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RAPID STABILIZING PROCESS FOR COLOR PHOTOGRAPHIC MATERIALS

Kinji Ohkubo and Katsumi Hayashi, Kanagawa, Japan, assignors to Fuji Photo Film Co., Ltd., Kanagawa, Japan

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ABSTRACT OF THE DISCLOSURE

A method for rapidly developing an exposed photographic material containing differently sensitized gelatino-silver halide emulsions and color formers capable of reacting with the oxidation products of a primary amine whereby said material is placed into a developing bath containing a primary aromatic amine, the developing process is stopped in a stop bath and the product is bleach-stabilized in a bath containing an anion of an iron (III) monohydrogen ethyl-diamine-N,N,N',N'-tetraacetate and ammonium thiosulfate and thereafter drying said material.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a rapid stabilizing process for color photographic materials.

(2) Description of the prior art

The demands for methods of providing photographic records in short periods of time recently increased considerably due to the latest technological advances. In particular, rapid processing of black and white silver halide photographic materials have been studied extensively, and are now employed widely, but rapid processing for coupler incorporated silver halide emulsions for recording colors has not been put to practice except in Polacolor (registered trade mark by International Polaroid Co.).

The use of coupler incorporated silver halide emulsions are advantageous for recording the visible spectrum, but conventional color processing systems require several steps including the developing of exposed silver halide, the termination of the developing process, bleaching of the developed silver, removal of the undeveloped silver halide, and removal of residual processing chemicals.

We have now discovered a method for stabilizing coupler containing color emulsions which has an improved processing rate and which does not require a washing operation.

A stabilizing process for color photographic materials has been described in U.S. Pat. No. 3,335,004 in which a color photographic material comprising differently sensitized gelatino-silver halide emulsions containing color formers is reacted with the oxidation product of a primary aromatic amine developer to form the dyes. The emulsion is developed in a developing bath containing the primary aromatic amine developer and the developing procedure is terminated by being passed through a stop bath. The product is thereafter bleach-stabilized with a bath containing an inorganic alkaline ferricyanide, an inorganic alkaline thiocyanate and an inorganic alkaline bichromate, which is stabilized in another bath of an inorganic alkaline thiosulfate and an inorganic alkaline bisulfite. This treatment, however, has the following disadvantages: (1) since the inorganic alkaline ferricyanides are strong oxidizing agents, it tends to decompose the solvent for the silver halide usually an inorganic alkaline thiocyanate, which remarkably reduces the shelf life of the bleaching-

stabilizing solution; (2) according to the process described in the specification of U.S. Pat. No. 3,335,004 additional stabilizing steps are required after the bleach-stabilizing procedure; and (3) since an inorganic alkaline thiocyanate is used as the solvent (stabilizing agent) for silver halide in the bleach-stabilizing bath, the light stable silver thiocyanate complex in the stabilized print is easily decomposed when contacted with water to a light-sensitive silver thiocyanate salt and therefore is easily contaminated by active radiation.

We have now found an improved photographic stabilizing process which obviates these various drawbacks.

One object of this invention is to provide an improved rapid process for color photographic materials.

Another object of the present invention is to provide an improved stabilizing process for color photographic materials in which the shelf life of the processing bath and the preservability of processed prints are good.

SUMMARY OF THE INVENTION

According to the present invention a rapid stabilizing process is provided for silver halide type color photographic materials comprising differently sensitized gelatino-silver halide emulsions containing color formers capable of reacting with the oxidation product of a primary aromatic amine developing agent. This type of material is developed according to this invention in a bath of the developing agent and thereafter bleach-stabilized in a bath containing an anion of iron (III) monohydrogen ethylenediamine - N,N,N'N'-tetraacetate and ammonium thiosulfate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The developing bath used in this invention may contain a primary aromatic amine developing agent of the p-phenylenediamine type in which two hydrogens on one of the amine groups is substituted by lower alkyl groups. For example N-ethyl-N-β-hydroxyethyl - p-phenylenediamine, N,N - diethyl - 2 - methyl-p-phenylene-diamine, and N-ethyl - N - (methanesulfonamidoethyl)-3-methyl-4-aminoaniline can be used. The developing bath may also contain hydroxylamine as an antioxidant and/or ammonium carbonate (or an alkali metal carbonate, such as sodium carbonate) or ammonium iodide (or an alkali metal iodide, such as potassium iodide).

