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

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PATENTS ABSTRACTS OF JAPAN, vol. 9, no. 68 (P-344)1791r, 28 March 1985; & JP - A - 59 201 056 (KONISHIROKU SHASHIN KOGYO K.K.) 14-11-1984

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Description

The present invention relates to a process for the production of a silver image including a stabilisation-fixing treatment of an image-wise exposed and developed photographic silver halide emulsion material to obtain an image having improved heat and/or light stability.

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, e.g. in 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.

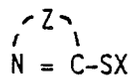
The fundamental difference between conventional and stabilising processing is that whereas in the former care is taken to remove the residual silver halide completely from the photographic material by dissolution in complexed form and diffusion, in the latter a considerable part of undeveloped silver halide is transformed 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 inter alia with the pH-value of the medium. Thus one compound may be effective as stabilising agent as well as a fixing agent depending on the pH-value of the processing bath.

According to the published JP-application 58—114035 fixation and stabilisation are carried out in subsequent steps, the processing of imagewise exposed black-and-white silver emulsion materials comprising the steps of:

(1) developing, optionally by alkali activated treatment,
(2) fixing, and
(3) image-stabilising treatment.

In the image-stabilising treatment a solution is used containing at least one compound (A) and (B). Compound (A) is an iodide of alkali metals and ammonium. Compound (B) corresponds to the following general formula:

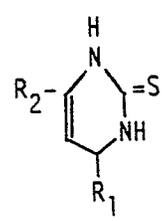


wherein:

X represents hydrogen, alkali metal, ammonium or organic amine, and

Z represents the non-metallic atoms necessary to form a 5- or 6-membered heterocyclic nucleus.

In FR—A—2 075 615 (claim 5) the stabilisation of photographic silver images has been described using compounds corresponding to the following general formula:

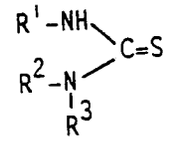


wherein:

R_1 represents an oxygen or sulphur atom,

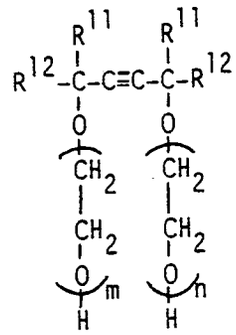
R_2 represents a C_1—C_6 alkyl group, preferably a C_1—C_3 alkyl group or carboxyl group.

According to JP—A—58 122 536 fixation speed of a silver halide photosensitive material is enhanced by a fixation solution containing $(NH_4)_2S_2O_3$ as principal agent and a compound according to one of the following general formulae:



(I)

or



(II)

wherein R^1, R^2 are each H, amino, lower alkyl, hydroxyalkyl or aryl, or each may combine to form a hetero ring;

R^3 is H, lower alkyl, hydroxyalkyl, or aryl when R^1 and R^2 do not form said ring, and when they do, it is H, amino, acylamino, lower alkyl, or hydroxyalkyl;

R^{11} and R^{12} are each alkyl, and

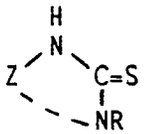
m and n are each 0 or 1.

As examples of cyclic thiourea compounds according to said general formula (I) ethylene thiourea and ethylene thiourea having a HO—CH_2—CH_2— substituent on its nitrogen atom have been given.

It is an object of the present invention to provide a stabilising-fixing treatment of exposed and developed photographic silver halide emulsion materials 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 stabilising-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 thiosulphate ions and a cyclic thiourea compound corresponding to the following general formula (X) or a corresponding tautomeric structure thereof:

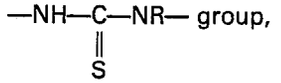


(X)

wherein:

R represents hydrogen, an unsubstituted hydrocarbon group, e.g. an alkyl, alkenyl, aryl or aralkyl group or a —CH_2—CH_2—OH group, and

Z represents a bivalent saturated hydrocarbon group including said group in substituted form forming a 5- or 6-membered heterocyclic ring with the



group,

characterized in that the thiosulphate ions stem from an alkali metal thiosulphate and no ammonium ions are present.

The following Table 1 contains a list of specific compounds within the scope of the above general formula (X) with a literature reference for their preparation.

Table 1

Compound No.	R	Z	Reference
1	H	$-CH_2-CH_2-$	US-P 3,801,330
2	H	$-CH(CH_3)-CH_2-CH_2-$	id.
3	$-CH_2-CH_2-OH$	$-CH_2-CH_2-$	id.
4	$-CH_2-CH=CH_2$	$-CH_2-CH_2-$	id.
5	$-C_6H_5$	$-CH_2-CH_2-$	id.
6	H	$-CH_2-CH_2-CH_2-$	id.
7	H	$-CH_2-CHOH-CH_2-$	GB-P 931,560
8	H	$-CH_2-CH_2-C(H_3C)(OH)-$	DE-AS 1,065,849
9	H	$-CH(C_6H_5)-CH_2-C(CH_3)(OH)-$	id.

