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PREVENTING FORMATION OF COLOR FOG
IN EMULSIONS

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This invention relates to color photography and particularly to a method for preventing the formation of color fog in photographic emulsions.

The incorporation of color forming components in silver halide emulsion layers was described by Fischer in U. S. Patent 1,102,028, granted June 30, 1914. These components are compounds such as phenolic hydroxyl compounds or compounds with reactive methylene groups, which are capable of reacting with the development product of aromatic amino photographic developers to produce dyes. The color formers may be added directly to the emulsion layers as described by Fisher or they may be incorporated in a separate medium which is insoluble in the carrier for the sensitive silver halide as described in Mannes and Godowsky U. S. Patent 2,304,940, granted December 15, 1942, and Jelley and Vittum U. S. Patent No. 2,322,027, granted June 15, 1943.

A difficulty frequently encountered in these processes is the formation of color fog or stain. With materials in which color forming compounds are incorporated in the sensitive layer, dye fog is formed along with the customary silver fog met in black and white photography but in addition fog is also formed from any oxidized developer formed by the action of air, oxidizing silver removal baths, etc. It is well known that in these processes the dye is formed when 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. Fog or stain arising from these causes is not readily controlled by the same procedures used to reduce or control silver fog.

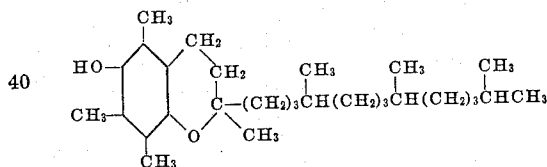
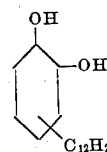
It is, therefore, an object of the present invention to provide a means for reducing or eliminating the formation of color fog in incorporated-coupler photographic emulsions. A further object is to provide a color forming photographic emulsion having non-diffusing couplers incorporated therein, which is less subject to the formation of color fog. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating in a photographic emulsion containing non-diffusing color formers, a non-coupling organic

ring compound having one or more hydroxyl substituents and functioning as a reducing agent. Our method is intended for use with emulsions which produce a negative image on development, whether they are used for direct exposure to a subject, or as a printing material for a negative or positive. Such materials may obviously be used to produce an image by reversal, but not to produce a positive image directly except after exposure to a negative. In the case of color-forming development, a colored negative image might be formed by direct development, or by reversal.

We have found that color fog or stain in incorporated coupler materials may be appreciably reduced by adding to the emulsion layers before coating or after coating and before processing a substance or substances having reducing properties as described above. It is believed that these substances exert an anti-oxidant action either by preventing the formation of extraneous oxidized developer or by reducing any extraneous oxidized developer before it has an opportunity to react with a color former. Whatever the mechanism of the reaction, we have found it possible in many cases to reduce markedly the fog or stain density without seriously damaging the densities of the dye developed images.

Compounds suitable for use according to our invention are hydroquinone and certain of its derivatives such as amyl hydroquinone, lauryl hydroquinone, heptyl hydroquinone, diamyl hydroquinone, and dioctyl hydroquinone. Other non-coupling organic carbon ring compounds containing at least one hydroxyl substituent which may be used are the following compounds:

 α -Tocopherol

Dodecyl catechol

55 The reducing agents used according to our invention may be incorporated in single layer coat-

ings or in one or more layers of a multi-layer coating. It may be desirable, for example, to have the reducing agent present in only one or two layers of a multi-layer coating and in this case a substance would be used which does not wander freely in gelatin such as lauryl hydroquinone or dioctyl hydroquinone. In cases where the reducing agent was desired to be uniformly distributed throughout the whole film, one might use compounds of lower molecular weight such as hydroquinone or its simple substitution products.

When the reducing agent is used with emulsions containing a coupler dissolved in agents insoluble in gelatin as in the processes described in Mannes and Godowsky Patent 2,304,940 and Jelley and Vittum Patent No. 2,322,027 it may be added either to the emulsion itself or to the coupler-carrier along with the coupler.

