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PROCESS FOR AVOIDING COLOR FOG ON PHOTOGRAPHIC COLOR MATERIAL

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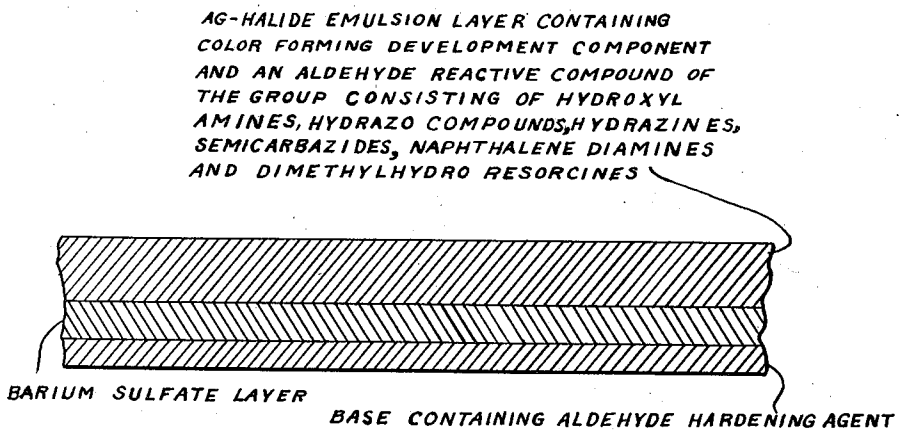

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PROCESS FOR AVOIDING COLOR FOG ON PHOTOGRAPHIC COLOR MATERIAL

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12 Claims. (Cl. 95—8)

This invention relates to a process for avoiding color-fog on photographic color material.

It is customary to use formaldehyde almost exclusively for the hardening of photographic emulsion layers, especially also of photographic papers. Also when manufacturing raw-paper and casting the bariumsulfate layer for photographic paper, formaldehyde is employed. If black- and-white-images are produced in such layers, the traces of formaldehyde remaining in the photographic material are not disturbing. It was found, however, that traces of formaldehyde influence considerably the whites of photographic emulsion layers containing color formers. The cause for it lies in the reactivity of the formaldehyde and other aldehydes with the color formers serving for the production of the color image. Pyrazolones for instance react with formaldehyde and oxidizing substances with the formation of intensely yellow-colored compounds. Since slight traces of formaldehyde are sufficient to produce the undesired color-fog, it is extremely difficult to eliminate the formaldehyde in the manufacturing process to such an extent, that no detrimental consequences appear.

It is an object of this invention to produce photographic color materials being free from color-fog.

Another object is the manufacture of photographic color paper which is free from color-fog.

These and other objects will become apparent from the following specification.

It has been found that it is possible to avoid the undesired color-fog in color photographic material containing color components in the photographic emulsion layers, if there be incorporated into the light sensitive emulsion layers, into the support of the emulsion layer, into the intermediate or backing layers, substances which react with aldehydes.

In selecting the substances which react with the formaldehyde, care must be taken, that no harmful effect is exerted on the emulsion. These substances for instance must not produce any fog in the emulsion nor decrease its sensitivity nor precipitate or deluster the emulsion. Suitable substances are for instance hydroxyl amines, hydrazine derivatives, for instance hydrazine-sulfo acid, hydrazine dicarboxylic acid ethyl ester, m-methylhydrazine, α-quinolylhydrazine, cyanacetylhydrazine, hydrazo derivatives, for instance hydrazoisobutyro nitrile, semicarbazides, for instance semi-carbazide hydrochloride, 1,4-phenylsemicarbazide, dimethylhydroresorcin and naphthylene diamines, for instance 1,8-naphthylene diamine-4-sulfo acid.

The photographic emulsion layers contain color formers reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, preferably those fast to diffusion according to the following U. S. patents: 2,178,612, 2,179,238, 2,179,244, 2,186,732, 2,186,849, 2,186,850 and 2,280,772; and U. S. application Ser. No. 327,628, filed April 3, 1940, applied for on behalf of Frölich et al.

The invention is further illustrated by the following example when taken with the accompanying self-explanatory drawing depicting in section a film according to the present invention.

To 1 kg. silver halide emulsion containing a pyrazolone derivative as color former there is added 1–2 grams of semicarbazide hydrochloride. This mixture is cast onto a support in a manner known per se.

