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METHOD OF PREVENTING AERIAL OXIDATION AND COLOR STAIN

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This invention relates to photography and particularly to a method for preventing aerial oxidation of photographic developers and color strain in photographic emulsions.

The method of color photography in which color-forming or coupler compounds combine with the development product of aromatic amino photographic developers to produce dyes is well known. The color formers or couplers may be added directly to the emulsion layers or may be incorporated in the developing solution, as described in Fischer U. S. Patent 1,102,028, granted June 30, 1914 or they may be incorporated in a water-permeable medium which is insoluble in the carrier for the silver halide, as described in Mannes & Godowsky U. S. Patent 2,304,940, granted December 15, 1942 and Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943.

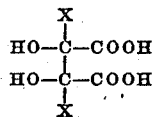
A difficulty frequently encountered in these processes is the formation of color fog or stain. When the exposed material is developed in a color forming developer, dye fog is frequently formed in the emulsion layer. This is because the developing agent has been oxidized to some extent by the action of the air and the oxidized developer tends to couple with the color-forming compound at places in the photographic material where no silver image is produced. It is well known that in these processes the dye should be formed only where the silver halide is reduced to metallic silver thereby oxidizing the developing agent to a form which couples with the color former. Once the developing agent is oxidized, it couples immediately with the color former whether a photographic image is present or not. Aerial oxidation of the developer or oxidation by means other than the photographic image therefore converts the developer to a form which will immediately react with the color former to produce a color fog or stain. This effect is especially noticeable in materials having couplers incorporated in the sensitive emulsion layer since there is no coupler in the developing solution to react with any developing agent which is oxidized by the action of the air. Fog or stain arising from these causes is not readily controlled by the same procedures used to control silver fog.

Methods for controlling color fog or stain have been described in Vittum and Wilder U. S. Patent 2,360,290 granted October 10, 1944 and in our prior Patent 2,356,486 granted August 22, 1944. Some of the compounds disclosed in these prior applications, when used to prevent aerial oxidation or color fog, cause a reduction in the

amount of dye image produced and some of the compounds, when incorporated in the sensitive emulsion, tend to render the resulting dye image unstable to the action of light.

It is, therefore, an object of the present invention to provide a novel means of reducing or eliminating the formation of color fog in photographic emulsions. A further object is to provide a novel means for reducing or eliminating the aerial oxidation of photographic developers. A still further object is to provide stain inhibitors for incorporation in photographic developing solutions or prebaths used prior to color-forming development. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating in the photographic developing solution or in a prebath used prior to color development, dihydroxy tartaric acid or dinitro tartaric acid or a salt, ester, or amide of these compounds. The compounds which we proposed to use have the following general formula:



where X is a hydroxyl group or a nitro group.

The salts of these compounds include the alkali metal salts such as the sodium salt. Esters may be used such as the methyl or ethyl esters of dihydroxy tartaric acid or dinitro tartaric acid. Amide derivatives of these compounds include the reaction products of these acids with an amine such as aniline. The action of dihydroxy tartaric acid may be due to their reaction products with the aqueous alkaline solutions, e. g., tartronic acid.

We have found that the aerial oxidation of both black and white and color developers may be appreciably reduced by adding to the developing solution a dihydroxy tartaric acid or dinitro tartaric acid or one of their salts, esters or amides. When used in color forming developers, these compounds also appreciably reduce the amount of color fog or stain produced in the emulsion, especially where the coupler compound is incorporated in the emulsion layer. It is believed that these compounds exert an antioxidant action either by preventing the formation of extraneous oxidized developer or by reducing any oxidized developer before it has an opportunity to react with the color former.

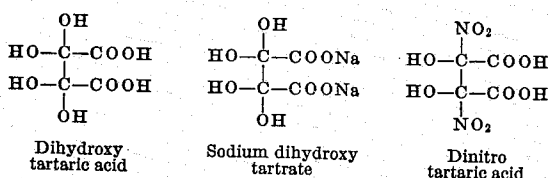
Whatever the mechanism of the reaction, we have found it possible to reduce markedly the fog or stain density without seriously reducing the densities of the developed dye images.

The agents used according to our invention may also be incorporated in the sensitive emulsion itself, such as one or more of the emulsion layers of a multi-layer coating. The stain preventing agent may be distributed uniformly throughout the emulsion or where it is intended to be non-diffusing in the gelatin an ester of an aliphatic alcohol containing at least five carbon atoms is preferably used. When incorporated in the emulsion, the stain inhibitor may be incorporated in the gelatin itself or in the water-permeable, water-insoluble coupler containing media such as described in Mannes & Godowsky U. S. Patent 2,304,940 and Jelley and Vittum U. S. Patent 2,322,027.

The stain inhibitors may also be incorporated in nonsensitive layers of the photographic material such as filter layers, interlayers or overcoating layers.

Where the stain inhibitor is used in a prebath prior to color development, it should be of such low molecular weight that it diffuses into the emulsion layer and it must be retained in the emulsion layer until color development begins. The photographic material should, accordingly, be bathed in a solution of the stain inhibitor just prior to the color development step. A similar result is obtained by incorporating the inhibitor in the color forming emulsion itself and stain prevention may, therefore, be accomplished by incorporating the inhibitor in a prebath just prior to color development or in the color developing solution itself.

