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STAIN PREVENTION IN COLOR
PHOTOGRAPHY

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11 Claims. (Cl. 95—6)

This invention relates to color photography and particularly to a method for preventing the formation of color fog or stain 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 sensitive silver salt as described in Mannes & Godowsky U. S. Patent 2,304,940, 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.

One method for controlling color fog or stain has been described in Vittum and Wilder U. S. patent application Serial No. 404,894, filed July 31, 1941. One disadvantage of the method of that application is that some of the compounds, when incorporated in an emulsion containing a coupler, tend to render the resulting dye unstable to the action of light. While the color fog or stain produced on development is eliminated, the resulting dye is in some cases less stable than it would be without the stain inhibitor in the emulsion.

It is, therefore, an object of the present inven-

tion to provide a novel means for reducing or eliminating the formation of color fog in photographic emulsions. A further object is to provide a color-forming photographic emulsion having non-diffusing couplers incorporated therein which is not subject to the formation of color fog. A further object is to provide stain inhibitors for incorporation in photographic emulsion layers containing couplers which do not impair the stability of the dyes produced in the emulsion layer. Other objects will appear from the following description of our invention.

These objects are accomplished by subjecting an exposed photographic emulsion to a color-forming development in the presence of dihydroxy maleic acid or an ester or amine salt of dihydroxy maleic acid.

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 non-diffusing ester or amine salt of dihydroxy maleic acid. 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 to reduce markedly the fog or stain density without seriously reducing the densities of the developed dye images.

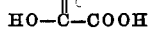
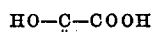
The agents used according to our invention may be incorporated in single layer coatings or in one or more layers of a multi-layer coating. It may be desirable, for example, to have the stain inhibitor present in only one or two layers of a multi-layer coating and in this case a substance would be used which does not wander frequently in gelatin. In cases where the reducing agent was desired to be uniformly distributed throughout the whole film, one might use compounds of lower molecular weight which diffuse to some extent throughout the film. When the inhibitor is intended to be non-diffusing in the gelatin, we preferably use a dihydroxy maleic acid ester of an aliphatic alcohol containing at least five carbon atoms.

When the stain inhibitor is used with emulsions containing a coupler dissolved in water-permeable, water-insoluble agents such as those described in Mannes and Godowsky U. S. Patent 2,304,940 and Jelley and Vittum, U. S. Patent 2,322,027, it may be added either to the emulsion itself or to the coupler-carrier along with the coupler.

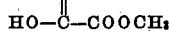
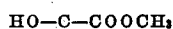
The stain inhibitors of our invention may also be incorporated in non-sensitive layers of the photographic material such as filter layers, inter-layer, and overcoating layers.

Where the stain inhibitor is introduced after coating and before processing, the photographic material should be bathed in a solution of the inhibitor just prior to the color development step. The inhibitor may be incorporated in a pre-bath prior to the color development step or in the development solution itself.

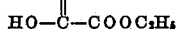
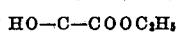
The following compounds are suitable for use according to our invention:



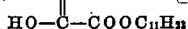
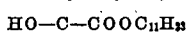
Dihydroxy maleic acid



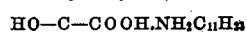
Dimethyl dihydroxymaleate



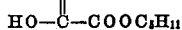
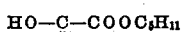
Dietethyl dihydroxymaleate



Dilauryl dihydroxymaleate



Laurylamine salt of dihydroxymaleic acid



Di-n-amyl dihydroxymaleate

The first three compounds are relatively soluble in water and may be used to reduce stain by incorporating them in a prebath or in a color developing solution. The latter three compounds are suitable for incorporation in the emulsion layer. When added to the emulsion layer, the stain inhibitors are usually employed in amounts of from $\frac{1}{16}$ to $\frac{1}{4}$ of the amount of coupler used although more or less of the stain inhibitor may be employed.

As a specific example of the incorporation of a stain inhibitor, according to our invention, in the sensitive emulsion layer 0.5 gram of dilauryl dihydroxy maleate may be added to the cellulose nitrate solution of Example 1 of Mannes and Godowsky U. S. Patent 2,304,940 and the emulsion prepared in the manner described in that example.

The following formula is suitable for a pre-bath of the stain inhibitor to be used prior to the color-forming development step if the inhibitor is not incorporated in the sensitive material:

Dihydroxymaleic acid-----	gram--	0.5
Sodium sulfite-----	do-----	2.0
Potassium bromide-----	do-----	5.0
Water to-----	cc--	1000

The colored photographic material is treated for one or two minutes in the prebath immediately before the color development step.

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 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 silver halide emulsion comprising a non-diffusing color coupler incorporated therein and, as an inhibitor of color fog, a dihydroxy maleic acid ester of an aliphatic alcohol containing at least five carbon atoms.
2. A color-forming photographic silver halide emulsion comprising a non-diffusing color coupler incorporated therein and, as an inhibitor of color fog, di-n-amyl-dihydroxy maleate.
3. A color-forming photographic silver halide emulsion comprising a non-diffusing color coupler incorporated therein and, as an inhibitor of color fog, dilauryl-di-hydroxymaleate.
4. 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 dihydroxy maleic acid selected from the class consisting of the free acid and the esters and amine salts of said 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 an ester of di-hydroxy maleic acid.
6. 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 an amine salt of dihydroxy maleic acid.
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 dihydroxy maleic acid.
8. The method of preventing the formation of color fog in a gelatino-silver halide emulsion which contains a non-diffusing color coupler comprising incorporating in said emulsion as an inhibitor of color fog a dihydroxy maleic acid ester of an aliphatic alcohol containing at least five carbon atoms.
9. The method of preventing the formation of color fog in a gelatino-silver halide emulsion which contains a non-diffusing color coupler, comprising incorporating in said emulsion as an inhibitor of color fog di-n-amyl-di-hydroxy maleate.
10. The method of preventing the formation of color fog in a photographic silver halide emulsion which contains a non-diffusing color coupler comprising bathing said emulsion after coating and just prior to a color-forming development step in a solution of a dihydroxy maleic acid selected from the class consisting of the free acid and its soluble esters.
11. The method of preventing the formation of color fog in a photographic silver halide emulsion which contains a non-diffusing color coupler comprising bathing said emulsion after coating and just prior to a color forming development step in a solution of dihydroxy maleic acid

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