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Lugosy et al.

[11] **3,762,922**

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[54] **SILVER HALIDE PHOTOGRAPHIC IMAGES**

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[52] **U.S. Cl.** ..... **96/56**, 96/22, 96/60 UX, 96/61 UX

[51] **Int. Cl.** **G03c 7/16**, G03c 7/00

[58] **Field of Search** 96/56, 22, 61, 60

[56] **References Cited**

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[57] **ABSTRACT**

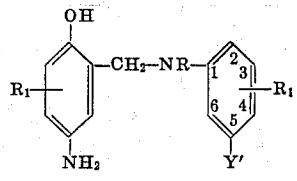
The image quality of photographic pictures containing, in addition to a silver image, a dye image resulting from developer, is improved by treatment with an alkaline solution containing a heavy metal complex.

10 Claims, No Drawings

SILVER HALIDE PHOTOGRAPHIC IMAGES

The subject of the present application is a process for improving the image quality of photographic pictures which contain a dye image in addition to the silver image.

In assignee's U.S. Pat. No. 3,622,629 by Lugosy, a process for producing photographic pictures is described which pictures contain, in addition to a silver image, a dye image resulting from the use of developer. The developer produces brown-black to blue-black colored dyes and includes compounds corresponding to the following general formula:



in which R is H, alkyl, aralkyl or carboxymethyl,

R_1 is H, an alkyl radical with one to four carbon atoms, Cl, Br or —COOH, and

Y′ is —OH or $—NH_2$, whereby at least one of the positions 2- and 4- is an unsubstituted, free coupling position.

With the aid of these compounds it is possible to develop black-and-white pictures with high density from films having coatings of greatly reduced silver halide content.

However, it has turned out to be a disadvantage that the dyes formed, which participate substantially in the image build up, do not correspond to the requirements of practice in all properties. Unsatisfactory, primarily, is the low stability of these dyes toward changes in pH. If, for example, after the development process, one subjects a picture produced by the process to further aftertreatment, under unfavorable circumstances, on going from alkaline to neutral or weakly acidic baths, or even in the washing process, undesirable color shade changes appear, for example, from black to brown or red, which also are usually connected with a loss in density.

Accordingly, the problem that is the basis of the invention is to stabilize these dyes against pH effects and, preferably, at the same time achieve a blackening of the image dye.

This problem is solved in the invention by treating the image dyes at any time after the development with alkaline solutions having a pH of at least 9 and containing heavy metals bound as complexes the stability of which is smaller than that of the dye-heavy metal complexes formed.

Suitable heavy metals for carrying out the process are Cu, Co, Ni, Cd, Zn and Ag, as examples. Especially well suited are Cu, Co and Ni since they effect an additional blackening of the image tone. As complex formers, ammonia, soluble amines, for example, di- and tri-ethanol amine, hydroxycarboxylic acids, for example, tartaric acid and citric acid as well as soluble mercapto compounds such as thioglycerol, thioglycol, thioglycollic acid, cysteine, etc. can be used. Indeed, from the German Auslegeschrift No. 1,125,279 and the German Pat. No. 1,099,349 it is known to treat photographic pictures that contain an image consisting of a dye with solutions of metal salts to improve the brilliance of the dyes formed and to stabilize against the effects of light and heat.

Therefore, it is not expected that in dye images that are produced by the process of self-coupling development, a treatment with heavy metal complexes, on the one hand would lead to stabilization of the image dye against pH changes and, on the other, a blackening and therewith a decrease in the brilliance of the dye could be achieved at the same time.

In accordance with the invention, a photographic picture which, in addition to the silver image, contains a dye image resulting from developer, as described, is treated so as to improve the image quality. This treatment comprises contacting said picture with an alkaline treatment solution with a pH of at least 9, said solution containing a heavy metal complex having a stability constant smaller than that of the dye-heavy metal complex formed. The dye of the color image, which results from the use of developer as described herein, is that which combines with the metal ions to form the dye-heavy metal complex referred to. The heavy metal complex is one which is capable of producing the dye-heavy metal complex, resulting in an image of increased optical density.

