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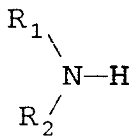
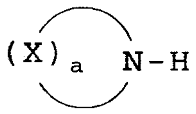
(54) Stabilizing solution for use in photographic processing.

(57) A stabilizing solution includes an aldehydic dye stabilizing agent and a soluble secondary amine in an amount sufficient to activate an aldehydic dye stabilizing agent. The secondary amine has the formula:



$$R_1R_2N{-}H$$

wherein each of R_1 and R_2 is an alkyl group having four or fewer carbon atoms, an aromatic group, a substituted aromatic group or an alkyl group containing solubilizing substituents and having up to seven carbon atoms or has the formula:



wherein the cyclic group has four to six carbon atoms, X is an oxygen or nitrogen atom and a is 0 or 1.

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Technical Field

This invention relates to silver halide photographic elements and, in particular, to compositions of a stabilizing solution which provide enhanced dye stability.

Prior Art

The processing of silver halide photographic elements generally involves the steps of color evolution, bleaching, fixing, stabilizing and drying. The stabilizing bath is used as the final step in the processing of photographic elements in order to reduce stain and/or to enhance dye stability. The stability of the dye image is believed to be affected by the presence of unreacted coupler in the emulsion layers, because the coupler and the dye can react slowly with one another in a redox reaction to degrade the color image. In particular, the image from magenta dye tends to fade much more rapidly than either the cyan or the yellow dye image. Stabilizing solutions are aqueous formulations that contain a compound which reacts with the residual dye coupler in the emulsion layer to deactivate it and prevents its reaction with the dye and subsequent degradation of the color image.

The present invention is particularly concerned with aldehydic dye stabilizing agents. Formaldehyde is a preferred aldehydic dye stabilizing agent because of its high volatility. Any residual formaldehyde on the photographic element is readily removed in a drying step. However in recent years concerns over the hazardous effects of formaldehyde have led to increased efforts in developing alternative dye stabilizing agents or in reducing the amount of formaldehyde used in the stabilizing solution without compromise to the stabilizing solution performance.

Assessment of the Art

It is an object of the present invention to provide novel aldehyde-based dye stabilizing solutions which can replace formaldehyde without negatively affecting dye stabilization.

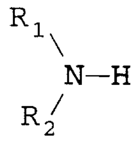
It is a further object of the present invention to provide a stabilizing solution having significantly reduced amounts of formaldehyde without negatively affecting dye stabilization.

Summary of the Invention

In accordance with the invention, a novel stabilizing solution is used to provide dye stability to photographic elements. The stabilizing solution advantageously prevents dye fade by deactivating the dye coupler remaining in the processed photographic elements. An aqueous stabilizing solution comprises an aldehydic dye stabilizing agent and a secondary amine in an amount sufficient to activate the aldehydic dye stabilizing agent. The use of a secondary amine in the stabilizing solution is based on the discovery that it activates the reaction between the aldehydic stabilizing agent and the dye coupler. By activating the aldehydic dye stabilizing agent, the rate of coupler deactivation is increased, thereby permitting use of reduced levels of dye stabilizing agent without compromise to the dye stabilizing properties of the solution or, alternatively, permitting use of aldehydic dye stabilizing agents containing higher aldehydes that were heretofore insufficiently active with respect to dye stabilization.

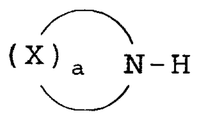
The term "secondary amine" is used herein in the conventional sense that the amine contains two nitrogen-carbon bonds, that is, $N(C\text{-}X)_2H$, where X is any substituent. By "higher aldehydes", as that term is used herein, it is meant aldehydes possessing a substituent group containing at least one carbon atom. By "reduced levels" as that term is used herein, it is meant that the amount of aldehydic dye stabilizing agent used in the stabilizing solution in the presence of a secondary amine is less than the amount that would be required to stabilize the dye in the absence of a secondary amine. By "insufficiently active", as that term is used herein, it is meant that the coupler deactivation reaction either does not occur at a perceptible rate or proceeds too slowly under the processing conditions described herein to be of practical use. The terms "activity" and "activation" are used herein with reference to the rate of dye coupler deactivation.