In the preparation of a treating liquid used according to the present invention the specified heterocyclic 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 cyclic thiourea compound.

According to a preferred embodiment the treating liquids used according to the present invention contain an anti-oxidizing agent to shield the cyclic thiourea compound from aerial oxidation. Suitable anti-oxidizing agents are ascorbic acid and compounds yielding sulphite ions such as 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 alkali metal thiosulphate ions and the cyclic thiourea compound corresponding to the general formula (X) 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 stabilising-fixing 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 stabilising-fixing treatment 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. Stabilising 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 stabilising-fixing 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.

Very advantageous results are obtained with a fixing-stabilising liquid wherein the above defined cyclic thiourea compound is present in a concentration of 1×10^{-4} mole to 1×10^{-1} mole per liter in conjunction with an alkali metal, e.g. sodium thiosulphate, in a concentration of 0.1 mole to 1.5 mole per liter.

It has been found advantageous to include a washing step to have still residual amounts of thiosulphate and complexed silver halide eliminated.

According to a particular embodiment the washing liquid likewise incorporates a said cyclic thiourea compound, e.g. in an amount up to 1×10^{-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 cyclic thiourea 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 example illustrates the present invention without, however, limiting it thereto.

Example 1

A photographic material having on a paper base a black-and-white gelatine-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 of 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 2.

Liquid no. 1 contained per liter 198.5 g (0.80 mole) of sodium thiosulphate.5 water and 25 g of potassium metabisulphite.

Liquid no. 2 had the same composition as liquid no. 1 but included in addition thereto per liter 10 g of 2-thio-hexahydropyrimidone-2.

Where indicated in Table 2 the fixing-stabilisation was followed by rinsing. The rinsing was effected by conveying the material for 10 s at 20°C through a tray containing plain water.

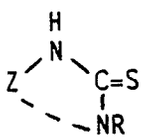
The efficiency of the stabilisation was determined by measuring the change in optical density (ΔD) obtained after keeping one strip (i) of the processed material for 3 days in the dark at 35°C at 80% relative humidity and another strip (ii) for 4 h in a XENOTEST (trade name) exposure apparatus wherein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

Table 2

Test No.	Liquid No.	Rinsing	ΔD (i)	ΔD (ii)
1	1	no	0.14	0.05
2	2	no	0.02	0.04
3	1	yes	0.08	0.01
4	2	yes	0.00	0.00

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 thiosulphate ions and a cyclic thiourea compound corresponding to the following general formula (X) or a corresponding tautomeric structure thereof:

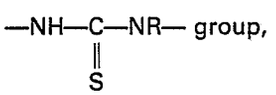


(X)

wherein:

R represents hydrogen, an unsubstituted hydrocarbon group or a $—CH_2—CH_2OH$ group, and

Z represents a bivalent saturated hydrocarbon group, including said group in substituted form, forming a 5- or 6-membered heterocyclic ring with the



group,

characterized in that the thiosulphate ions stem from an alkali metal thiosulphate and no ammonium ions are present.

2. Process according to claim 1, wherein Z is $—CH_2—CH_2—CH_2—$.

3. Process according to claim 1 or 2, wherein the cyclic thiourea compound is 2-thio-hexahydro-pyrimidone-2.

4. Process according to any of claims 1 to 3, wherein the alkali metal thiosulphate is sodium thiosulphate.

5. Process according to any of claims 1 to 4, wherein said solution contains said cyclic thiourea compound in a concentration of 1×10^{-4} mole to 1×10^{-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.

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

7. Process according to claim 6, wherein said water contains said mercapto-triazole in dissolved state in an amount up to 1×10^{-1} mole per liter.

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

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

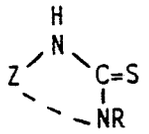
10. Process according to any of the preceding claims, wherein the silver halide of said silver halide emulsion material contains at least 50 mole% of silver chloride.

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.

