

United States Patent

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[54] DEVELOPER MONOBATH FREE FROM
FORMATION OF COLORED SLUDGE

[75] Inventors: Noboru Itoh; Senji Tosa; Hirokazu
Tsukahara; Norio Kobayashi, all of
Kyoto, Japan

[73] Assignee: Mitsubishi Paper Mills, Ltd., Tokyo,
Japan

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96/66.5, 52, 66.3

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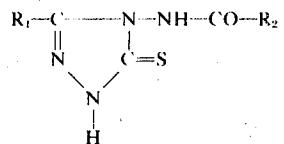
Primary Examiner—Norman G. Torchin

Assistant Examiner—M. F. Kelley

Attorney—Cushman, Darby & Cushman

[57] ABSTRACT

Colored sludge due to silver colloids is prevented by adding at least one of 3-substituted derivatives of 4-acylamido-1,2,4-triazoline-5-thione represented by the general formula:



wherein R₁ and R₂ are selected from lower alkyl, aryl and aralkyl groups having seven or less carbon atoms, to a developer containing a silver complex-forming agent such as thiosulfates, thiocyanates and alkanolamines, and such a preventive state can be maintained for a prolonged period of time.

1 Claim, No Drawings

DEVELOPER MONOBATH FREE FROM FORMATION OF COLORED SLUDGE

This invention relates to a developer capable of preventing formation of colored sludge, which has been often a great trouble for photographic treatment with the so-called monobath developing-fixing agent containing thiosulfates as a fixing agent and a liquid developer containing a water-soluble, silver complex-forming agent.

It has been well known since the early days in the history of the photography to add such a water-soluble, silver complex-forming agent as sodium thiosulfate, ammonium thiosulfate, potassium thiocyanate, ammonium thiocyanate, ammonia, ethanolamine, etc., which have been widely used as a fixing agent to a liquid developer and use the resulting monobath developing-fixing agent, which is capable of carrying out the development and fixing at the same time, in a treatment of a photographic emulsion. Recently, the mono-bath developing-fixing agent has been applied not only to the development of films for the general pictures, but also to the development of microfilms or to a rapid treatment for regenerating a print from the developed negative, that is, a printing of necessary portions of investigating the negative on a reader printer. As compared with the heretofore widely used two-bath type developing and fixing treatment, the mono-bath treatment is particularly effective, because it is quite enough to use only a single bath. Further, in the conventional two-bath type reader printer consisting of an activator bath and a stabilization bath, these two baths are mixed together, where not only brown contamination is brought about, but also it is inconvenient to exchange the solution. Usually, the stabilization bath is strongly acidic and a thiocyanate is used in the stabilization bath. Therefore, the metallic parts of an apparatus is liable to be corroded. Furthermore, the finished print is often liable to be faded. These are the disadvantages of the two-bath type, developing and fixing treatment. On the other hand, in the mono-bath developing-fixing agent, these disadvantages are almost eliminated and thus the mono-bath deems to be very advantageous.

However, the mono-bath developing-fixing treatment has also disadvantages. The greatest disadvantage is a formation of a large amount of colored sludges during continuous photographic treatment. Such formation not only makes the solution dirty, but also the colored sludges stick to surfaces of prints and films and makes the surfaces dirty. Therefore, the solution must be often exchanged or filtered. The colored sludge is formed according to the following manner: silver halide in a film or photographic paper to be treated is dissolved and entered into a developer solution by action of a silver complex-forming agent contained in the solution, and the silver halide is reduced to silver colloid by the developer. The silver colloid is formed in the solution. A portion thereof is coagulated and settled, but the most portion thereof is suspended in the solution in a form of blackish brown, dirty sludge floc. The formation of such colored sludge can be retarded by lowering a temperature of the developer solution, but in that case the developing as well as fixing speed is also retarded. Thus, it is not practical to lower the temperature.

Accordingly, various methods have been heretofore attempted to control the colored sludge in the mono-

bath developing-fixing agent. For example, there has been proposed a method for preventing coloring of the solution by adding colloidal silver, which is known as "Carcy Lee silver," etc., to the agent in advance to rapidly coagulate colored sludge and thereby form coarse coagulates and allow them to settle down on the bottom of the vat.

However, the proposed method is not directed to the prevention of formation of the sludge itself, and thus 10 sludge is successively formed and a satisfactory effect cannot be attained. When a vigorous stirring is effected of filtration of the solution is not carried out, the sludge is liable to stick to the surface of the print and the stuck sludge is hard to remove. In the proposed 15 method such new disadvantages are encountered. Therefore, it is necessary to prevent formation itself of the sludge to avoid the serious influences by the colored sludge.

