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[56] References Cited			
UNITED STATES PATENTS			
2,310,223	2/1943	Eaton et al.....	96/61
2,871,121	1/1959	Kimura et al.	96/61
3,257,208	6/1966	Van Paesschen et al.	96/111

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[54] **PHOTOGRAPHIC STABILIZER BATH**
COMPRISING THIOCYANATE AND AN
INORGANIC HARDENER COMPLEX
5 Claims, No Drawings

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ABSTRACT: Photographic images are produced by imagewise exposure of supported silver halide emulsion layers, development and treatment with a stabilizing bath to convert the light-sensitive silver salt in the unexposed and undeveloped areas into light-insensitive reaction products. The stabilizing bath contains as inorganic hardeners complex compounds of zirconium, aluminum and chromium.

PHOTOGRAPHIC STABILIZER BATH COMPRISING THIOCYANATE AND AN INORGANIC HARDENER COMPLEX

The invention relates to a process for the production of photographic images by exposure, development and subsequent stabilization. The invention also relates to a stabilizer bath for carrying out the process.

It is known to stabilize developed photographic images with complex forming compounds in rapid photographic reproduction processes as a substitute for conventional fixing with sodium thiosulfate followed by washing. In contrast to the method of fixing with sodium thiosulfate, in these stabilizing processes the silver salts remain in the unexposed and developed parts of the layer in the form of a light-insensitive reaction product of the stabilizing compound with the original silver halides.

For example the conventional stabilizer baths contain water-soluble thiocyanates as stabilizers, particularly ammonium thiocyanate, which reacts with the silver halide to form a silver thiocyanate complex which is insensitive to light. Although the said complex compound is soluble in water, most of this complex remains in the image-bearing layer because the treatment time in the stabilizer bath is very short and the general final washing is omitted in photographic processes of this kind.

This two-bath process is of particular importance for rapid processing of photographic materials. In order to obtain photographic images of satisfactory quality and to achieve rapid penetration of the processing baths into the exposed silver halide emulsion layers, the said layers are comparatively little hardened. When processing with the usual stabilizer baths which contain, for example, ammonium thiocyanate, potassium metabisulfite, sodium acetate, glacial acetic acid and small quantities of special additives particularly heterocyclic mercapto compounds which serve to improve the image tone or increase the stability upon storage of the silver image, the image-containing layers obtained have a marked tendency to be sticky and are difficult to dry. Even after the layer has been dried, the layers tend to become sticky again at higher humidity. Photographic images are therefore liable to stick together and to be damaged when separated. Even layers which have been thoroughly hardened show the same disadvantages when processed in these baths although to a less extent.

Since even a thorough hardening of the layers cannot prevent sticking completely and because excessive hardening is a disadvantage because it impairs the photographic properties, such as the gamma, image tone, etc., rapid hardening compounds are added to the stabilizer baths. The known organic hardeners are, however, of limited utility for this purpose, particularly for physiological reasons, formaldehyde cannot be used because of the unpleasant odor and insufficiently rapid hardening. Inorganic hardeners have therefore been proposed for this purpose, in particular aluminum sulfate. When such baths are used, the images which are obtained are immediately hardened enough to be unaffected by touch and dry very rapidly.

Aluminum sulfate has, however, other disadvantages which limit its application, particularly in automatic photographic processes. Development is performed in an alkaline bath before stabilization and the stabilization bath is contaminated with small quantities of the alkaline developer baths being carried into this stabilizing bath. This causes the pH of the stabilizing bath to rise from an original value of about 3 to values of up to about 4 to 5. Aluminum hydroxide starts to flocculate at pH values of about 4 or which leads to the precipitation of solid, jellylike masses which deleteriously effect the stabilization and in development machines cause blockage in pipes and circulating pumps.

It is among the objects of the invention to provide stabilizer baths for two-bath processes which yield sufficiently hardened and nonsticky photographic images of satisfactory quality.

An aqueous stabilizer bath has now been found which contains thiocyanates in dissolved form as stabilizers and mixed

complexes of zirconium, aluminum and chromium salts as hardeners, the ratio of these metal salts, expressed in terms of the metal oxide $ZrO_2:Al_2O_3:Cr_2O_3$ being 100:5-50:2-30 parts by weight, preferably 100:10-20:3-8 parts by weight.

The stabilizer baths according to the invention may, for example, have the following composition:

250 to 300 g. of a water-soluble thiocyanate by an alkali metal thiosulfate or preferably ammonium thiocyanate,
60 to 100 g. of an alkali metal metabisulfite, in particular potassium metabisulfite,
40 to 60 g. of an alkali metal acetate, in particular sodium acetate,
30 to 80 g. of the zirconium aluminum chromium mixed complex,

and small quantities of other conventional additives for improving the image tone or stability of the image, in particular heterocyclic mercapto compounds, e.g. of the type described in German Pat. application Ser. No. P 19 19 045.5 and German Auslegeschrift 1 299 221.

The baths according to the invention have a pH of between 3 and 4.5. This is adjusted by addition of an acid, preferably acetic acid.

Silver images of excellent quality are obtained when using the stabilizer baths according to the invention. The layers are sufficiently hardened and nonsticky. They are not liable to stick together even when kept at high humidity.

The usual photographic materials containing one or more silver halide emulsion layers on a suitable layer support, preferably paper, are suitable for use in the process with the stabilizer bath according to the invention. The silver halides used may be silver chloride or silver bromide, if desired in admixture with each other or if desired together with small quantities of silver iodide. Gelatine is particularly suitable for use as binder for the layers but may be partly replaced by other water-soluble natural or synthetic binders such as alginic acid or its derivatives, in particular its salts, esters or amides, cellulose derivatives, e.g. carboxymethyl cellulose, or hydroxyethyl cellulose, starch or derivatives thereof, and polyvinyl pyrrolidone, polyvinyl alcohol or copolymers containing vinyl alcohol units.

