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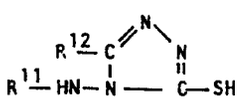
(54) **Process for the production of silver images including a stabilisation-fixing treatment.**

(57) A process for the production of a silver image including a stabilisation-fixing treatment of said image formed by development of an imagewise exposed photographic silver halide emulsion material, wherein the imagewise exposed and developed silver halide emulsion material is treated with an aqueous solution containing an alkali metal thiosulphate and a mercapto-triazole compound corresponding to the following general formula (A):



(A)

wherein:

$R^{11}$ represents hydrogen or $-CO-R^{33}$, wherein $R^{33}$ is $C_1$-$C_2$ alkyl, and

$R^{12}$ represents hydrogen, $C_1$-$C_2$ alkyl or amino.

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# Process for the production of silver images including a stabilisation-fixing treatment

The present invention relates to a process for the production of silver images including a stabilisation-fixing treatment.

Stabilising baths for exposed and developed photographic silver halide emulsion layers which contain a large variety of organic mercapto compounds are state of the art and particulars concerning such baths are described in, e.g. the book "Modern Photographic Processing" Vol. 2 of Grant Haist - A Wiley Interscience Publication - (1979) New York - p. 210-227.

An effective stabilising agent showing no unwanted side effects should meet some demands which are i.a. :

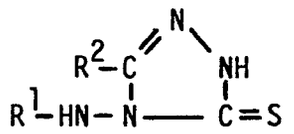
1. to be stable in alkaline and/or acid processing conditions,
2. to be odourless, non-toxic, non-deliquescent and non-corrosive,
3. to react rapidly with silver ions without changing the binding properties of the gelatin in the emulsion layer,
4. to form a colourless compound with silver ions, preferably a colourless transparent compound when treating silver halide on a transparent support,
5. to form a compound with silver ions that is resistant to change, especially in hot, humid conditions and under light-exposure, and
6. to reduce as less as possible the optical density of the photographic silver image.

No compound, unfortunately has yet satisfied all these requirements and thus a constant search for new stabilising agents or advantageous new combinations of already known stabilising agents is still going on.

The fundamental difference between a conventional fixing agent and stabilising agent is that whereas the former removes the residual silver halide completely from the photographic material by dissolution in complexed form and diffusion, the latter transforms a considerable part of undeveloped silver halide into a non-light sensitive substance that remains in the photographic material.

It follows from the above that the only distinction between the agents in question is that the stabilising agent forms an insoluble non-lightsensitive silver compound while the fixing agent forms a soluble silver complex. However, the solubility of said compounds in a given medium varies with the pH-value of the medium. Thus one compound may be effective as stabilising agent as well as a fixing agent; it depends inter alia on the pH-value of the processing bath.

From the published JP-applic. 58-122535 it is known to prevent the lowering of the fixation speed even after processing of a good deal of developed film by the use of ammonium thiosulphate as fixing agent in conjunction with an organic mercapto compound corresponding to the following general formula :

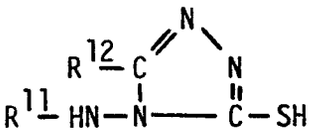


wherein :
$R^1$ is H, -CO-$R^3$, $R^3$ being lower alkyl, and
$R^2$ is H, lower alkyl or amino.

It is one of the objects of the present invention to provide a process for the production of silver images including a stabilisation-fixing treatment yielding particularly stable images under conditions of heat, high relative humidity and light exposure.

Other objects and advantages of the present invention will appear from the further description.

In accordance with the present invention a process for the production of a silver image including a stabilisation-fixing treatment of said image formed by development of an imagewise exposed photographic silver halide emulsion material is provided, wherein the imagewise exposed and developed silver halide emulsion material is treated with an aqueous solution containing an alkali metal thiosulphate and a mercapto-triazole compound corresponding to the following general formula (A) :



(A)

wherein :
$R^{11}$ represents hydrogen or -CO-$R^{33}$, wherein $R^{33}$ is $C_1$-$C_2$ alkyl, and
$R^{12}$ represents hydrogen, $C_1$-$C_2$ alkyl or amino.

Representatives of said mercapto-triazole compounds are disclosed in thione form in said already mentioned published JP-application.

The procedure for preparing said mercapto-triazole compounds is known to those skilled in the art.

More particularly, for the preparation of 3-mercapto-4-amino-1,2,4-triazole and 3-mercapto-4-amino-5-methyl-1,2,4-triazole reference is made to Ann. Chem. 637, (1960) 140-141. For the preparation of 4,5-diamino-3-mercapto-1,2,4-triazole reference is made to J. Chem. Soc., (1952), 4817.

Acyl derivatives within the scope of the above general formula can be prepared by known acylation procedures.

In the preparation of the aqueous treating liquids used according to the present invention the specified mercapto compounds are simply dissolved in water together with the other ingredients.

According to a preferred embodiment the pH of the treating liquid is in the acidic range, e.g. in the range of 6 to 4. Small amounts of water-soluble solvents, e.g. acetic acid and water-miscible alcohols may be added to improve the dissolution of the mercapto-compound.

