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STABILIZATION OF PROCESSED PHOTOGRAPHIC EMULSIONS TO HIGH TEMPERATURES AND HUMIDITIES

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8 Claims. (Cl. 95—88)

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This invention relates to photography and particularly to the rapid processing of photographic materials.

Photographic processing of the customary silver halide emulsions after exposure includes the essential steps of development, fixing, washing and drying. Optional steps such as reduction toning, etc., may be included but are not essential to the formation of a photographic image. These essential steps consume an appreciable amount of time and in many cases the time required for completion of each step cannot be shortened without harming the quality of the final picture.

Yackel U. S. application, Ser. No. 594,589, filed May 18, 1945, describes a rapid processing method according to which a developed silver image is stabilized by treatment with a solution of a compound which does not react with metallic silver and which forms a light-inert silver complex by reaction with undeveloped silver halide. The stabilization bath is used only until the silver halide has been substantially completely converted to a complex with the stabilizing compound and the complex is left in the emulsion layer, the layer being dried without any further treatment, such as washing. While the method of the Yackel application is satisfactory for the stabilization of images which are not to be stored under adverse conditions, it has the disadvantage that the silver images tend to fade when stored under conditions of high temperature and humidity. A further disadvantage is that certain of the stabilizing agents such as thiosulfates tend to crystallize on the surface of the photographic emulsion.

It is therefore an object of the present invention to provide a rapid processing method for silver halide emulsion layers which produce prints stable to high temperature and humidity. A further object is to prevent crystallization of the stabilization agent on the emulsion layer during or after stabilization by my method. Other objects will appear from the following description of my invention.

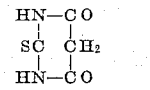
These objects are accomplished by the technique described herein which includes stabilizing the image in the presence of a metal below silver and above osmium in the electromotive series, without washing the print.

According to the stabilizing process described in Yackel U. S. application, Serial No. 594,589, a silver halide emulsion, preferably a gelatino-silver halide emulsion is exposed in the usual way and is then developed in the customary silver halide developing agent. If the emulsion is coated on a paper or other porous support, it is desirable to wipe the surface of the emulsion with a sponge, a

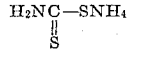
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rubber roll, or other applicator wet with the developing solution so that the paper support is not soaked with the developing solution. After development has taken place, the excess developing agent present on the surface of the print is removed by any convenient means such as a squeegee and the print treated with a stabilizing solution. The purpose of the stabilizing agent is to make the undeveloped silver halide substantially incapable of further photo-sensitivity. The stabilizing agent must be a compound which does not react readily with metallic silver and which forms a light-inert silver complex by reaction with the undeveloped silver halide in the emulsion layer. The resulting silver complex should be light-colored or transparent so that it does not interfere with the viewing or printing of the final image.

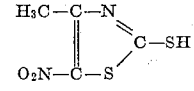
Stabilizing agents described for this purpose in the Yackel application, Serial No. 594,589, are compounds containing doubly-bonded sulfur or an SH linkage, such as alkali metal and ammonium thiosulfates and thiocyanates, thiourea and thioglycolic acid. Additional stabilizing agents which I have found suitable for this process include the following:



