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STABILIZATION OF PHOTOGRAPHIC EMULSIONS

William L. Brice, Oak Ridge, Tenn., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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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 thiourea tend to crystallize on the surface of the photographic emulsion.

It is therefore the principal object of this invention to provide a rapid processing method for silver halide emulsion layers which produces prints stable to high temperature and humidity.

This object is accomplished by the method described herein which includes stabilizing the image with a soluble thiocyanate 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, Ser. 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 rubber roll, or other applicator wet with the developing solution so that the paper support is

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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 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 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.

According to my invention, I use an alkali metal thiocyanate, including ammonium thiocyanate, as the stabilizing agent 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, chloroplatinic acid (H_2PtCl_6). These compounds may be present in the stabilizing bath or in the emulsion layer. When used in the stabilizing baths, suitable amounts are from 0.1 to 10 grams per liter of solution. An amount of the order of 0.04 gram per liter of wet emulsion is suitable for use in the emulsion. The alkali metal thiocyanate may be present in an amount of between about 5% and 10% of the weight of the solution.

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

Example 1

Water	cc.	750
Auric chloride	grams	0.24
Ammonium thiocyanate	do	60
Acetic acid (glacial)	cc.	10
Water to 1 liter.		

Example 2

Iridium sesquichloride	grams	0.301
Ammonium thiocyanate	do	30
Water	cc.	500

Example 3

Palladium chloride ($PdCl_2$)	grams	0.1525
Ammonium thiocyanate	do	30
Water	cc.	500

Example 4

Chloroplatinic acid (H_2PtCl_6)	grams	0.325
Ammonium thiocyanate	do	30
Water	cc	500

Example 5

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 that of Example 1 without the gold chloride. A check emulsion without the gold chloride was treated in the same way 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.

As in the case of the process described in Yackel application, Ser. 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 according 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 time 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.

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 an alkali metal thiocyanate, 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.

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 an alkali metal thiocyanate, 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 gold chloride, with an alkali metal thiocyanate, 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 thiocyanate, 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 with a solution of an alkali metal thiocyanate containing a soluble salt of a metal below silver and above osmium in the electromotive series, 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.

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 with a solution of an alkali metal thiocyanate containing a chloride of a metal below silver and above osmium in the electromotive series, 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 with a solution of an alkali metal thiocyanate 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 with a solution of ammonium thiocyanate, 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.

9. 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 with a 5% to 10% solution of an alkali metal thiocyanate containing from about 0.01% to about 0.1% of 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.

WILLIAM L. BRICE.

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