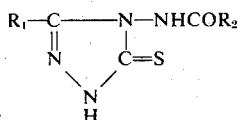
Heretofore, a few mercapto compounds having a hetero ring such as 1-phenyl-5-mercaptopentrazol, 2-thiazoline-4-carboxylic acid, etc. have been disclosed as being capable of preventing the formation of such colored sludge, but according to the experiments made by the present inventors, it has been found that most of 20 these compounds can indeed retard the formation speed of the colored sludge to some extent, but a large amount of sludge, which is equal to that of the sludge formed when no sludge formation retardant is added, is formed when the solution is left standing for 1 to 2 days after the developing treatment. In a treatment of 25 negative films, where a developing solution, which has been subjected to filtration before it is used, is employed, such is no more problem. However, in most cases the developing solution is usually used without any filtration for a continuation of over a few days to 30 prepare small number of prints a day, though there are a few cases that the solution is used continuously as in the case of the monobath developing-fixing solution for reader printer. To prevent the colored sludge from 35 sticking to the apparatus, a possible duration of the well-known art is only few days and thus has no significance almost at all.

According to the well known art, an action enough 40 to prevent the formation of colored sludge is attained 45 by adding an increased amount of the additive to the solution, but in that case the developing speed is extremely retarded with no exception, and the desirable density of developed silver is not obtained. For example, when 2.0 g of 1-phenyl-5-mercaptopentrazol is 50 added to 1/1 of the solution, the action to prevent the formation of colored sludge can be maintained for about a few days, but the maximum density of developed silver is extremely lowered, for example, the optical density 1.3 at the non-addition of the additive falls 55 down to 0.6. Thus, the solution becomes unpractical.

An object of the present invention is to provide a developer containing an additive capable of preventing a formation of colored sludge due to silver colloid and 60 keeping such preventive state for a prolonged period of time without changing a developability almost at all in a developer solution containing such a silver complex-forming agent as thiosulfates, thiocyanates, alkanolamine, etc.

As a result of various studies and researches on the 65 disadvantages of the prior art for a long period of time, the present inventors have found that, among many mercapto compounds other than the well known ones,

compounds of 4-acylamido-1,2,4-triazoline-5-thione series can prevent formation of silver colloid without giving any influence to the developability and can maintain its preventive action for a prolonged period of time, even if the number of films or prints to be treated is increased or the solution is used after some day, and have accomplished the present invention. The present additive is a 3-alkyl or 3-aryl or 3-aralkyl derivative of 4-acylamido-1,2,4-triazoline-5-thiones having the following general structure.



wherein R_1 and R_2 are selected from lower alkyl, aryl and aralkyl groups having 7 or less carbon atoms.

The present compounds have already separately applied for a patent by the present inventors as a toner or a silver image and a developing accelerator for silver complex salt diffusion transfer, but the effectiveness of these compounds as an inhibitor for formation of colored sludge in the monobath developer solution was clarified by the successive studies, and in this respect the present invention has a great significance.

Particularly effective among these compounds are 4-acetoamido-3-heptyl-1,2,4-triazoline-5-thione, 4- propionamido-3-pentyl-1,2,4-triazoline-5-thione, 4- benzamido-3-phenyl-1,2,4-triazoline-5-thione, 4- benzamido-3-pentyl-1,2,4-triazoline-5-thione, 4- phenylacetamido-3-heptyl-1,2,4-triazoline-5-thione, 4-phenylacetamido-3-butyl-1,2,4-triazoline-5-thione, etc.

The amount of the present inhibitor for formation of colored sludge can be changed between 0.01 and 1.0 g per one liter of the solution, but a sufficient preventive effect can be usually attained by adding 0.1 to 0.5 g of the present inhibitor to one liter of the solution, without giving influences upon the developability and other photographic characteristics almost at all.

Among the well known inhibitors for formation of the colored sludge, some inhibitors are only effective for a high speed negative emulsion, but the present compounds are effective for any of silver bromide, silver chloride, silver chloride-bromide, silver bromide-iodide emulsions.

So long as the developer solution contains such a water-soluble silver complex-forming agent as sodium thiosulfate, it is possible to prevent the formation of colored sludge in quite the same principle even for the developing solution for a silver complex diffusion transfer process.

The developing solution containing no developing ingredients, which has been recently used in said process and is called "activator," is an alkali solution containing a sulfite or further sodium thiosulfate, but the developing ingredients or the silver complex-forming agent is dissolved into the solution from the prints (negative and positive papers) during the developing treatment, and silver halide of the emulsion is dissolved therein. Thus, colored sludge due to the silver colloid is likewise formed. However, such formation can be prevented by adding the present compound thereto.

Now, the present invention will be explained hereunder in detail, referring to examples, but will not be limited thereto.

