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3,326,684

METHOD FOR STABILIZING DEVELOPED PHOTOSENSITIVE MATERIALS

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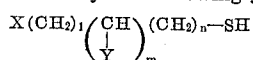
This invention relates to a method for stabilizing the developed image and more particularly to a method for stabilizing the developed image without fixing with sodium thiosulfate and then washing with water.

Fixing is carried out in order to remove silver halide in the non-exposed parts after development. However, because silver-thiosulfate complex formed during fixing is unstable to light, it must be removed by washing with water.

Many complex-forming agents which are effective as stabilizer have been already reported in technical literatures (for example; H. D. Russel, B. C. Yackel, G. B. Bruce, Photographic Science and Technical Journal, August, 1950, p. 59—62). Usually ammonium thiocyanate is often used. In such a case silver complex represented by the general formula $(\text{NH}_4)_x\text{Ag}(\text{CNS})_y$ is formed.

This salt is a transparent crystal and locates at white or transparent parts. Since this salt is stable for light it is unnecessary to remove by washing with water (ref. B.P. No. 867,242, F.P. No. 1,206,359, No. 1,239,429 or No. 1,258,356). Such treatment for stabilization enables rapid treatment but it is attended by many disadvantages in the quality of image. In order to secure the stabilization for light silver complex-forming agent is used in excess amount than the theoretical one. Because of hygroscopic property of the agent, the surface of processed emulsion layer tends to become sticky. The silver complex-forming agent gradually oxidizes metallic silver constituting the image, converting it into silver complex and decreasing the density of image or vanishing the image. In other words, if photosensitive materials subjected to the stabilizing treatment is placed in air, the decrease in density, and the change in color from black to brown or yellow becomes remarkable with the lapse of time, and in an extreme case the image disappears. Such fading phenomenon is often observed when the material is preserved under high humidities. If the exposure is effected before the completion of reaction between unexposed silver halide and silver complex-forming agent, the photolysis of unstable silver complex salt and unstabilized silver halide occurs and the white part or the transparent part is contaminated.

This invention is characterized in that the stabilizing treatment on the developed image is effected by using the compound represented by the following general formula;



wherein X, Y each represent hydrogen, hydroxyl group, alkoxyl group, amino group, alkylamino group, carboxyl group, carbalkoxyl group, thiol group, sulfonic acid, halogen, alkyl group, aryl group or heterocyclic ring, and l, m, n , each represent 0, 1 or 2, and $(l+m+n)$ is an integer larger than 0 and that the decrease in density of image, the changing in tone, or the contamination of white part or transparent part by photolysis is prevented even when image is preserved in air.

This invention is also characterized in that the decrease in density, or the change in tone of image or the contam-

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ination of white part or transparent part by light is prevented by stabilizing the image with silver complex forming agent and then by immersing for several seconds or more in a solution containing the above-mentioned compounds.

The said compounds are also effective when they are used along with the salts of heavy metal, such as Ni, Co, Cd, Zn and Au, which can form soluble or insoluble complex salt with the silver-complex forming agent and can stabilize the image. For photographic materials containing gelatine as the binder, the said compounds are effective even when employed jointly with both hardening agent and alcohols. It is also possible to stabilize the image by immersing photo-sensitive materials in a solution containing the said compounds after the stabilizing treatment with another silver-complex forming agent.

The compound used in this invention are, for example, 2-mercaptoethanol, 1-thioglycerol, 2-mercaptoethylamine hydrochloride, 2-diethylaminoethanethiol hydrochloride, thioglycolic acid, 2-mercaptopropionic acid, thiomalic acid, sodium-2-mercaptoethanesulfonate, thiobenzylalcohol and the like.

These compounds are dissolved in water, lower aliphatic alcohol such as methanol, ethanol, isopropanol and the like, acetone, dioxane and the like, and used in the form of solution.

In order to facilitate the understanding of this invention, examples will be given hereafter. It should be understood that this invention is not limited by such examples but limited by the appended claim.