According to a preferred embodiment the treating liquids used according to the present invention contain an anti-oxidizing agent to shield the mercapto-triazole compound from aerial oxidation. Suitable anti-oxidizing agents are ascorbic acid and compounds yielding sulphite ions, e.g. sodium sulphite and potassium metabisulphite.

The present image-stabilising process makes it possible to eliminate the customary washing procedure and yet to obtain a satisfactory stable print.

The treatment of the developed silver image with the above aqueous solution containing an alkali metal thiosulphate and a mercapto-triazole compound corresponding to the general formula (A) may be preceded by a rinsing treatment but such is not strictly necessary.

The image-stabilising liquids used according to the present invention do not alter the binding properties of gelatin, so that no sticky gelatin silver halide emulsion layers are obtained as is the case when using stabilising liquids based on thiocyanates. Further no particular odour is produced and toxicity and corrosivity are very low.

The fixing-stabilisation treatment according to the present invention is particularly effective for the stabilisation of silver images obtained by means of silver halide emulsion layers wherein the silver halide is for at least 50 mole % silver chloride. The present fixing-stabilisation processing is very effective when used in conjunction with silver halide emulsion layers

having a silver halide coverage, the silver halide being expressed in an equivalent amount of silver nitrate, not higher than 4 g per sq.m.

The treatment according to the present invention provides image stabilisation in a short time. Fixing-stabilisation treatment according to the present invention may be terminated in 30 s at room temperature (20°C) and may be terminated in 15 s at 35 °C.

The fixing-stabilisation treatment can be used for photographic black-and-white papers and films, e.g. graphic art film materials, but is likewise applicable for the image stabilisation of photographic colour materials wherein residual silver halide may not remain.

The photographic materials may contain already before the exposure some or all of the developing agent(s) used in the development step. When the developing agents are present already in the photographic material during the exposure the development may be carried out with a so-called activator bath which is an alkaline aqueous liquid being free from developing agents and activates these agents already present in the photographic material.

The silver images stabilised according to the present invention show a very low darkening in the non-image area under circumstances of heat, humidity and/or light-exposure. Such is demonstrated furtheron in comparative tests including the use of stabilising liquids comprising ammonium thiosulphate.

Very advantageous results are obtained with a fixing-stabilising liquid wherein the above defined mercapto-compound is present in a concentration of $1x10^{-4}$ mole to $1x10^{-1}$ mole per liter in conjunction with the alkali metal thiosulphate in a concentration of 0.1 mole to 1.5 mole per liter.

Further it has been established experimentally that the exhaustion of alkali metal thiosulphate fixing agent in a common fixing bath, e.g. containing 0.1 mole to 1.5 mole per liter of sodium thiosulphate, is counteracted by using therein said mercapto-triazole, e.g. in a concentration up to $1x10^{-1}$ mole per liter. It has been found advantageous to include a washing step to have the still residual amounts of thiosulphate and of complexed silver halide eliminated.

According to a particular embodiment the washing liquid likewise incoporates the mercapto-triazole compound, e.g. in an amount up to $1x10^{-1}$ mole per liter.

The application of the treating liquids used in the processing of photographic silver halide emulsion materials may proceed by immersion but more advantageously proceeds by meniscus coating using a lick-roller, sponge

or resilient roller to limit the volume of applied liquid .

In the processing of an image-wise exposed silver halide emulsion material according to the present invention it is in favour of effective stabilisation to keep the pH of the liquid(s) containing said mercapto-triazole compound in the acidic range and therefore to eliminate as much as possible of the alkaline developing or development activating liquid from the material before applying the stabilising liquid. Such may proceed by squeegee, e.g. with rollers or by applying an intermediate rinsing step.

The following comparative example illustrates the present invention without, however, limiting it thereto.

Example

A photographic material having on a paper base a black-and-white gelatin-silver halide emulsion layer the silver halide of which contains 97.6 mole % of chloride, 2 mole % of bromide and 0.4 % of iodide at a coverage equivalent to 2.7 g of $AgNO_3/m^2$ and having a gelatin to $AgNO_3$ ratio of 0.56 and containing in a layer subjacent to the silver halide emulsion layer and in a top layer thereto a total amount of 0.71 $g/m^2$ of hydroquinone and 0.16 $g/m^2$ of 1-phenyl-3-pyrazolidinone was prepared.

Said photographic material was treated in unexposed state for 10 s at 20°C with an alkaline aqueous activator liquid having the following composition :

| | |
|---|---|
| sodium hydroxide | 0.75 mole |
| sodium sulphite | 0.40 mole |
| potassium bromide | 0.017 mole |
| ethylen diamine tetra-acetic acid sodium salt | 1.5 g |
| water up to | 1000 ml |
| | pH : 13.5 |

The developed material was led between squeegee rollers to remove the major part of adhering alkaline liquid and was then dipped for 5 s at 20 °C into a fixing or stabilising-fixing liquid as defined in the following Table.

