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(54) **Photographic processing.**

(57) A fixing process for photographic material comprises treatment with an alkali metal sulphite and a water soluble quaternary nitrogen compound.

EP 0 411 760 A1

PHOTOGRAPHIC PROCESSING

This invention relates to photographic processing and, in particular, to a method of fixing.

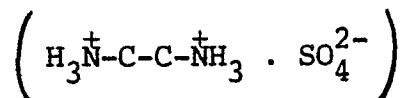
Photographic silver halide materials are employed to form images by first imagewise exposing the material, e.g. in camera, and then processing to form a visible image. The processing steps usually include (a) a development step in which the exposed areas of the material form a visible image and (b) a fixing step whereby the undeveloped silver halide is removed by treatment with a fixer solution which contains a silver halide solvent.

The most widely used fixer solutions are based on alkali metal or ammonium thiosulphates. Under certain conditions some colour couplers (as used in colour materials) can continue to couple in a thiosulphate fixer. Further, thiosulphate fixer solutions are unstable and can precipitate sulphur.

Our International application PCT EP90/00607 proposes to use alkali metal sulphite solutions to remove silver chloride from photographic materials in acceptable processing times. However fixing is relatively slow in comparison with thiosulphate fixers. Reference is also made to our International Application PCT EP/90/00725 and to our International Application PCT EP 90/00726.

In accordance with the present invention there is provided a fixing method of removing silver halide, especially silver chloride, from a photographic material during processing which comprises treatment with an aqueous solution containing an alkali metal sulphite and a water soluble quaternary nitrogen compound.

The quaternary nitrogen compound should have a relatively strong conjugate base so that, at the pH prevailing in a fixing solution, in the region of 8, it is protonated and cationic. One suitable compound is ethylenediammonium sulphate



We have found that particularly in sodium and potassium sulphite fixing solutions incorporating these quaternary ammonium compounds the fixing rate is surprisingly enhanced.

The following example illustrates the present invention and the accompanying drawing is a graph of residual silver against fixing time.

EXAMPLE 1

A coloured paper coated with silver was produced from silver chloride. The following are the silver coating weights: 0.1076 mg/dm² the red and green sensitive layers and 0.4306 mg/dm² in the blue sensitive layer layer, giving a total silver laydown of 0.6459 mg/dm².

Sample strips of this coated paper were swollen in a 25g/l potassium carbonate buffer pH 10.1 to simulate a developer. The strips were then plunged into a fixing solution in accordance with the invention (25 °C) and processed for varying times. The strips were then washed for 2 minutes in water and treated with a 5g/l sodium sulphide solution to reveal any residual silver chloride as silver sulphide. The strips were then washed for a further 2 minutes, then hung up to dry. The blue reflection density of each strip was measured. It was found that the maximum density for the unfixed sample was 0.30 and for a totally fixed sample, 0.05. Atomic adsorption measurements of the silver showed that there was a good linear correlation between blue reflection density and residual silver. From the density measurements, it was therefore possible to estimate the residual silver in the paper.

Three fixing solutions were made up and the pH of all of them was adjusted to 8.0 ± 0.1, see the table below. The results are shown in the drawing. The gradient of the best fit straight line through the experimental points is taken as a measure of the relative fixing rate of the materials and is included in the table below.

Component	Fix 1	Fix 2	Fix 3
Sodium sulphite	20g/1	0g/1	20g/1
Ethylene diammonium sulphate	0g/1	25g/1	25g/1
Relative fixing rate	.096	.014	.352

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10 It can be seen that the fixing rate by the solution containing the quaternary salt and the sulphite (Fix 3) is three times greater than the sum of the two rates in the fixer containing the separate components, indicating that the two are working synergistically.

The fixing action of the ethylenediammonium sulphate is probably by the free base ethylenediamine which is present at small concentrations at pH8.0.

15 A Similar experiment was carried out with n-methyl pyridinium chloride. This substance has no fixing action in itself. A 20g/1 sulphate fixing solution containing 5g/1 of this salt had a relative fixing rate of 0.27 calculated on a similar basis to the above.

The fixing method and solution as described are useful with photographic silver halide elements known in the photographic art. A description of illustrative examples of such photographic materials is found in, for instance, Research Disclosure, Item No. 17,463 Vol. 176, pages 22 - 31 (December 1978).

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Claims

25 1. A fixing method of removing silver halide from a photographic material during processing such method comprising treatment with an aqueous solution containing an alkali metal sulphite characterised in that the solution also contains a water soluble quaternary nitrogen compound.

2. A method as claimed in Claim 1 wherein the silver halide is silver chloride.

3. A method as claimed in either Claim 1 or Claim 2 wherein the quaternary compound has a strong conjugate base.

30 4. A method as claimed in either Claim 1 or Claim 2 wherein the quaternary compound is ethylenediammonium sulphate.

5. A photographic element fixed by treatment with an aqueous solution containing an alkali metal sulphite and a water soluble quaternary nitrogen compound.