Example 1

A photosensitive paper prepared by coating a paper with the photographic emulsion of silver halide which contains gelatine and hydroquinone was exposed, developed, and then subjected to the stabilizing treatment using the solution having the following composition:

Ammonium thiocyanate	-----g--	175
Borax	-----g--	2
Potassium metabisulfite	-----g--	130
Formalin (20%)	-----ml--	150
1% alcoholic solution of 2-mercaptopropionic acid	-----ml--	60
Water to make	-----ml--	1000

The procedure for preparing the solution was as follows: potassium metabisulfite was dissolved in 300 ml. of water and then formalin was added. After the temperature of the solution was lowered to room temperature, 1% alcoholic solution of 2-mercaptopropionic acid was added, then water was added until the total amount of the solution was attained to 1000 ml.

The image stabilized with this solution showed sufficient stability after drying. Even when preserved under a severe condition of high humidity such as 100% RH the decrease in density of image was less than that of image treated with a solution which contains the agents listed above excepting 2-mercaptopropionic acid, that is, the preservation property was better.

The result of test carried out under a condition of 100% RH at a room temperature is as follows:

	Decrease in density	
Stabilizing solution without	after 4 hours	
2-mercaptopropionic acid	-----	0.61
Stabilizing solution containing		
2-mercaptopropionic acid	-----	0.22

Example 2

A photosensitive paper of silver chloride was treated with a stabilizing solution having the following composition in the same way as in Example 1.

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Ammonium thiocyanate -----g--	175
Borax -----g--	2
Potassium metabisulfite -----g--	130
Formalin (20%) -----ml--	150
1% aqueous solution of diethylaminoethanethiol HCl salt -----ml--	60
Water to make -----ml--	1000

The test result was as follows:

	Decrease in density after 4 hours
Stabilizing solution without 2-diethylaminoethanethiol HCl salt -----	0.61
Stabilizing solution containing 2-diethylaminoethanethiol HCl salt -----	0.25

The print was exposed to the light of a fluorescent lamp of 1,000 lux for 24 hours immediately after drying. Contamination of white parts was apparently less than the case when a stabilizing solution without 2-diethylaminoethanethiol HCl salt was employed.

Example 3

A photosensitive paper of silver chloride was treated with a stabilizing solution having the following composition in the same way as in Example 1.

Ammonium thiocyanate -----g--	175
Borax -----g--	2
Potassium metabisulfite -----g--	130
Formalin (20%) -----ml--	150
1% aqueous solution of 2-mercaptoethylamine HCl salt -----ml--	60
Water to make -----ml--	1000

The test result was as follows:

	Decrease in density after 4 hours
Stabilizing solution without 2-mercaptoethylamine HCl salt -----	0.61
Stabilizing solution containing 2-mercaptoethylamine HCl salt -----	0.36

Example 4

A photosensitive paper of silver chloride was treated with a stabilizing solution having the following composition in the same way as in Example 1.

Ammonium thiocyanate -----g--	175
Borax -----g--	2
Potassium metabisulfite -----g--	130
Formalin (20%) -----ml--	150
NiCl ₂ -----g--	5
1% alcoholic solution of 2-mercaptopropionic acid -----ml--	60
Water to make -----ml--	1000

The test result was as follows:

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	Decrease in density after 4 hours
Stabilizing solution without 2-mercaptopropionic acid -----	0.51
Stabilizing solution containing 2-mercaptopropionic acid -----	0.19

What we claim as our invention are:

1. A process for the production of a photographic image in a silver halide photographic emulsion layer which comprises developing the emulsion layer and stabilizing the undeveloped portions in the layer with a stabilizing solution containing a silver-complex forming agent and a thiol compound, said silver complex forming agent being a member selected from the group consisting of an alkali metal thiocyanate and ammonium thiocyanate, and said thiol compound being represented by the general formula



wherein X and Y are each selected from the group consisting of hydrogen, hydroxyl, alkoxy, amino, alkylamino, carboxyl, carbalkoxyl, thiol, sulfonic acid, halogen, alkyl, aryl and heterocyclic ring, and *l*, *m* and *n* represent respectively an integer of 0, 1, or 2 and (*l*+*m*+*n*) is an integer larger than 0.

2. A process according to claim 1, wherein the thiol compound is 2-mercapto-propionic acid.

3. A process according to claim 1, wherein the thiol compound is diethylaminoethanethiol.

4. A process according to claim 1, wherein the thiol compound is 2-mercaptoethylamine.

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