Neither during the manufacturing process nor during prolonged storage could a color-fog be observed on these emulsion layers.

What we claim is:

1. In a method of processing photographic color material comprising a support carrying a silver halide emulsion layer containing a color former reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, and an aldehyde hardening agent for the emulsion tending to react with said color former to produce color fog, the improvement which comprises inhibiting the formation of said color fog by contacting said color material with an organic substance reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semicarbazides, naphthalene diamines, and dimethylhydroresorcines.

2. Photographic color material comprising a support carrying a silver halide emulsion layer containing a color former reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, and an aldehyde hardening agent tending to react with said color former to produce color fog, said material also containing an organic substance reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semicarbazides, naphthalene diamines, and dimethylhydroresorcines.

3. A photographic material for color forming development comprising a support layer, at least

one silver halide emulsion layer containing a color former reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, at least one intermediate layer, and a backing layer, at least one of said layers containing traces of an aldehyde hardening agent having the tendency to produce color fog with said color former, at least one of said layers containing a compound reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semi-carbazides, naphthalene diamines, and dimethyl-hydroresorcines.

4. A photographic material for color forming development comprising a support layer substantially consisting of a paper support and a barium sulfate layer, at least one silver halide gelatin emulsion layer containing a color former reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, at least one intermediate layer, and a backing layer, said paper support and said emulsion layer containing traces of an aldehyde hardening agent having the tendency to produce color fog with said color former said paper support additionally containing a compound reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semi-carbazides, naphthalene diamines, and dimethyl-hydroresorcines.

5. A photographic material for color forming development comprising a support layer substantially consisting of a paper support and a barium sulfate layer, at least one silver halide gelatin emulsion layer containing a color former reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, at least one intermediate layer and a backing layer, said barium sulfate layer and said emulsion layer containing traces of an aldehyde hardening agent having the tendency to produce color fog with said color former, said barium sulfate layer additionally containing a compound reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semi-carbazides, naphthalene diamines, and dimethylhydroresorcines.

6. A multi-color photographic paper comprising a gelatino silver halide emulsion layer which contains a color former reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, a barium sulfate layer and a paper support for the photographic emulsion and said barium sulfate layer, said photographic paper containing in at least one of said layers an aldehyde hardening agent tending to react with the color former to produce color fog, and said gelatino silver halide emulsion also containing an organic substance reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semi-carbazides, naphthalene diamines and dimethyl-hydroresorcines.

7. Multi-color photographic paper comprising a gelatino silver halide emulsion layer containing a color former reactive with the oxidation products of an aromatic developer to form a dye in situ with the silver image, a barium sulfate layer, and a paper support for the photographic emulsion and the barium sulfate layer, said photographic material containing in at least one of said layers an aldehyde-hardening agent tending to react with the color former to produce color fog, said barium sulfate layer containing an organic substance reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semi-carbazides, naphthalene diamines, and dimethylhydroresorcines.

8. A multi-color photographic paper comprising a gelatino silver halide emulsion layer containing a color former reactive with the oxidation products of an aromatic amino developer to form a dye in situ with the silver image, a barium sulfate layer, at least one of said layers containing an aldehyde hardening agent, tending to react with the color former to produce color fog, said paper support containing an organic substance reactive with the aldehyde hardening agent and selected from the class consisting of hydroxyl amines, hydrazines, hydrazo compounds, semi-carbazides, naphthalene diamines, and dimethyldroresorcines.

9. The process as defined in claim 1 wherein the organic substance reactive with the aldehyde hardening agent is a semi-carbazide.

10. The article as defined in claim 2 wherein the organic substance reactive with the aldehyde hardening agent is a semi-carbazide.

11. The article as defined in claim 2 wherein the organic substance reactive with the aldehyde hardening agent is a semi-carbazide and the color former is a pyrazolone.

12. The article as defined in claim 2 wherein the organic substance reactive with the aldehyde hardening agent is semi-carbazide hydrochloride and the color former is a pyrazolone.

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CERTIFICATE OF CORRECTION.

Patent No. 2,309,492. January 26, 1943.

FRITZ ALBERS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 38-39, claim 8, for "dimethyldroresorcines" read --dimethylhydroresorcines--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of December, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.