accelerator eg, Japanese specifications 61/250647A and 61/261739A. In spite of all these suggestions no such solution has ever been used commercially.

Redox amplification processes have been described, for example in British Specification Nos. 1,268,126, 1,399,481, 1,403,418 and 1,560,572. In such processes colour materials are developed to produce a silver image (which may contain only small amounts of silver) and then treated with a redox amplifying solution (or developer-amplifier) to form a dye image. The redox amplifying solution contains a reducing agent, for example a colour developing agent, and an oxidising agent which will oxidise the colour developing agent in the presence of the silver image which acts as a catalyst. Oxidised colour developer reacts with a colour coupler (usually contained in the

photographic material) to form image dye. The amount of dye formed depends on the time of treatment or the availability of colour coupler rather than the amount of silver in the image as is the case in conventional colour development processes. Examples of suitable oxidising agents include peroxy compounds including hydrogen peroxide, cobalt (III) complexes including cobalt hexammine complexes, and periodates. Mixtures of such compounds can also be used. A particular application of this technology is in the processing of silver chloride colour paper, especially such paper with low silver levels.

If the level of silver halide employed in the photographic material is low enough it may be possible to dispense with any bleaching and/or fixing steps. At present, however, it is often necessary to have such processing steps in a redox amplification process. The present inventor has found that an aqueous hydrogen peroxide solution optionally containing some acid will perform as an efficient bleach solution when following redox amplification dye image formation.

According to the present invention there is provided a method of processing an imagewise exposed photographic silver halide material which includes a redox amplification dye image-forming step and a bleach step using an aqueous solution of hydrogen peroxide or a compound capable of releasing hydrogen peroxide.

The present bleach solutions are considerably more ecologically acceptable than traditional bleach solutions based on ferricyanides or ferric EDTA. Moreover, in a system already using a hydrogen peroxide amplification solution, the supply thereof to the amplification and bleach solutions could come from a common source thus saving on chemical storage.

In a preferred embodiment of the present invention, the bleach step follows immediately after image formation with or without an intermediate acid stop bath comprised for example of dilute acetic acid.

A hydrogen peroxide bleach for a silver image produced in a redox amplification may contain from 20 to 400 ml of 100 vol hydrogen peroxide solution per litre of bleach solution, preferably from 30 to 100 ml/litre. Such a solution may additionally contain an acid, eg acetic acid in a concentration of from 0.05 to 10.0 ml/litre. Its pH may be in the range 1 to 6, preferably from 3.0 to 5.5 High levels of acetic acid are not good for the environment and an alternative may be to use low levels of sodium bisulphate. This is acid and somewhat buffered. It may be possible to use more dilute peroxide at a higher processing temperature.

To fix the material it is immersed in concentrated sulphite fixer, either with or without a low level of sodium thiosulphate, eg 2 g/l, present. Alternatively a conventional thiosulphate fixer may be used.

The following Examples are included for a better understanding of the invention.

EXAMPLE 1

A multilayer coating containing approx 1.18 mg/dm^2 total silver was fogged to light and then developed in SOLUTION A for 3 min at 18°C. The ascorbic acid was present to suppress the formation of dye image. A good grey silver image was obtained.

Control—A strip of this developed silver was stopped in 2% acetic acid for 1 min followed by treatment in a ferric EDTA bleach-fix solution. The silver was

Control—A strip of this developed silver was stopped in 2% acetic acid for 1 min followed by treatment in a ferric EDTA bleach-fix solution. The silver was completely removed in 15 seconds at 18°C. The strip was then washed and dried. Testing for silver was carried out by adding a drop of solution B (a dilute solution of sodium sulphide) to the bleached/fixed area. No brown stain was observed indicating that all the silver had been removed. When the untreated coating was tested, a heavy brown stain was observed indicating the presence of silver (chloride).

Invention— A strip of the same multilayer coating was developed as above to give a grey silver image. After development the strip was stopped by immersing it in a stop bath of 2% acetic acid for 1 min. It was then immersed at 18°C in solution C (a 30 VOL of hydrogen peroxide containing a little acetic acid). After agitating for 30 secs the grey silver image turned white. On completion the strip was immersed in the fixer solution D for 30 secs. The strip was washed and dried and tested for silver using sodium sulphide as above. No brown stain was observed indicating that the silver had been completely removed (bleached and fixed).

EXAMPLE 2

Example 1 was repeated as far as the acetic stop bath for 1 min. The strip was then immersed in the fixer solution D for 30 secs followed (without washing) by immersing in the hydrogen peroxide bleach solution C for 30 secs. The image did not turn white (bleach) where it had been previously immersed in the fixer but did turn white above indicating that the fixer had "poisoned" the silver image and prevented it from

bleaching. This experiment shows why it is necessary to pass straight from the acetic stop bath to the peroxide bleach in order to get the bleaching effect.

SOLUTIONS

Solution A— Colour developer

Sodium sulphite	1.88g
Sodium carbonate(anhydrous)	21 g
Color Developer CD3	7.60g
1-hydroxyethylidene-1,1-diphosphonic acid	1.20g
N,N-diethylhyroxylamine	0.74g
Sodium hydroxide	2.29g
Ascorbic acid	14 g
Water to	1000 ml
pH	10.1

Solution B—— Test solution

Sodium sulphide	0.25g
Water to	100 ml

Solution C—— Hydrogen peroxide bleach

100 VOL Hydrogen peroxide	333 ml
Water	666 ml
Glacial acetic acid	1.7 g
Final Volume	1000 ml
pH to approx	3.5

Solution D—— Sodium sulphite/ Hypo fixer

Sodium sulphite	60 g
Sodium thiosulphate	2.0g
Water to	1000 ml

CLAIMS:

1. A method of processing an imagewise exposed photographic silver halide material which includes a redox amplification dye image-forming step and a bleach step using an aqueous solution of hydrogen peroxide or a compound capable of releasing hydrogen peroxide.

2. A method of photographic processing as claimed in claim 1 in which the bleach solution has a pH of from 1 to 6.

3. A method of photographic processing as claimed in claim 2 in which the bleach solution has a pH of from 3.0 to 5.5.

4. A method of photographic processing as claimed in any of claims 1-3 in which the bleach solution contains from 20 to 400 ml of 100 vol hydrogen peroxide solution per litre of bleach solution.

5. A method of photographic processing as claimed in any of claims 1-6 in which the bleach solution contains from 30 to 100 ml of 100 vol hydrogen peroxide solution per litre of bleach solution.

6. A method of photographic processing as claimed in any of claims 1 to 5 in which the bleach step is followed by a fix step.

7. A bleach solution as defined in any of claims 1-5.

8. The use of a bleach as defined in any of claims 1-5 for the bleach step of a redox amplification process.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/01377

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G03C7/42 ; G03C7/30

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	G03C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	DE,A,2736886 (KONISHIROKU PHOTO INDUSTRY) 02 March 1978 see page 30, lines 12 - 20 see page 43, lines 5 - 10; claim 1 (cited in the application)	1-8
Y	US,A,4113490 (M.FUJIWHARA ET AL.) 12 September 1978 see column 6, lines 21 - 31 see column 10, lines 28 - 39; claim 1	1-8

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
23 SEPTEMBER 1991	18. 10. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	PHILOSOPH L.

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP9101377
SA 49494

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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