35 6. A fixing solution comprising an alkali metal sulphite characterised by the presence of a water soluble quaternary nitrogen compound.

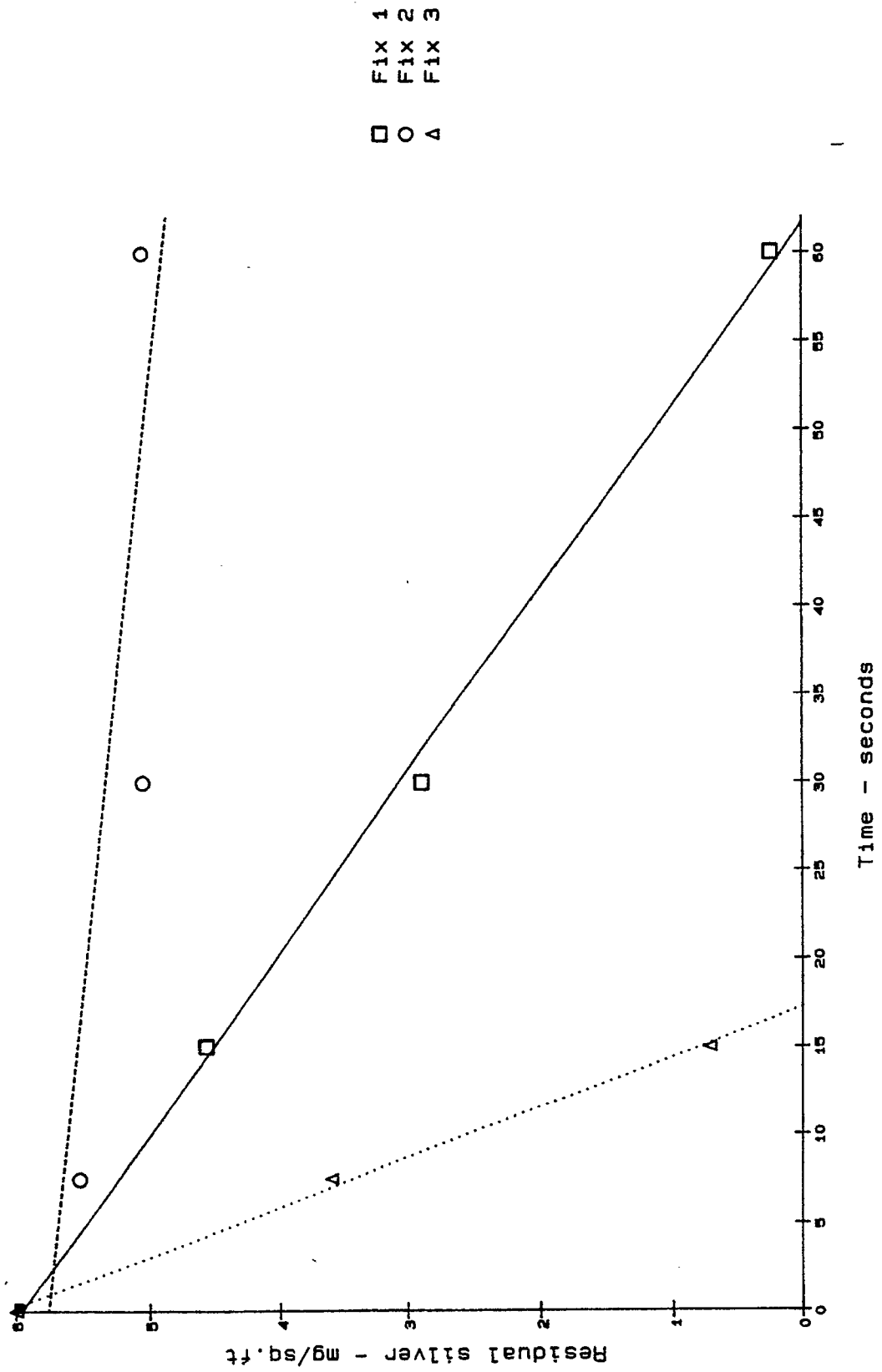
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Figure 1. Fixing in Sulphite Fixers





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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 6895

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	G.HAIST: "MODERN PHOTOGRAPHIC PROCESSING Volume 1" 1979, JOHN WILEY AND SONS, NEW YORK * page 598, line 12 - page 599, line 13 * ---	1-6	G03C5/38
Y	R.S.SCHULTZE: "SCIENCE AND APPLICATIONS OF PHOTOGRAPHY" 1955, ROYAL PHOTOGRAPHIC SOCIETY OF GB, LONDON "Acceleration of the fixing process by active cations" pp177-180. *Page 177 and Page 178* ---	1-6	
X	US-A-2515122 (GENERAL ANILINE AND FILM CORPORATION) * claim 1 * ---	1	
X	US-A-2174494 (AMERICAN CYANAMID CO.) * column 2, lines 46 - 57 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05 OCTOBER 1990	Examiner BOLGER W.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons ----- & : member of the same patent family, corresponding document			