EXAMPLE 1

One liter of a monobath developing-fixing solution consisting of the following compounds was prepared:

10	Water	750 ml
	1-Phenyl-3-pyrazolidone	2 g
	Hydroquinone	14 g
	Sodium sulfite (anhydrous)	40 g
	Sodium hydroxide	5 g
	Sodium metaborate	20 g
	Trisodium phosphate	50 g
	Sodium thiosulfate (pentahydrate)	120 g
15	Total with addition of water 1/	

Another solution containing 0.2 g of 4-benzamido-3-pentyl-1,2,4-triazoline-5-thione in addition according to the above recipe was prepared at the same time.

20 sheets (A4 of Japan Industrial Standard) each of photographic papers coated with a silver chloride emulsion by means of these monobaths were exposed and developed in these 2 kinds monobath developers.

25 The thus obtained prints had sufficient densities and had no fogs for both kinds. No print-out took place under direct sun beams. There was no substantial difference in color tone between these two kinds of the prints, because the necessary color toner was added to the emulsion. After the treatment, these solutions were left standing at room temperature, but the solution containing no inhibitor for formation of colored sludge started to be colored after one hour and was changed to genuine black after 24 hours. The colored sludge

30 due to the silver colloid stuck to the equipment.

However, the solution containing 4-benzamido-3-pentyl-1,2,4-thiazoline-5-thione was kept almost transparent even after 24 hours, and only yellowish brown precipitates appeared after 5 days. A very great effect 40 upon the prevention of formation of colored sludge was observed.

EXAMPLE 2

Added to the recipe according to Example 1 was 0.3 g/l of 4-phenylacetamido-3-butyl-1,2,4-triazoline-5-thione as an inhibitor for formation of the colored sludge due to the silver colloid.

On the other hand, a solution containing 0.3 g/l of 1-phenyl-5-mercaptopotetrazole, the well-known inhibitor, in place of the present inhibitor for formation of the colored sludge was prepared as a reference. After the treatment in the same manner as in Example 1, the residue solutions were left standing at room temperature.

55 The solution containing the well known 1-phenyl-5-
mercaptotetrazole was only slightly color-changed
after one hour, but a considerable amount of sludges
was formed after 24 hours. After 48 hours, the sludge
formation was not so different as that of the solution
60 containing no inhibitor as in Example 1.

On the other hand, the solution containing 4-phenylacetamido-3-butyl-1,2,4-triazoline-5-thione did not produce colored sludge almost at all even after three days, but started to be only slightly color-changed to yellowish after 5 days. A very great effect upon the prevention of formation of colored sludge was observed.

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EXAMPLE 3

Added to the recipe according to Example 1 was 0.3 g/l of 4-acetamido-3-heptyl-1,2,4-triazoline-5-thione as an inhibitor for the formation of colored sludge. On the other hand, another solution containing 0.3 g of the well-known DL- α -thiocetic acid was prepared as a reference. After the treatment in the same manner as in Example 1, the residue solutions were left standing at room temperature. All the prints were formed good.

The solution containing DL- α -thiocetic acid started to form colored sludge after 7 hours and changed to black after 24 hours, and became equal to the solution containing no inhibitor as in Example 1. On the other hand, the solution containing 4-acetamido-3-heptyl-1,2,4-triazoline-5-thione started to be changed to slightly yellowish after 24 hours, but the coloring did not proceed thereafter. The solution was not so changed after 5 days or 10 days almost at all as after one day. A very great effect upon the prevention of formation of colored sludge due to the silver colloid was observed.

EXAMPLE 4

One liter of a monobath developing-fixing solution containing the following compounds was prepared.

Water	750 ml
1-Phenyl-3-pyrazolidone	1 g
Hydroquinone	16 g
Sodium sulfite (anhydrous) 80 g	
Sodium carbonate (monohydrate)	30 g
Sodium thiosulfate	110 g
Sodium hydroxide	5 g
Total with addition of water	1 l

A solution according to the above recipe, which contained, in addition, 0.3 g/l of 2-mercaptop-5-phenyl-1,3,4-oxadiazole, the well-known inhibitor for formation of colored sludge, was prepared as a reference, whereas a solution according to the above recipe, which contained, in addition, 0.3 g/l of 4-benzamido-3-phenyl-1,2,4-triazoline-5-thione, was prepared. These solutions were used for the print treatment. The thus obtained prints were good for both solutions. No print-out took place under direct beams of the sun.