In preferred embodiments, the secondary amine has the formula:



wherein each of R_1 and R_2 is an alkyl group, a substituted alkyl group, an aromatic group or a substituted aromatic group. The alkyl group may contain four or fewer carbon atoms. The substituted alkyl group may have solubilizing moieties, in which case there may be up to seven carbon atoms in the alkyl group. A most preferred amine is diethanolamine.

In another preferred embodiment, the secondary amine is a cyclic amine having the formula:



wherein the cyclic group contains four to six carbon atoms, X is an oxygen or nitrogen atom and a is 0 or 1. Most preferably, the cyclic amine is morpholine or piperidine.

In yet another preferred embodiment, a solubilizing agent is added to the solution in an amount sufficient to solubilize the secondary amine. Preferred solubilizing agents include co-solvents such as ethylene glycol and diethylene glycol.

Detailed Description of the Invention

The stabilizing solution of this invention can be used to provide improved dye stability with any of a wide variety of color photographic elements. Thus, for example, the stabilizing solution can be advantageously employed in the processing of photographic elements designed for reversal color processing or in the processing of negative color elements or color print materials. The stabilizing solution can be employed with photographic elements which are processed in color developers containing couplers or with photographic elements which contain the coupler in the silver halide emulsion layers or in layers contiguous thereto. The photosensitive layers present in the photographic elements processed according to the method of this invention can contain any of the conventional silver halides as the photosensitive material, for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, and mixtures thereof. These layers can contain conventional addenda and be coated on any of the photographic supports, such as, for example, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polycarbonate film, polystyrene film, polyethylene terphthalate film, paper, polymer-coated paper, and the like.

The photographic elements which are advantageously treated with the stabilizing solution of this invention are elements comprising a support having thereon at least one, and typically three or more, hydrophilic colloid layers containing a dye image. Any of a wide variety of colloids can be utilized in the production of such elements. Illustrative examples of such colloids include naturally occurring substances such as proteins, protein derivatives, cellulose derivatives, for example, cellulose esters, gelatin, for example, alkali-treated gelatin (cattle bone or hide gelatin) or acid treated gelatin (pig-skin gelatin), gelatin derivatives - for example, acetylated gelatin, phthalated gelatin and the like, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodion, agar-agar, arrowroot albumin and the like.

In the production of color photographic images, it is necessary to remove the silver image, which is formed coincident with the dye image. This can be done by oxidizing the silver by means of a suitable oxidizing agent, commonly referred to as a bleaching agent, in the presence of halide ion followed by dissolving the silver halide so formed in a silver halide solvent, commonly referred to as a fixing agent. Alternatively, the bleaching agent and fixing agent can be combined in a bleach-fixing solution and the silver removed in one step by use of such solution.

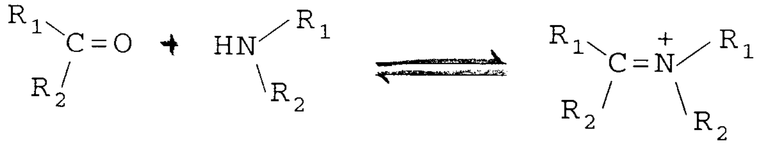
Color print papers are most commonly processed by use of a bleach-fixing solution. Color negative films are most commonly processed by use of separate bleaching and fixing solutions. The bleaching agent is typically a ferric complex of an aminopolycarboxylic acid, for example, the ferric complex of ethylenediaminetetraacetic acid (EDTA) or the ferric complex of 1,3-propylenediaminetetraacetic acid

(PDTA) or a mixture of the ferric complex of EDTA and the ferric complex of PDTA. The fixing agent is typically a thiosulfate, such as sodium thiosulfate or ammonium thiosulfate, or a thiocyanate, such as ammonium thiocyanate, or a mixture of a thiosulfate and a thiocyanate.