The photographic materials may also be optically or chemically sensitized in the usual manner.

In addition, the emulsions may contain developers or developer combinations of the polyphenol type, for example hydroquinone or pyrocatechol of the aminophenol series, for example p-aminophenol or p-methylamino phenol compounds of the pyrazolidone series, phenylene diamine derivatives and the like, antioxidants for the developer, e.g. potassium metabisulfite, aldehyde and ketone bisulfite, matting agents and brightening agents.

Development is carried out in the usual manner, using known developers. According to a preferred method of carrying out the invention, the developer is added to the photographic material and development is initiated by treatment with an alkaline aqueous bath, hereinafter referred to as an activator bath.

The method of preparation of the mixed complexes for use according to the invention has been described in U.S. Pat. No. 3,423,162.

EXAMPLE

A light-sensitive photographic material having a silver iodobromide gelatin emulsion layer (2.5 mols percent of silver iodide) containing 1.8 g. of silver in the form of silver halide and approximately 2.5 g. of hydroquinone per m^2 on a support of baryta-coated paper is exposed in a sensitometer customarily employed in the art and developed by treatment with the following activator bath:

1,000 ml. of water,
100 g. of sodium hydroxide,
50 g. of sodium sulfite,
2 g. of potassium bromide.

Samples of the developed material are then treated in the following stabilizer baths:

I. Bath according to the invention

1,000 ml. of water,
300 g. of ammonium thiocyanate,
85 g. of potassium metabisulfite,
30 g. of cyclohexanone bisulfite,
50 g. of sodium acetate, anhydrous,
70 g. of a mixed Zr-Al-Cr-sulfate complex (containing 100 parts of ZrO_2 to 14 parts of Al_2O_3 and 7 parts of Cr_2O_3),
15 ml. of glacial acetic acid.

The mixed complex is prepared as follows: 100 parts of a commercial zirconium sulfate containing 23 percent of ZrO_2 and about 1 mol of silicic acid and about 1 mol of sodium sulfate per mol of ZrO_2 and having a basicity of about 10 percent are stirred up with about 200 parts of water and mixed with an aqueous solution of 21.5 parts of a commercial aluminum sulfate (containing 15 percent of Al_2O_3) and 8.9 parts of a commercial Cr(III) sulfate dye (containing 18 percent of Cr_2O_3 and having a basicity of 44 percent) in about 30 parts of water. This mixture is heated for 15 minutes at $80^\circ C.$, cooled and dried by the spray drying process. The powder obtained contains the metal oxides in the following proportions: 100 parts of ZrO_2 to 14 parts of Al_2O_3 to 7 parts of Cr_2O_3 .

II.

215 g. of ammonium thiocyanate,
85 ml. of glacial acetic acid,
25 g. of sodium acetate,
30 g. of sodium aluminum sulfate, water up to 1 liter.

III.

250 g. of ammonium thiocyanate,
100 g. of potassium metabisulfite,
50 g. of sodium acetate,
15 ml. of glacial acetic acid, water up to 1 liter.

The treatment time is about 3 seconds. The silver images obtained using the stabilizer baths I and III have a good image quality, whereas the image whites obtained with bath II are unsatisfactory. Furthermore, it is found that after prolonged storage, the images produced with bath II fade.

If the above photographic material is processed in a conven-

tional development apparatus for two-bath processes, it is found that solutions I and III can be used for processing approximately 10 to 12 $m.^2$ of the photographic material described above before the stabilizing effect of the solution diminishes. This indicates that only insignificant precipitation, if any, has taken place in bath I of the invention. The stabilizing effect of bath II is already exhausted after about 6 to 8 $m.^2$ of the photographic material have been passed through it. Marked precipitation occurs after only about 4 $m.^2$. This precipitation has become so serious after processing about 6 $m.^2$ that on further use the rollers become severely contaminated and the quality of the picture is impaired. For both these reasons, the bath cannot be used any more.

The layers obtained using baths I and II are sufficiently hardened and nonsticky, whereas those obtained with bath III are sticky and useless for practical purposes.

We claim:

1. Aqueous photographic stabilizer bath containing water-soluble thiocyanates as stabilizers and mixed complexes of zirconium, aluminum and chromium salts, the ratio of these metal salts, expressed in terms of the metal oxide $ZrO_2:Al_2O_3:Cr_2O_3$ being 100:5 to 50:2 to 30 parts by weight as hardener.

2. The bath of claim 1 wherein the ratio of these metal salts in the mixed complexes of zirconium, aluminum and chromium salts, expressed in terms of the metal oxides, is 100:10 to 20:3 to 8 parts by weight.

3. In a process for the production of photographic images by exposure of a photographic material containing at least one supported silver halide emulsion layer, development and stabilization in an aqueous stabilizer bath which contains in dissolved form thiocyanates and hardeners, the improved consisting of treating the developed layer with a stabilizer bath which contains as hardener a mixed complex compound of zirconium, aluminum and chromium salts, the ratio of these metal salts, expressed in terms of the metal oxides $ZrO_2:Al_2O_3:Cr_2O_3$, being 100:5 to 50:2 to 30 parts by weight.

4. The process of claim 3, wherein the ratio of these metal salts in the mixed complexes of zirconium, aluminum and chromium salts expressed in terms of the metal oxides, is 100:10 to 20:3 to 8 parts by weight.

5. The process of claim 3, wherein the silver halide emulsion layer contains a photographic developer compound and wherein development is performed by treatment with an aqueous alkaline bath.

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