In general, the reducing agents are used in quantities ranging from 0.1 gram to 1.0 gram per liter of gelatin silver halide emulsion. These values are, however, only illustrative. As a specific example of the incorporation of a reducing agent into a silver halide emulsion containing coupler, the following is suitable: To 50 cc. of green sensitized silver bromide emulsion containing 0.25 gram of magenta coupler, 1-phenyl-3-pentadecyl-5-pyrazolone, there was added, before coating, 0.02 gram of diamyl hydroquinone.

Where it is desired to introduce the reducing agent after coating and before processing, the sensitive material may be bathed in an aqueous solution of the reducing agent such as the following pre-bath:

Hydroquinone-----	grams--	0.2
Potassium bromide-----	do-----	2.0
Sodium sulfite-----	do-----	2.0
Water to-----	cc--	1000

The reducing agent may be added to one of the film processing baths such as a prebath or the first developer bath. In the case of negative development as disclosed, for example, in Jelley and Vittum U. S. Patent 2,322,027, the first developer is a color-forming developer. The reducing agent may, therefore, be used in a color-forming developer such as a diethyl-p-phenylenediamine developer. Our method is intended for use principally with emulsions which produce a negative image upon direct development, that is, emulsions in which a negative image would be formed upon development after exposure under a positive image or in which positive images would be formed on direct development after exposure under a negative image. It may also be used for reversal color development.

Our process is particularly useful with paper materials, where it is especially important to reduce the minimum (fog) densities. This applies both to negative-developed paper and to reversal paper and transparency materials.

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

We claim:

1. A color forming photographic emulsion which produces a negative image on development, comprising a non-diffusing coupler incorporated therein and as an inhibitor of color fog a hydroquinone having a carbon chain of at least five carbon atoms.

2. A color forming photographic emulsion

which produces a negative image on development, comprising a non-diffusing coupler incorporated therein and as an inhibitor of color fog an amyl hydroquinone.

3. A color-forming photographic emulsion which produces a negative image on development, comprising a non-diffusing coupler incorporated therein and as an inhibitor of color fog amyl hydroquinone.

4. A color-forming photographic emulsion which produces a negative image on development, comprising a non-diffusing coupler incorporated therein and as an inhibitor of color fog lauryl hydroquinone.

5. The method of preventing the formation of color fog in a photographic silver halide emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising exposing said emulsion and developing it with a primary aromatic amino developing agent in the presence of a non-coupling hydroxy benzene.

6. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising incorporating in said emulsion as an inhibitor of color fog a non-coupling hydroxy benzene, exposing said emulsion and developing it with a primary aromatic amino developing agent.

7. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising incorporating in said emulsion as an inhibitor of color fog a non-coupling hydroxy benzene and a carbon chain of at least five carbon atoms, exposing said emulsion and developing it with a primary aromatic amino developing agent.

8. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising incorporating in said emulsion as an inhibitor of color fog a hydroquinone having a carbon chain of at least five carbon atoms.

9. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising incorporating in said emulsion as an inhibitor of color fog amyl hydroquinone.

10. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising incorporating in said emulsion as an inhibitor of color fog lauryl hydroquinone.

11. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising bathing said emulsion after exposure and before development in a solution of a non-coupling hydroxy benzene, and incapable of developing a visible image therein, and then developing said emulsion with a primary aromatic amino developing agent.

12. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising bathing said emulsion after exposure and before development in a solution of hydroquinone incapable of developing a visible image therein

and then developing said emulsion with a primary aromatic amino developing agent.

13. The method of preventing the formation of color fog in a photographic emulsion which produces a negative image on development and which contains a non-diffusing coupler therein, comprising bathing said emulsion after exposure and

before development in a solution containing about 0.2 gram per liter of hydroquinone, and then developing said emulsion with a primary aromatic amino developing agent.

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