Production of the treatment solutions of the invention can be accomplished in a known manner. Thus, for example, the complex former and the metal salt can be dissolved separately in water, the two solutions can be combined and subsequently the pH can be raised to at least 9 through the addition of an alkali.

However, one can also first produce the complex salt in solid form, such as, for example, is described for copper tetramine sulfate in L. Vanino, Handbuch der praeparativen Chemie, Vol. I, page 516 (Stuttgart 1925). Then, before use the complex compound can be dissolved in water and the pH of this solution can subsequently again be increased to at least 9 through addition of an alkali.

Suitably, the concentration of the metal ion should be between 0.005 and 0.5 mol/l., whereas, the concentration of the complex former preferably should be between one-half and five times the value of the metal ion concentration. To achieve the desired action, only complexes are suitable the stability constants of which are smaller than those of the dye-metal complexes, since otherwise no metal ions will be given off to the image dye.

The treatment of the image dye with the complex heavy metal solution can take place at any time after the development. For example, it can be carried out between development and fixing process, between fixing process and final washing or after the final washing of the developed film. In a preferred embodiment of the process, the treatment can take place simultaneously with the fixing, if one uses a combination bath which contains the fixing agent and the metal complex compounds in alkaline medium. However, in this case, it is recommended to introduce an acid stop bath between developing and fixing.

However, one can also avoid this stop bath if one adds to the combination bath a substance that is capable of stopping the development process in alkaline solution. It was found that a good stopping effect can be achieved with low-molecular-weight thiol compounds that possess at least one hydrophilic group. Especially suitable, for example, are thioglycerol, thioglycol, thio-

glycollic acid, cysteine and thiazolidine-4-carboxylic acid.

As already described above, some of these thiol compounds are themselves suitable as complex formers for the metal salts. If one uses such a heavy metal-thiol complex in an alkaline combination bath, one achieves an adequate stopping therewith, so that in this case a separate addition of a thiol compound is not necessary. On the contrary if one uses one of the other complex formers, to achieve an adequate stopping it is necessary to add one of the above-mentioned soluble thiol compounds to the alkaline combination bath. These compounds preferably are used in amounts of 0.01 to 0.5 mol/l.

In addition, the presence of a soluble mercapto compound in the alkaline combination bath, in addition to the stopping action, may effect a desirable blackening of the color shade of the dye image formed.

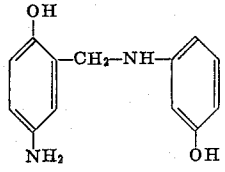
The invention will be illustrated in greater detail by means of the following examples.

EXAMPLE 1

A photographic film base was coated on both sides with a high-sensitivity gelatin-silver halide emulsion (AgBr: AgI = 60:1, gelatin:silver halide = 1:1) in such a way that the total coating amounted to 72 mg $AgBr/dm^2$.

Sample A of this film was exposed at a distance of 1.2 m for 0.2 sec in a gray-wedge sensitometer (wedge constant 0.15 cm^{-1}, exposure intensity on the wedge 30 lx) with the filters BG 3 (1.8 mm) and BG 38 (1.5 mm) using two Osram lamps (Wi 9, 2,660°K.), and developed for 2 min at 22° C. in a solution having the following composition and circulated by nitrogen blown in intermittently:

Solution I: Hydrochloride of N-(2'-hydroxy-5'-aminobenzyl)-3-hydroxy-aniline



16.0 g.

1-Phenyl-3-pyrazolidone		0.2 g
Sodium metaborate (tetrahydrate)		140.0 g
Sodium hydroxide		4.8 g
Sodium sulfite, anhydrous		50.0 g
Ascorbic acid		0.4 g
Potassium bromide		8.0 g
Ethylene glycol		2 ml
Tetrasodium salt of ethylenediamine tetraacetic acid		1.0 g
Water	make up to	1 l.

The film was then washed for 3 min in running water, fixed for 3 min in a 20 percent solution of $Na_2S_2O_3 \cdot 5H_2O$ in water, washed for 5 min and dried.