If desired or where exceptional results are required, a stop bath such as those used in conventional photographic processes may be used in the process of this invention. Conventional stop baths generally contain acetic acid and alkali metal acetates. If desired, an alkali metal bisulfite can also be added to the bath.

The bleach-stabilizing bath oxidizes the developed silver and converts the oxidized silver and undeveloped silver halide to a light stable silver complex. The leuco dye, which is the intermediate product of the coupling reaction between the color developing agent and the color former, is simultaneously converted to the colored form. The bleach-stabilizing bath contains an anion of iron (III) monohydrogen ethylenediamine tetraacetate as the oxidizing agent for the developed silver. Either an alkali metal salt of iron (III) monohydrogen ethylenediamine tetraacetate, or a combination of ferric chloride and sodium ethylenediamine tetraacetate can produce the foresaid anion in the solution. The oxidizing agent is preferably used in the solution in an amount of between 1–50 g./liter. A larger concentration may contaminate the print. An ammonium thiosulfate has been found to be a suitable stabilizing agent. The bleach-stabilizing bath may contain an alkali metal thiosulfate as an accelerator for stabilization.

The concentration of stabilizing agent depends upon the amount of silver halide on the support, preferably 100–500 g./liter can be used. The bleach-stabilizing bath preferably has a pH of between 4 and 8. The thiosulfate will be decomposed in the bleach-stabilizing bath of a pH of less than 4. If the pH of the bath is more than 8, a fog will be produced which will contaminate the prints subsequently formed. A suitable combination of an alkali metal hydrogen phosphate, an alkali metal carbonate, an alkali metal hydrogen sulfite and boric acid may be employed so that the bath has a buffering action in the foresaid range of pH. Besides the foresaid components, 0.3–10 g./liter of thiourea and potassium iodide may be added to the bath as oxidizing accelerators for the developed silver.

Since in the process of this invention, an anion of iron (III) monohydrogen ethylenediamine tetraacetate is used as the oxidizing agent in the bleach-stabilizing bath, the anion can be present at the same time with the solvent for the silver halide without reaction. The shelf life of the bleach-stabilizing bath is therefore considerably improved in comparison to baths wherein potassium ferricyanide is added as the oxidizing agent. The oxidizing ability of iron (III) monohydrogen ethylenediamine tetraacetate is weaker than that of potassium ferricyanide, but by employing a proper oxidizing accelerator, the oxidizing ability may be maintained at the necessary level.

When the stabilizing bath of this invention is used, no further treatment is necessary, which is a particularly desirable aspect of this invention. Furthermore, the process of this invention permits the use of ammonium thiosulfate as a stabilizing agent which is known as a fixing agent in conventional light-sensitive silver halide photographic materials. Ammonium thiosulfate can form a silver complex which is stable to dilution and is not converted into a light sensitive silver salt when it is brought into contact with water.

The rapid stabilizing process of the present invention not only eliminates the various disadvantages encountered in the conventional processes, but also provides a print having a better preservability since the stabilized print can be rinsed for a shorter time due to the stability of the silver complex to dilution.

The invention will be more fully explained by reference to the following examples, which are presented for purposes of illustration only and are not intended to be limiting in any manner.

EXAMPLE 1

The following emulsions were applied to a photographic baryta paper; a blue sensitive silver iodo-bromide emulsion containing a yellow color former [3,5-dicarboxy-2-(4-steroylamide benzoyl)acetanilide], a green sensitive silver chloro-bromide emulsion containing a magenta color former [1-(3-sulfo-4-phenoxyphenyl)-3-stearoyl-5-pyrazolone] and a red sensitive silver chlorobromide emulsion containing a cyan color former [N-n-octadecyl-1-hydroxy-4-sulfo-2-naphthamide] in the above order. The layer was then coated with a gelatin overcoat. In preparing the above emulsions, each of the color formers was added to the corresponding emulsion in thier alkaline aqueous solution.

The photographic light-sensitive color printing paper thus prepared was exposed to an image on a negative color film and thereafter developed for 60 seconds in a developing bath, at 40° C., having the following composition:

Solution A:

Ethylenediamine tetraacetic acid 2Na—2 g.
Sodium Carbonate (anhydrous)—84 g.
Potassium bromide—1 g.
Sodium sulfite—1 g.
Water—600 ml.