The residue solutions were left standing at room temperature. The solution containing the well known 2-mercaptop-5-phenyl-1,3,4-oxadiazole did not undergo color change after one hour, but a considerable amount of colored sludge was formed after 24 hours. On the other hand, the solution containing 4-benzamido-3-phenyl-1,2,4-triazoline-5-thione of the present invention did not produce any sludge almost at all after one hour or even after 24 hours. Only a very small amount of sludges was observed after 5 days. A very great effect upon the prevention of formation of colored sludge was observed.

EXAMPLE 5

A mono-bath (mono-bath developing-fixing solution for developing microfilms having the following composition was used:

Water	750 ml
Sodium sulfite (anhydrous)	36 g
1-Phenyl-3-pyrazolidone	1.2 g
Hydroquinone	12.0 g
Sodium metaborate	0.5 g
Sodium carbonate (monohydrate)	30.0 g
Sodium thiosulfate (pentahydrate)	20.0 g

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Sodium thiocyanate	0.7 g
1 % 4-benzamido-3-heptyl-1,2,4-triazoline-5-thione solution	20 ml
Total with addition of water	1 l

As a reference, a solution containing the same amount of 4-azolidine-4-carboxylic acid, the well-known inhibitor for formation of colored sludge, as that of the present inhibitor, 4-benzamido-3-heptyl-1,2,4-triazoline-5-thione, in place of the present inhibitor was used. No difference was observed between the present solution and the reference solution during the treatment, and there was no fear for the sticking of the sludge onto the film surfaces. However, when the treated solutions were reused after they had been reserved for one week, the present solution could be used as it was, whereas there was a small amount of sludges in the reference solution, and filtration was necessary. In the solution according to the above recipe except for the inhibitor, a small amount of sludge was already formed during the development and stuck to the film surface. Thus, it was necessary to carefully wipe the film surfaces with soft cotton during the water washing to remove the sludge sticking to the film surfaces.

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EXAMPLE 6

For a mono-bath (mono-bath developing-fixing solution) for a highly sensitive negative film, it was possible to use the solution prepared according to the recipe of Example 5, except that the amount of sodium thiosulfate therein was changed to about 60 – 100 g according to the composition of a film emulsion, but the following recipe was suitable for the specific purpose development:

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Water	750 ml
Phenylone	4.0 g
Hydroquinone	12.0 g
Sodium sulfite (anhydrous)	50.0 g
Sodium thiosulfate (pentahydrate)	110.0 g
Sodium hydroxide	4.0 g
1 % 4-benzamido-3-heptyl-1,2,4-triazoline-5-thione	30 ml
Total with addition of water	1 l

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A solution prepared according to the above recipe except for the inhibitor 4-propionacetamido-3-heptyl-1,2,4-triazoline-5-thione, was used as a reference. No difference was observed between the present solution and the reference solution during the development, but when the treated solutions were reused after the solutions had been reserved for 7 days, the reference solution contained a considerable amount of sludge and it was necessary to filter the reference solution. On the other hand, no sludge was formed at all in the present solution.

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EXAMPLE 7

The following recipe, where the present inhibitor was added to a developing solution for silver complex diffusion transfer, was preferable.

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Water	750 ml
Hydroquinone	12 g
1-Phenyl-3	1 g
Sodium sulfite (anhydrous)	60 g
Sodium hydroxide	12 g
Potassium bromide	1.5 g
Sodium thiosulfate (pentahydrate)	10 g
1 % 4-propionamido-3-methyl-1,2,4-triazoline-5-thione	

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ethanol solution
Total with addition of water

20 ml
1 l

A manuscript was copied with a photo-sensitive paper (for example, "Hishirapid" negative paper NL made by Mitsubishi Paper Mills Ltd. Japan), placed on a transfer sheet (for example, "Hishirapid" positive paper P made by Mitsubishi Paper Mills Ltd. Japan) so that the film surface of one paper might face with that of another, and treated with a specific purpose, developing machine (for example, "Hishiracopy" processor, made by Mitsubishi Paper Mills Ltd. Japan). After a large number of sheets had been treated, the solutions were observed the next day. The solution containing no inhibitor of the present invention, 4-propionamido-3-methyl-1,2,4-triazoline-5-thione, was colored to black and contained a considerable amount of sludge, whereas the present solution was only slightly color-changed, and contained no sludge almost at all.

What is claimed is:

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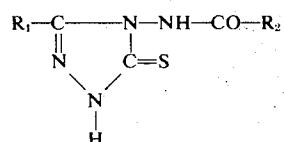
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1. In a monobath developing composition containing at least one member of the group consisting of thiosulfates thiocyanates and alkanol amines as the fixing agent or silver complex forming agent, a developer and a colored sludge preventive agent, the improvement in which said developing composition further contains as the colored sludge preventive agent the 3-substituted 4-acylamido-1,2,4-triazoline-5-thione having the general formula:



where R_1 and R_2 are both phenyl.

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