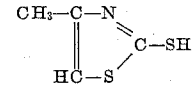
Thiobarbituric acid



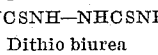
Ammonium dithiocarbamate



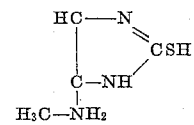
2-Mercapto-4-methyl-5-nitrothiazole



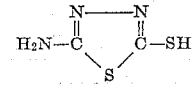
2-Mercapto-4-methyl-thiazole



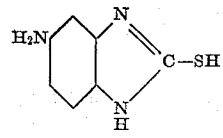
Dithio biurea



4-Aminomethyl-2-mercapto imidazole



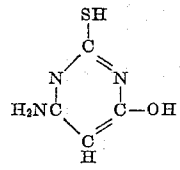
5-Amino-2-mercapto-1,3,4-thiodiazole



2-Mercapto-5-amino-benzimidazole

$HS.CH_2COOH$

Thioglycolic acid



6-Amino-2-thio-4-hydroxy-pyrimidine

$H_2NSC—CSNH_2$

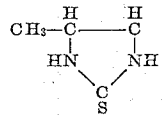
Dithio oxamide

$C(CH_3)_3CSNH_2$

Thio trimethyl acetamide

$CH_2SHCHNH_2COOHHCl$

Cysteine hydrochloride



Propylene thiourea

CH_3CSNH_2

Thioacetamide

$CH_3CH_2CSNH_2$

Thiopropionamide

$HS—CH_2CONHNH_2$

Thioglycolic hydrazide

The essential feature of the present invention is the stabilization with these agents in the presence of a metal below silver and above osmium in the electromotive series. The metals of this class include palladium, platinum, gold, iridium and rhodium (see Mellor, "Modern Inorganic Chemistry," 1925, page 433). Suitable compounds are gold chloride, palladium chloride, iridium sesquichloride and chloroplatinic acid (H_2PtCl_6). These compounds may be present in the stabilizing bath or in the emulsion layer. When used in the stabilizing bath, suitable amounts are from 0.01 to 10 grams per liter. An amount of the order of 0.04 gram per liter of wet emulsion is suitable for use in the emulsion.

My invention will be further illustrated by reference to the following examples.

Typical stabilizing solutions are represented by the following examples.

Example 1

Thiourea	grams	40
Acetic acid	milliliters	60
Gold chloride	gram	1
Water to	liter	1

Example 2

Thiourea	grams	40
Gold chloride	grams	5
Citric acid	grams	15
Sodium citrate	grams	10
Water to	liter	1

Example 3

Sodium thiosulfate	grams	150
Sodium bisulfite	grams	15
Gold chloride	gram	1
Water to	liter	1

Example 4

Ammonium thiosulfate	grams	100
Sodium bisulfite	grams	15
Acetic acid	milliliters	10
Gold chloride	gram	0.25 to 1
Water to	liter	1

Example 5

Water	cc	750
Gold chloride	gram	0.24
Ammonium thiocyanate	grams	60
Acetic acid (glacial)	cc	10
Water to	liter	1

The following example illustrates the incorporation of my compounds in the emulsion layer.

Example 6

To a gelatino-silver halide emulsion there was added just before coating 0.2 gram of gold chloride per 5000 cc. of wet emulsion. This emulsion was coated, developed and treated with a stabilizing bath such as those of Example 4 or Example 5 without the gold chloride. A check emulsion without the gold chloride was treated in the same way after processing and upon storage at 100° F. and 90% relative humidity for six days was found to bleach to a brownish-yellow image. The emulsion containing the gold chloride showed greatly improved resistance to bleaching under similar conditions.

The use of salts of metals below silver and above osmium in the electromotive series to improve the heat and high humidity stability of images treated with alkali metal and ammonium thiocyanates is not a part of my invention but is the invention of William L. Brice as described in application, Serial No. 624,570 filed concurrently herewith, now Patent No. 2,448,857, September 7, 1948.

I have found that while many of the stabilizing solutions described herein are satisfactory when used on paper emulsions as regards crystallization of salts on the prints, in certain cases, the stabilizing agent crystallizes on the surface of the emulsion on drying. This is particularly true in the case of film emulsions coated on transparent cellulosic supports and stabilized with thiosulfate solutions. I have found that this crystallization may be prevented by incorporating certain hydroxy-substituted aliphatic amines in the stabilizing bath. The hydroxy aliphatic amine may be added to the thiosulfate solution and sufficient acid then added to neutralize the solution or they may be added as the amine thiosulfate, replacing all or part of the ammonium thiosulfate. The amines do not increase the stability of the silver complex formed with the stabilizing agent or prevent the fading of the silver image but are used only to prevent crystallization on the surface of the emulsion.