Sample B of the above-described film was exposed and processed as A, but before drying it was dipped for 1 minute in an alkaline solution with the following composition, (Solution II), and then dried.

Solution II:		
Sodium metaborate (tetrahydrate)		30 g
Seignette salt (potassium sodium tartrate)		100 g
Water	make up to	1 l.
The pH is adjusted to 13 with 50% NaOH		

Sample C of the above-described film was exposed and processed as B, but before drying it was washed for an additional 5 min in running water and then dried.

Sample D of the above-described film was exposed and processed as A, but before drying additionally was dipped for 3 min in a solution with the following composition (Solution III), thereafter washed for 5 min in running water and then dried.

Solution III:		
Copper sulfate (pentahydrate)		40 g
Seignette salt (potassium sodium tartrate)		100 g
Sodium metaborate (tetrahydrate)		30 g
Water	make up to	1 l.
The pH is adjusted to 13 with 50% NaOH		

The color shades resulting in the four samples are presented in Table 1.

TABLE 1.

Sample	Final treatment	Color shade
A	Washing	red-brown
B	Alkaline bath	blue-black
C	Alkaline bath + washing	red-brown
D	Alkaline copper complex bath and washing	blue-black

It is observed that the color change from blue-black to red-brown caused by the washing process does not appear when the film is treated after development with a copper complex bath.

EXAMPLE 2

Sample A of the X-ray film described in Example 1 was exposed as explained there, and developed for 2 min at 22°C. in Solution I of Example 1. The development was stopped by dipping for 30 sec in a 2% $KHSO_4$ solution. Thereafter, the film was fixed for 3 min in a 20 percent solution of crystalline sodium thiosulfate (pentahydrate), washed 3 min in running water, treated for 3 min with Solution III of Example 1, washed for 5 min and dried.

Sample B was exposed, developed and stopped as sample A; thereafter however, it was dipped for 3 min in a solution with the composition below (Solution IV), washed for 5 min and dried.

Solution IV:		
Copper sulfate (pentahydrate)		40 g
Siegnette salt (potassium sodium tartrate)		100 g
Sodium metaborate (tetrahydrate)		30 g
Sodium thiosulfate (pentahydrate)		200 g
Water	make up to	1 l.
The pH is adjusted to 13 with 50% NaOH		

The two film samples had a blue-black image tone and could not be differentiated.

EXAMPLE 3

Exposed film samples were prepared as described in Example 1 and developed for 90 sec. at 22°C. in Solution I of Example 1.

Sample A, after the development, was bathed for 3 min in Solution IV as in Example 2, washed for 5 min in running water and dried.

Sample B, after the development was stopped for 30 sec in 2 percent potassium hydrogen sulfate solution, treated with Solution IV of Example 2 for 3 min, washed for 5 min and dried.

Sample C, after the development, was treated for 3 min with a bath having the following composition (Solution V), washed for 5 min and dried.

Solution V:		
Copper sulfate (pentahydrate)		40 g
Thioglycerol		15 ml
Sodium thiosulfate (pentahydrate)		200 g
Seignette salt (potassium sodium tartrate)		100 g
Sodium metaborate (tetrahydrate)		30 g
Water	make up to	1 l.
The pH is adjusted to 13 with 50% NaOH.		

Fog and maximum density of all three samples are compiled in Table 2.

TABLE 2.

Sample	Fog	Maximum density
A	0.41	3.8
B	0.12	3.2
C	0.11	3.2

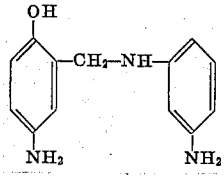
From the table it is evident that the development process is carried further after introduction of the film in the alkaline Solution IV through the developer substance remaining in the gelatin, through which a somewhat higher density results because of the simultaneous presence of fixer but also an unacceptable higher fog. This phenomenon disappears when the development is stopped by a known acid bath and the developer substance is dissolved out (Sample B). Practically the same effect, without an additional stopping bath, is achieved through the use of the mercapto compounds of the invention (Sample C).