Processes employing the stabilizing solution of this invention can vary widely in regard to the particular processing steps utilized. For example, the process can comprise only the two steps of color developing and bleach-fixing, followed by the stabilizing step, or it can comprise the three steps of color developing, bleaching, and fixing, followed by the stabilizing step. Alternatively, it can be a color reversal process in which the processing baths utilized are a first developer, a reversal bath, a color developer, a bleach, and a fix, followed by the stabilizing bath.

The stabilizing solution of the present invention prevents dye fade by providing a dye stabilizing agent which deactivates the dye coupler remaining in the photographic element after treatment as described above. Use of a secondary amine in the stabilizing solution serves to enhance the activity of the aldehydic dye stabilizing agent. The secondary amine interacts with the aldehydic dye stabilizing agent to form a highly reactive, positively charged intermediate which, in turn, readily reacts with and thereby deactivates the dye coupler. It has been discovered that secondary amines are effective catalysts for reactions of the aldehydic dye stabilizing agent with the dye coupler. The reaction may involve the intermediate formation of a cationic Schiff base according to eq. 1. An uncharged Schiff base intermediate which is less reactive does not form when using a secondary amine.

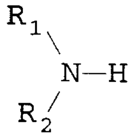
(1)



According to the invention, an increase in the rate of magenta dye coupler deactivation by the aldehydic dye stabilizing agent was observed in the presence of a secondary amine. A five-fold increase in the rate of magenta dye coupler deactivation was observed for formaldehyde. The increased rate of dye coupler deactivation permits a five-fold decrease in the formaldehyde level without degradation of the stabilizing solution properties. Reduced formaldehyde levels are highly desirable due to the growing concerns regarding the health hazards of formaldehyde. Typical prior art stabilizing solutions have formaldehyde levels ranging from 0.75 to 2.0 g/L. The stabilizing solution of the present invention possesses acceptable dye stabilizing performance with formaldehyde levels below 0.5 g/L and preferably in the range of 0.1-0.5 g/L. The secondary amine can be used at levels approximately at least one tenth the molar concentration of the dye stabilizing agent and typically in the range 0.05 to 0.20 the molar concentration of the dye stabilizing agent.

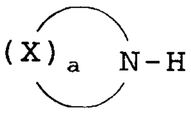
Higher aldehydes in general are not as reactive as formaldehyde in dye coupler deactivation reactions. For example, no acceptable level of activity is observed with acetaldehyde in the absence of a secondary amine unless the process is carried out with high excesses of the aldehyde. According to the invention, the addition of a secondary amine increases the activity of the aldehyde, which is defined as the rate of the dye coupler deactivation, so that the claimed aldehydes can be used under the processing conditions described hereinabove. The aldehyde is present at its solubility limit or preferably at a level of 5.0 g/L. The secondary amine is present at a level sufficient to activate the aldehyde. Typically, the amine is approximately one tenth the molar concentration of the aldehyde. The amine may be used at a concentration in the range of 0.05 to 1.00 g/L.

The amine can be any secondary amine that is soluble in the stabilizing solution. Secondary amines that are preferred for use in the stabilizing baths of this invention have the formula:



wherein each of R_1 and R_2 is an alkyl group, a substituted alkyl group, an aromatic group or a substituted aromatic group. Solubility of the amine in the stabilizing solution is obtained in several ways. If the alkyl group is nonpolar, it should contain four or fewer carbon atoms. However, if the substituted alkyl group contains solubilizing substituents, the amount of carbon atoms in the alkyl group can increase to seven. Solubilizing substituents can include, for example, hydroxy, sulfoxy and carboxyl groups. Diethanolamine is a preferred secondary amine.