Patentansprüche

1. Verfahren zur Herstellung eines Silberbildes, das eine Stabilisier-Fixierbehandlung des erzeugten Bildes durch Entwicklung eines bildmäßig belichteten photographischen Silberhalogenidemulsions-

materials umfaßt, wobei das bildmäßig belichtete photographische Silberhalogenidemulsionsmaterial behandelt wird mit einer wäßrigen Lösung, welche Thiosulfat-Ionen und eine cyclische Thioharnstoffverbindung der folgenden allgemeinen Formel (X) oder einer übereinstimmenden tautomeren Struktur davon enthält:



(X)

in der bedeuten:

R Wasserstoff, eine unsubstituierte Kohlenwasserstoffgruppe oder eine —CH_2—CH_2OH Gruppe, und

Z eine zweiwertige gesättigte Kohlenwasserstoffgruppe einschließlich einer solchen Gruppe in substituierter Form, die mit der —NH—CS—NR— Gruppe einen 5- oder 6-gliedrigen heterocyclischen Ring bildet,

dadurch gekennzeichnet, daß die Thiosulfat-Ionen von einem Alkalimetallthiosulfat stammen und keine Ammonium-Ionen anwesend sind.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Z —CH_2—CH_2—CH_2— ist.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die cyclische Thioharnstoffverbindung 2-Thiohexahydropyrimidon-2 ist.

4. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Alkalimetallthiosulfat Natriumthiosulfat ist.

5. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Lösung die cyclische Thioharnstoffverbindung in einer Konzentration von 1×10^{-4} Mol bis 1×10^{-1} Mol pro Liter in Anwesenheit des Alkalimetallthiosulfats in einer Konzentration von 0,1 Mol bis 1,5 Mol pro Liter enthält.

6. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Behandlung durch eine Spülbehandlung mit Wasser gefolgt wird.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Wasser das Mercaptotriazol in gelöstem Zustand in einer Menge bis 1×10^{-1} Mol pro Liter enthält.

8. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Lösung einen pH-Wert im Bereich 6—4 hat.

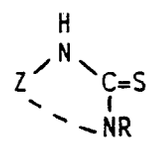
9. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Lösung ein Oxidationsschutzmittel enthält.

10. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Silberhalogenid des Silberhalogenidemulsionsmaterials mindestens 50 Mol-% Silberchlorid enthält.

11. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Silberhalogenidemulsionsmaterial eine Menge Silberhalogenid enthält, welche, ausgedrückt in äquivalentem Silbernitrat, nicht größer ist als 4 g pro m^2.

Revendications

1. Procédé pour la formation d'une image argentique, ce procédé comprenant un traitement de stabilisation-fixage de cette image formée par développement d'un matériau d'émulsion photographique à l'halogénure d'argent exposé sous forme d'une image, procédé dans lequel ce matériau exposé et développé sous forme d'une image est traité avec une solution aqueuse contenant des ions thiosulfate et un composé de thiourée cyclique répondant à la formule générale (X) ci-après ou une structure tautomère correspondante de ce composé:

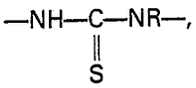


(X)

où

R représente un atome d'hydrogène, un groupe d'hydrocarbure non substitué ou un groupe —CH_2—CH_2OH, et

Z représente un groupe d'hydrocarbure saturé bivalent, y compris ce même groupe sous forme substituée, formant un noyau hétérocyclique pentagonal ou hexagonal avec le groupe



caractérisé en ce que les ions thiosulfate proviennent d'un thiosulfate d'un métal alcalin, tandis qu'il n'y a pas d'ions ammonium.

2. Procédé selon la revendication 1, caractérisé en ce que Z représente $—CH_2—CH_2—CH_2—$.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le composé de thiourée cyclique est la 2-thio-hexahydro-pyrimidone-2.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le thiosulfate d'un métal alcalin est le thiosulfate de sodium.

5. Procédé suivant l'une quelconque des revendications 1 à 4, caractérisé en ce que la solution précitée contient le composé de thiourée cyclique en une concentration de 1×10^{-4} mole à 1×10^{-1} mole par litre en présence du thiosulfate d'un métal alcalin en une concentration de 0,1 mole à 1,5 mole par litre.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que le traitement est suivi d'un traitement de rinçage avec de l'eau.

7. Procédé selon la revendication 6, caractérisé en ce que l'eau contient le mercapto-triazole à l'état dissous en une quantité allant jusqu'à 1×10^{-1} mole par litre.

8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que la solution a un pH se situant dans l'intervalle allant de 6 à 4.

9. Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que la solution contient un agent antioxydant.

10. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'halogénure d'argent du matériau d'émulsion à l'halogénure d'argent contient au moins 50% molaires de chlorure d'argent.

11. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le matériau d'émulsion à l'halogénure d'argent contient 4 g/m^2 maximum d'halogénure d'argent, exprimé en une quantité équivalente de nitrate d'argent.