EXAMPLE 4

Film samples were produced and exposed as in Example 1.

Sample A of the film was developed for 90 sec at 22°C. in a solution (Solution VI) having the following composition:

Solution VI: Sulfate of N-(2'-hydroxy-5'-amino-benzyl)-3-aminoaniline



13 g.

Sodium metaborate (tetrahydrate)		50 g
Sodium hydroxide		7 g
Sodium sulfite, anhydrous		50 g
Potassium bromide		5 g
Water	make up to	1 l.

The film was then washed for 3 min in running water, fixed for 3 min in a 20 percent solution of crystalline sodium thiosulfate (pentahydrate), washed for 5 min and dried.

Sample B of the film was developed and washed as Sample A, but then treated for 3 min with Solution IV of Example 2, washed for 5 min and dried.

The optical densities measured with a color densitometer with various filters in the same place on the wedge are compiled in Table 3.

TABLE 3.

Sample	Density without filter	Density with red filter	Density with green filter	Density with blue filter
A	1.00	1.06	1.12	0.82
B	1.00	1.05	1.00	0.95

The film B treated with the copper complex bath, compared to the control, shows an appreciable blackening.

EXAMPLE 5.

On the final processed film Samples B and C from Example 3, color densities were measured as described in Example 4. The results are contained in Table 4.

TABLE 4.

Sample	Density without filter	Density with red filter	Density with green filter	Density with blue filter
B	1.00	1.03	0.94	1.06
C	1.00	1.01	0.99	1.01

The film C treated with the bath containing thioglycerol (Solution V) is practically neutral black in contrast to the control.

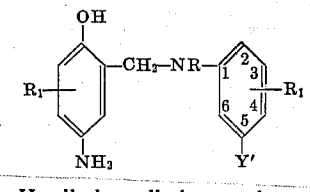
The advantages achievable with the present invention lie chiefly in that through the treatment with the metal complexes as described herein one arrives at pH-stable image dyes, which also do not undergo any changes in tone on going from alkaline to neutral or slightly acid treating baths. Rather, the desired dark color shades are maintained and beyond this even undergo a further blackening.

We claim:

1. Process for improving the image quality of an exposed photographic picture which, in addition to the silver image, contains a dye image resulting from developer, comprising treating said picture with an alkaline solution with a pH of at least 9, said solution containing a heavy metal complex having a stability constant smaller than that of the dye-heavy metal complex formed.

2. A process according to claim **1** wherein said heavy metal complex is formed from a metal selected from the group consisting of copper, cobalt, nickel, cadmium, zinc and silver.

3. A process according to claim **2** wherein said developer is a compound having the formula:

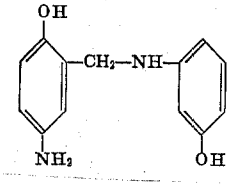


in which R is H, alkyl, aralkyl or carboxymethyl,

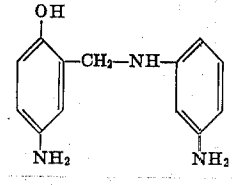
R_1 is H, an alkyl radical with one to four carbon atoms, Cl, Br or —COOH, and

Y' is —OH or —NH_2, whereby at least one of the positions 2- and 4- is an unsubstituted, free coupling position.

4. A process according to claim **3**, said developer being:



5. A process according to claim **3**, said developer being:



6. A process according to claim **3**, wherein the complex former of said heavy metal complex is selected from the group consisting of ammonia, soluble amines,

hydroxycarboxylic acids and soluble mercapto compounds.

7. A process according to claim **1**, said alkaline solution containing a fixing agent.

8. A process according to claim **7**, said complex former being a mercapto compound.

9. A process according to claim **8**, said mercapto compound being selected from the group consisting of thioglycerol, thioglycol, thioglycollic acid and cysteine.

10. A process according to claim **3**, wherein said heavy metal complex is formed from copper sulfate and potassium sodium tartrate.

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