Other preferred secondary amines are cyclic amines having the formula:



wherein the cyclic group contains four to six carbon atoms, X is an oxygen or nitrogen atom and *a* is 0 or 1. Cyclic amines are particularly preferred because the reduced steric hindrance associated with cyclic compounds promotes the formation of the reactive intermediate. Preferred cyclic amines include morpholine and piperidine.

Any of the well known aldehydic dye stabilizing agents can be used in the stabilizing solution of the invention. Secondary amines have been found to accelerate the reactions of most aldehydic dye stabilizing agents. Particularly useful agents include aliphatic aldehydes such as formaldehyde, paraformaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glutaraldehyde and valeraldehyde and aromatic aldehydes such as benzaldehyde, furfural, vanillin and anisaldehyde.

The ingredients utilized in making up the stabilizing solution of this invention can be used in any suitable amount and the optimum amount of each will vary widely depending on a number of factors such as the particular compounds employed, the manner of treating the photographic element with the stabilizing solution and the particular type of photographic element to be treated.

Other additives can also be incorporated into the stabilizing solution with beneficial results. Examples of useful additives include wetting agents, buffering agents and biocides. Wetting agents are particularly useful when processing color negative film to avoid water spotting. Organosiloxane wetting agents are especially beneficial. Biocides are useful to prevent microbial growth in both processes for color films and processes for color papers. A particularly useful class of biocides for this purpose are the thiazole compounds, especially isothiazolines such as 1,2-benzisothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, 2-octyl-4-isothiazolin-3-one and 5-chloro-N-methyl-4-isothiazolin-3-one.

The invention is further illustrated by the following examples.

Examples

Fresh solutions for the appropriate Color Developer, Bleach and Fix were prepared according to directions. A stabilizing solution was prepared as shown in Tables 1 and 2.

Screening tests were performed by developing KODAK VERICOLOR III Professional Film according to the standard process with the above solutions in lieu of the standard stabilizing solution. The developed film was evaluated by a liquid chromatographic method for determining residual dye coupler and by an accelerated image stability fade test to determine dye fade.

The accelerated dye fade test was accomplished by an oven keeping method in which the film is incubated to 77° C at 40% relative humidity to accelerate the redox reaction responsible for dye fade. The film is then evaluated against a neutral dye patch. Dye intensities are determined and reported in Table 1 as densities corrected to a density of 1.0. Negative numbers indicate a loss of dye intensity. Performances were judged by comparison to stabilizing solutions to control solutions.

Table 1

Exp. No.	formalin (mL/L)	Secondary amine, mL/L	density (corrected)[a]	[amine]/[CH_2O]
1	0.50	morpholine, 0.00	-16	0.00
2	0.50	morpholine, 0.01	-13	0.02
3	0.50	morpholine, 0.05	-4	0.09
4	0.50	morpholine, 0.07	0	0.13
5	0.75	morpholine, 0.07	-7	0.09
6	1.00	morpholine, 0.07	+1	0.06
7	1.25	morpholine, 0.07	+1	0.05
8	0.50	DEA[b], 0.00	-17	0.00
9	0.50	DEA, 0.05	-13	0.09
10	0.50	DEA, 0.07	-11	0.12
11	0.50	DEA, 0.09	-10	0.15
11	0.75	DEA, 0.09	-5	0.10
12	1.00	DEA, 0.09	-2	0.08
13	1.25	DEA, 0.09	+1	0.06
14[c]	5.00	-	0	-
15[d]	2.50	-	-1	-

[a] 1.0 above D_{min};
[b] DEA-diethanolamine;
[c] FLEXICOLOR Stabilizer;
[d] FLEXICOLOR Stabilizer II

Comparison of the experiments in Table 1 for reactions with formaldehyde illustrates the advantages of the invention. Formaldehyde levels are reported in Table 1 as mL/L of formalin, which is 37% w/w formaldehyde. Clearly, acceptable dye fade stability was obtained at significantly reduced levels of formaldehyde. Experiments 14 and 15 provide comparison to the standard stabilizing solutions (controls). The solution of experiment 1, with reduced formaldehyde level and no added amine, is clearly unacceptable. However, addition of even small amounts of the secondary amine, morpholine, (Exp. 3) resulted in stabilization of the dye coupler. At levels as low as 1.00 mL/L formaldehyde (see Exp. 5, 6 and 12), superior dye fade stabilization is observed. Overall, morpholine provided better dye fade stabilization than diethanolamine. This is consistent with the observation that cyclic secondary amines more greatly accelerate the deactivation reaction of the magenta dye coupler.