Solution B:

Hydroxylamine hydrochloride—2 g.
N-ethyl-N-β-hydroxyethyl-p-phenylene diamine sulfate—4.5 g.
Water—100 ml.

Solutions A and B were mixed immediately before use, and diluted with water to a total volume of 1 liter.

The color printing paper thus developed was immersed for 30 seconds in a stop bath containing 10 ml. of glacial acetic acid, and 20 grams of sodium acetate (anhydrous), and enough water to make a solution of 1 liter in volume, at 40° C.

The printing paper was then processed in a bleach-stabilizing bath at 40° C. for 20 seconds. The bath has the following composition:

Sodium salt of iron (III) monohydrogen ethylenediamine tetraacetate—10 g.
Sodium carbonate monohydrate—10 g.
Boric acid—45 g.
Ammonium thiosulfate, 69.9%—358 ml.
Thiourea—5 g.
Remainder—water to render 1 liter of solution

The stabilized print thus obtained was free from any residual silver image, and had an excellent color image. The print was highly stable to actinic radiation.

EXAMPLE 2

A light sensitive color printing paper prepared as in Example 1 was developed and stopped as in Example 1, and then processed for 60 seconds at 40° C., in a bleach-stabilizing bath having the following composition:

Sodium salt of iron (III) monohydrogen ethylenediamine tetraacetate—25 g.
Ammonium thiosulfate, 69.9%—172 ml.
Sodium thiosulfate—5 g.
Potassium dihydrogen phosphate—15 g.
Sodium bisulfite—2 g.
Potassium iodide—1 g.
Remainder—water to render 1 liter of solution

The stabilized print thus obtained had an excellent color image and showed high stability to actinic radiation.

EXAMPLE 3

A color printing paper prepared as in Example 1 was developed and stopped as in Example 1, and then processed for 40 seconds at 35° C. in a bleach-stabilizing bath having the following composition:

Sodium salt of iron (III) monohydrogen ethylenediamine tetraacetate—2 g.
Ammonium thiosulfate, 69.9%—570 ml.
Sodium carbonate monohydrate—10 g.
Sodium bisulfite—45 g.
Thiourea—9 g.
Remainder—water to render 1 liter of solution

The stabilized print thus obtained showed the same excellent characteristics as that of Example 1.

What is claimed is:

1. A method for rapidly developing an exposed photographic material comprising differently sensitized gelatino-silver halide emulsions containing color formers capable of reacting with the oxidation product of a primary aromatic amine to form a dye, which process comprises placing said exposed material into a developing bath containing a primary aromatic amine developing agent, arresting the developing process by passing said material through a stop bath, bleach-stabilizing said material with a bath containing an anion of an iron (III) monohydrogen ethylenediamine-N,N,N',N'-tetraacetate and ammonium thiosulfate, and immediately thereafter drying said material.

2. The method of claim 1 wherein said developing agent is a p-phenylenediamine in which two hydrogens on one of the amine groups is substituted with lower alkyl groups.

3. The method of claim 1 wherein said developing agent is selected from the group consisting of N-ethyl-N-β-hydroxyethyl-p-phenylenediamine, N-N-diethyl-2-methyl-p-phenylene-diamine and N-ethyl-N-(methanesulfoneamidoethyl)-2-methyl-4-aminoaniline.

4. The method of claim 1 wherein said developing bath contains an antitoxidant.

5. The method of claim 1 wherein said bleach-stabilizing bath is prepared from ferric chloride and sodium ethylenediamine tetraacetate.

6. The method of claim 1 wherein said anion is present in an amount of between 1–50 g./liter.

7. The method of claim 1 wherein the ammonium thiosulfate is used in an amount of between 100–500 g./liter.

8. The method of claim 1 wherein the bleach-stabilizing bath is maintained at a pH of between 4 and 8.

9. The method of claim 1 wherein the bleach-stabilizing bath contains between 0.3–10 g./liter of thiourea and potassium iodide as oxidizing accelerators.

10. The method of claim 1 wherein said photographic material is placed in a bleach-stabilizing bath for 20 seconds at 40° C. wherein said bath comprises the sodium salt of iron (III) monohydrogen ethylenediamine tetraacetate, sodium carbonate monohydrate, boric acid and 69.9% ammonium thiosulfate.

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NORMAN G. TORCHIN, Primary Examiner

A. T. SUROPICO, Assistant Examiner

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