The following compounds are suitable for use according to our invention:



When incorporated in a prebath or in a developing solution, these compounds are used in amounts ranging from about 1 gram to about 5 grams per liter of solution. More or less than these amounts may be employed but in general less than 1 gram produces very little result and the solubility limit is reached in the neighborhood of 5 grams per liter.

Our invention will be further illustrated by reference to the following specific examples:

Example 1

The following formula is a standard hydroquinone developer containing one of the inhibitors according to our invention:

Hydroquinone	grams	11.25
Sodium bisulfite	do	11.25
Potassium bromide	do	11.25
Sodium hydroxide	do	26.25
Sodium dihydroxy tartrate	do	5
Water to	liter	1

The sodium dihydroxytartrate was not completely dissolved in these developers but the solution displayed improved properties with respect to aerial oxidation.

Example 2

The following example illustrates the incorporation of our compounds in a staining pyrogallol developer:

Pyrogallol	grams	2.8
Sodium sulfite (anhydrous)	do	1.4
Sodium carbonate (anhydrous)	do	5.3
Dinitro tartaric acid	do	5
Water to	liter	1

Example 3

The following formula is suitable as a prebath for use just prior to color-forming development:

Sodium sulfite (desiccated)	grams	5
Sodium carbonate (monohydrate)	do	20
Potassium bromide	do	5
Sodium dihydroxytartrate	do	1
Water to	liter	1

Example 4

The following formula illustrates a color developer containing one of our inhibitors:

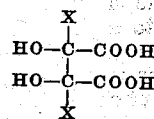
2-amino-5-diethylamino toluene HCl	grams	3
Sodium sulfite (desiccated)	do	20
Sodium carbonate (monohydrate)	do	10
Sodium metaborate	do	40
Potassium bromide	do	1
Dinitro tartaric acid	do	2
Water to	liter	1

Our process is particularly useful with paper materials where it is especially important to reduce the minimum or fog densities. This applies both to negative developing paper and to reversal paper as well as transparency materials.

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

We claim:

1. A photographic developing solution having a reduced tendency toward aerial oxidation, comprising a photographic developing agent and a compound soluble in said developing solution selected from the group consisting of dihydroxy tartaric acid, dinitro tartaric acid, and the salts, esters and amides of said acids.
2. A photographic developing solution having a reduced tendency toward aerial oxidation comprising a photographic developing agent and a compound having the following general formula:



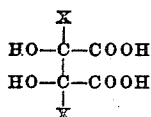
where X is selected from the class consisting of hydroxyl and nitro groups.

3. A photographic developing solution having a reduced tendency toward aerial oxidation comprising a photographic developing agent and sodium dihydroxytartrate.
4. A photographic developing solution having a reduced tendency toward aerial oxidation comprising a photographic developing agent and dinitro tartaric acid.

5. The method of preventing the formation of color fog in a photographic silver halide emulsion which is developed by a color forming development step, comprising subjecting said emulsion to the color forming development in the presence of a compound soluble in the developing solution selected from the group consisting of dihydroxy

tartaric acid, dinitro tartaric acid and the salts, esters and amides of said acids.

3. The method of preventing the formation of color fog in a photographic silver halide emulsion which is developed by a color forming development step, comprising subjecting said emulsion to the color forming development in the presence of a compound having the general formula:



where X is selected from the class consisting of hydroxyl and nitro groups.

7. The method of preventing the formation of color fog in a photographic silver halide emulsion which is developed by a color forming development step, comprising subjecting said emulsion to the color-forming development in the presence of sodium dihydroxy tartrate.

8. The method of preventing the formation of color fog in a photographic silver halide emulsion which is developed by a color-forming development step, comprising subjecting said emulsion to the color forming development in the presence of dinitro tartaric acid.

9. A color-forming photographic paper developer capable of developing a colored image in the presence of a coupler compound, comprising a primary aromatic amino developing agent and a compound soluble in the developing solution selected from the group consisting of dihydroxy tartaric acid, dinitro tartaric acid and the salts, esters and amides of said acids.

10. A color-forming photographic developer capable of developing a colored image in the presence of a coupler compound, comprising a primary aromatic amino developing agent and sodium dihydroxy tartrate.

11. A color-forming photographic developer capable of developing a colored image in the presence of a coupler compound, comprising a primary aromatic amino developing agent and dinitro tartaric acid.

12. The method of preventing the formation of color fog in a silver halide emulsion which contains a non-diffusing coupler, comprising bathing said emulsion after coating and just prior to a color-forming development step in a solution of a soluble compound selected from the group consisting of dihydroxy tartaric acid, dinitro tartaric acid and the salts, esters and amides of said acids.

13. The method of preventing the formation of color fog in a silver halide emulsion which contains a non-diffusing coupler, comprising bathing said emulsion after coating and just prior to a color-forming development step in a solution of sodium dihydroxy tartrate.

14. The method of preventing the formation of color fog in a silver halide emulsion which contains a non-diffusing coupler, comprising bathing said emulsion after coating and just prior to a color forming development step in a solution of dinitro tartaric acid.

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