Suitable hydroxy aliphatic amines which I have used for this purpose are ethanolamine, diethanolamine, triethanolamine, β-diethylamino ethyl alcohol, trimethylolaminomethane, 2-amino-2-methyl-1-propanol and 2-amino-2-methyl-1,3-propanediol.

As in the case of the process described in Yackel application, Serial No. 594,589, hardened emulsions must be used with the present process. Positive emulsions such as are used on photographic papers are generally hardened and no further hardening treatment is required. However, in the case of certain negative film emulsions, the emulsion must be hardened before stabilizing ac-

cording to my invention. This can be done with a formaldehyde hardening bath before or after development or in any other suitable way.

Although the emulsion may be immersed in the developing and stabilizing solutions, I prefer merely to moisten the surface of the emulsion with the solutions except in the case of films and plates. Thus in the case of paper supports, moistening the surface of the emulsion only, prevents the support from becoming wet and the drying done is thereby greatly reduced.

It will be apparent from the foregoing description of my invention that all or a major part of the silver remains in the emulsion after stabilization. This differs from the customary fixing and washing in which the intent is to remove the residual silver halide from the emulsion. The unexposed silver halide is converted to a complex with the stabilizing agent and it is desirable that this complex be as stable and permanent as possible so that there is little fading or discoloration of the final image.

It will be understood that the examples and modifications included herein are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

I claim:

1. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it in the presence of a metal below silver and above osmium in the electromotive series, with a compound selected from the class consisting of compounds containing sulfur doubly bonded to a single carbon atom and SH linkages bonded to a carbon atom which does not react readily with metallic silver and which forms a light-inert silver complex by reaction with undeveloped silver halide, only until the silver halide has been substantially completely converted to a complex by reaction with said compound, leaving said complex in said layer and drying said stabilized image without any further treatment.

2. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it in the presence of a chloride of a metal below silver and above osmium in the electromotive series, with thiourea, only until the unexposed silver halide is substantially completely converted to a light inert silver complex by reaction with the stabilizing material, and drying said stabilized image without any further treatment.

3. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it in the presence of a chloride of a metal below silver and above osmium in the electromotive series with ammonium thiosulfate, only until the unexposed silver halide is substantially completely converted to a light inert silver complex by reaction with the stabilizing material, and drying said stabilized image without any further treatment.

4. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it in the presence of gold chloride, with ammonium thiosulfate, only until the unexposed silver halide is substantially completely converted to a light inert silver complex by reaction with the stabilizing material, and drying said stabilized image without any further treatment.

5. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it by treatment with a solution of a compound selected from the class consisting of compounds containing sulfur doubly bonded to a single carbon atom and SH linkages bonded to a carbon atom which does not readily react with metallic silver and which forms a light-inert silver complex by reaction with undeveloped silver halide, only until the silver halide has been substantially completely converted to a complex with said compound, said solution containing a metal below silver and above osmium in the electromotive series, leaving said complex in said layer and drying said stabilized image without any further treatment.

6. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it by treatment with a solution of thiourea containing gold chloride, only until the unexposed silver halide is substantially completely converted to a light inert silver complex by reaction with the stabilizing material, and drying said stabilized image without any further treatment.

7. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it by treatment with a solution of ammonium thiosulfate containing gold chloride, only until the unexposed silver halide is substantially completely converted to a light inert silver complex by reaction with the stabilizing material, and drying said stabilized image without any further treatment.

8. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent and stabilizing it by treatment with a solution of ammonium thiosulfate containing gold chloride and a hydroxy aliphatic amine, only until the unexposed silver halide is substantially completely converted to a light inert silver complex by reaction with the stabilizing material, and drying said stabilized image without any further treatment.

HAROLD D. RUSSELL.

REFERENCES CITED

The following references are of record in the file of this patent:

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