Liquid no. 1 contained per liter 198.5 g (0.8 mole) of sodium thiosulphate.5 water and 10 g of sodium sulphite.

Liquid no. 2 had the same composition as liquid no. 1 but included in addition thereto per liter 1 g of 3-mercapto-4-amino-1,2,4-triazole.

Liquid no. 3 had the same composition as liquid no. 1 but included per liter 3 g of 3-mercapto-4-amino-5-methyl-1,2,4-triazole.

Liquid no. 4 contained per liter 118.5 g (0.8 mole) of ammonium

thiosulphate and 10 g of sodium sulphite.

Liquid no. 5 had the same composition as liquid no. 4 but included in addition thereto per liter 1 g of 3-mercapto-4-amino-1,2,4-triazole.

Where indicated in the following Table the fixing-stabilisation was followed by rinsing. This rinsing was effected by conveying the material for 10 s at 20 °C through a tray containing plain water.

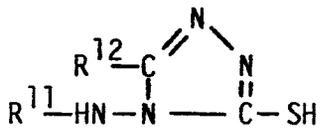
The efficiency of the stabilisation was determined by measuring the change in optical density ( $\Delta$ D) obtained after keeping one strip (i) of the processed material for 3 days in the dark at 35 °C at 80 % relative humidity and another strip (ii) for 4 h in a XENOTEST (trade name) exposure apparatus wherein the strip was subjected to a white light illumination of 180,000 lux.

Table

| Test No. | Liquid No. | Rinsing | $\Delta$ D (i) | $\Delta$ D (ii) |
|---|---|---|---|---|
| 1 | 1 | no | 0.14 | 0.05 |
| 2 | 2 | no | 0.02 | 0.03 |
| 3 | 2 | yes | 0.04 | 0.00 |
| 4 | 3 | no | 0.02 | 0.02 |
| 5 | 3 | yes | 0.03 | 0.01 |
| 6 | 4 | no | 0.64 | 0.08 |
| 7 | 4 | yes | 0.26 | 0.07 |
| 8 | 5 | no | 0.66 | 0.08 |
| 9 | 5 | yes | 0.28 | 0.07 |

Claims

1. A process for the production of a silver image including a stabilisation-fixing treatment of said image formed by development of an imagewise exposed photographic silver halide emulsion material, wherein the imagewise exposed and developed silver halide emulsion material is treated with an aqueous solution containing an alkali metal thiosulphate and a mercapto-triazole compound corresponding to the following general formula (A) :



(A)

wherein :
$R^{11}$ represents hydrogen or -CO-$R^{33}$, wherein $R^{33}$ is $C_1$-$C_2$ alkyl, and
$R^{12}$ represents hydrogen, $C_1$-$C_2$ alkyl or amino.

2. Process according to claim 1, wherein the mercapto-triazole is 3-mercapto-4-amino-1,2,4-triazole, 3-mercapto-4-amino-5-methyl-1,2,4-triazole or 4,5-diamino-3-mercapto-1,2,4-triazole.

3. Process according to claim 1 or 2, wherein the alkali metal thiosulphate is sodium thiosulphate.

4. Process according to any of claims 1 to 3, wherein said solution contains said mercapto-compound in a concentration of $1x10^{-4}$ mole to $1x10^{-1}$ mole per liter in the presence of the alkali metal thiosulphate in a concentration of 0.1. mole to 1.5 mole per liter.

5. Process according to any of claims 1 to 3, wherein said treatment is followed by a rinsing treatment with water.

6. Process according to claim 5, wherein said water contains said mercapto-triazole in dissolved state in an amount up to $1x10^{-1}$ mole per liter.

7. Process according to any of claims 1 to 6, wherein said solution has a pH in the range of 6 to 4.

8. Process according to any of claims 1 to 7, wherein said solution contains an anti-oxidizing agent.

9. Process according to claim 8, wherein said anti-oxidizing agent is ascorbic acid or a compound yielding sulphite ions.

10. Process according to any of the preceding claims, wherein the silver halide of said silver halide emulsion material contains at least 50 mole % of silver chloride.

11. Process according to any of the preceding claims, wherein the silver halide emulsion material contains an amount of silver halide expressed in an equivalent amount of silver nitrate not higher than 4 g per sq.m.

European Patent Office

# EUROPEAN SEARCH REPORT

0189603
Application number

EP 85 20 0095

## 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.4) |
|---|---|---|---|
| D,Y | PATENTS ABSTRACTS OF JAPAN, vol. 7, no. 234 (P-230) [1379], 18th October 1983; & JP - A - 58 122 535 (MITSUBISHI SEISHI K.K.) 21-07-1983 | 1-7,10 ,11 | G 03 C 5/39 |
| Y | US-A-3 854 947 (E.R. RITCHEY) * Claim 1 * | 3 | |
| Y | GB-A-1 285 696 (KODAK) * Claims * | 8,9 | |

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

G 03 C

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 02-10-1985 | PHILOSOPH L.P. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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