Table 2

Exp. No.	aldehyde[a]	amine[b] present	residual dye coupler (mg/ft^2)
16	acetaldehyde	no	51.7
17	acetaldehyde	yes	4.8
18	propionaldehyde	no	87.0
19	propionaldehyde	yes	42.6
20	butyraldehyde	no	33.0
21	butyraldehyde	yes	0.4
22	valeraldehyde	no	48.2
23	valeraldehyde	yes	1.1
24	blank[c]	no	160[d]
25	control[e]	no	1.0

[a] 5.0 g/L;
[b] morpholine at 0.1 mL/L;
[c] water;
[d] out of calibration limits;
[e] FLEXICOLOR Stabilizer

Comparison of the experiments in Table 2 for reactions with a variety of higher aldehydes further illustrates the advantages of the invention. All higher aldehydes were used at a level of 5.0 g/L. Morpholine was used in all the experiments shown in Table 2 because it had worked best with formaldehyde (see Table 1). All of the aldehydes tested showed some capability in removing residual dye coupler from the photographic element, as evidenced by the reduced residual dye coupler as compared to a blank sample (#24). Both acetaldehyde and butyraldehyde in the presence of morpholine exhibited significantly improved dye stabilization as compared to samples without morpholine. Butyraldehyde, in particular, showed performance that equaled the current stabilizing solution.

Claims

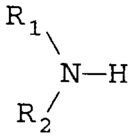
1. An aqueous stabilizing solution for use in the color processing of photographic elements, comprising:
   an aldehydic dye stabilizing agent; and
   a secondary amine, the secondary amine being present in an amount sufficient to activate the aldehydic dye stabilizing agent to effect dye stabilization.

2. The aqueous stabilizing solution of claim 1 characterized in that the aldehydic dye stabilizing agent is formaldehyde, formaldehyde being present at a level of less than 0.5 g/L.

3. The aqueous stabilizing solution of claim 1 characterized in that the aldehydic dye stabilizing agent is a higher aldehyde, the higher aldehyde present at its solubility limit.

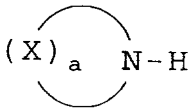
4. The aqueous stabilizing solution of claim 1, 2, or 3 characterized in that the secondary amine is present at a level at least one tenth in molar ratio to the aldehydic dye stabilizing agent.

5. The aqueous stabilizing solution of claim 1, 2, or 3 characterized in that the secondary amine has the formula I or II:



I

wherein each of R_1 and R_2 is an alkyl group, a substituted alkyl group, an aromatic group or a substituted aromatic group;



II

wherein the cyclic group has four to six carbon atom, X is an oxygen or nitrogen atom and a is 0 or 1.

6. The aqueous stabilizing solution of claim 5 characterized in that the alkyl group of the secondary amine of formula I contains 4 or fewer carbon atoms.

7. The aqueous stabilizing solution of claim 1, 2, 3, 4 or 5 characterized in that the secondary amine is diethanolamine, morpholine, or piperidine.

8. The aqueous stabilizing solution of claim 1, further comprising:
   a solubilizing agent in an amount sufficient to solubilize the secondary amine which is not soluble in the aqueous solution.

9. The aqueous stabilizing solution of claim 8 characterized in that the solubilizing agent is a co-solvent.

10. The aqueous stabilizing solution of claim 8 characterized in that the solubilizing agent is selected from the group containing diethylene glycol and ethylene glycol.