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PRODUCTION OF COLORED DIRECT-POSITIVE IMAGES

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Int. Cl. G03c 1/40, 5/24
U.S. Cl. 96—100 15 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to the production of colored direct-positive images in light-sensitive silver halide emulsions containing aromatic 1,2-dihydrazones in soluble, diffusion-resistant form stabilized by an additional content of an aliphatic aromatic hydroxyl derivative.

The process for the production of direct positive color-photographic images by means of photographic silver halide emulsion layers containing aromatic 1,2-dihydrazones is described in British patent specification 916,657. In this process the aromatic 1,2-dihydrazones remain unchanged at the unexposed areas of the silver halide emulsion layers during color-forming development with primary aromatic amines of the p-phenylendiamine type, for example 4-aminodiethyl aniline, and are then oxidized to form colored compounds in a bleaching bath by means of alkali metal ferricyanide, while at the exposed areas the dihydrazones react with the oxidation products of the color-forming developer to form colorless or almost colorless compounds which are stable against oxidation by ferricyanide ions. The above process is of limited utility, since many formulations are not sufficiently stable when the photographic material is stored under the simultaneous influence of heat and moisture. This results in a decrease in the maximum color densities and in a corresponding flattening of the characteristic curve during color-forming development.

In the most unfavourable instances the above undesired effects even occur upon drying the photographic layer during their production.

The object of the present invention is to provide photographic elements which contain the above 1,2-dihydrazones, but which are stable against the effects of heat and moisture.

It has now been found that compounds of the following formula

R—NHOH

are particularly suitable for stabilizing the foregoing formulations. In this formula, R represents

(a) A linear or branched alkyl radical with up to 20 carbon atoms which may be substituted as desired, but preferably with phenyl, e.g. in a benzyl- or phenylethyl grouping, carboxy or sulfo,

(b) An aromatic ring grouping, preferably aryl rings, in particular naphthyl or phenyl; these groups may in turn be substituted as desired, for example, with halogen, preferably chlorine or bromine, alkoxy groups with up to 18 carbon atoms, hydroxy, carboxy, esterified carboxy whereby the ester grouping is preferably derived from an aliphatic alcohol with up to 20 carbon atoms, sulfo, amino which may be substituted, for example, with acyl radicals, in particular those derived from aliphatic carboxylic acids

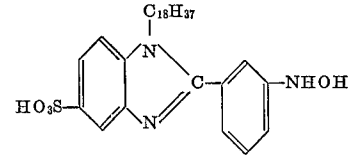
with up to 20 carbon atoms or from phenyl sulfonic acids, or with alkyl radicals of up to 20 carbon atoms, sulfamyl groupings, in which case the amide radical may be substituted as indicated above in respect of the amino groups, or with phenyl radicals or alkyl radicals with up to 20 carbon atoms.

Preferred are phenyl-hydroxylamine derivatives particularly those containing water-solubilizing groups such as —SO_3H or —COOH and long-chain alkyl radicals with 7 to 20 carbon atoms. These substituents may be linked to the phenyl ring either directly or via any intermediate members, for example, a phenyl sulfonamide grouping.

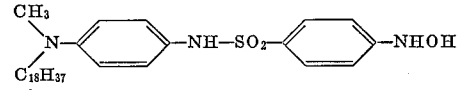
The aromatic 1,2-dihydrazones described in British patent specification No. 916,657 are stabilized by the above hydroxylamines against the simultaneous effect of heat and moisture. This effect is unexpected inasmuch as the simple hydroxylamine or its salts do not produce any improvement in stability. In addition, other additives with a comparable reducing action such as aromatic hydrazines, hydroxamic acids, ascorbic acid and pyrocatechol, are practically ineffective.

The following compounds exhibit particular utility:

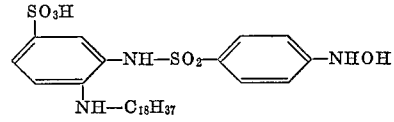
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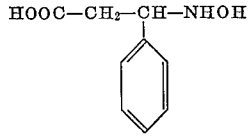
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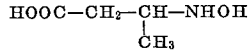
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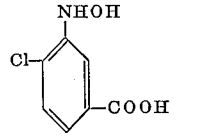
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V



VI



The hydroxylamine derivatives are preferably added to the emulsions in amounts from 15% to 60% by weight, based on the aromatic 1,2-dihydrazone; that is about 10 to 750 mg. per square meter of the layer. They do not deleteriously affect the silver halide emulsion. According to British patent specification 916,657 or U.S. Patent 3,186,840 the aromatic dihydrazones are added in amounts of 1–20 g. per liter of silver halide emulsion; that is about 4.5 to 90 g. per mol silver halide. The aromatic dihydrazones suitable for the photographic materials of the present invention are described in the above patent specification and patent as well as in British patent specification 916,658 and U.S. Patent 3,162,643.

The hydroxylamines may be prepared by methods described in the literature, starting from the corresponding nitro compounds. In cases where the water solubility is reduced, for example by fairly long alkyl radicals, it is

advisable to reduce the nitro compounds in pyridine with zinc powder and hydrochloric or acetic acid. These generally applicable methods are described in the following with regard to 2-(m-hydroxylaminophenyl)-1-octadecyl-benzimidazole-5-sulphonic acid.

EXAMPLE 1

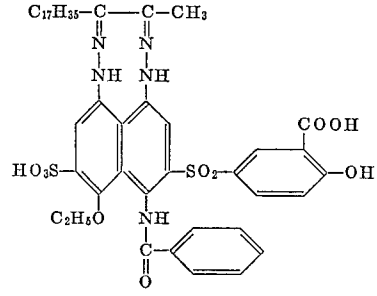
Preparation of the hydroxylamine derivative:

100 g. of 1-octadecyl-2(m-nitrophenyl)-benzimidazole-5-sulfonic acid were dissolved in 500 ml. of pyridine. 130 ml. of 5-N-hydrochloric acid were added to the solution and 25 g. of zinc powder were introduced with stirring at 25 to 30° C. over a period of 30 minutes. After stirring for another 15 minutes, the reaction mixture was suction-filtered. Ice was added to the filtrate and the reaction product was precipitated with hydrochloric acid, suction-filtered, washed repeatedly with water and, finally, stirred with acetone and sucked dry.

Yield: 74 g. of 1-octadecyl-2-(m-hydroxyaminophenyl)-benzimidazole-5-sulfonic acid.

Photographic application:

To a gelatino-silver iodobromide emulsion of average sensitivity containing about 5 mol percent of silver iodide were added 40 ml. of a 7.5% aqueous solution of saponine, 10 ml. of a 5% methanolic solution of tris-acroleyl-perhydrotriazine and 25 ml. of a 1% aqueous solution of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and an aqueous solution of a dihydrazone of the following formula, so that the final layer contained 55 g. of that compound per mol silver halide.



The above emulsion was applied onto a transparent support of celluloseacetobutyrate. The dried layer contained 0.55 g. of Ag per m.^{2} and had a thickness of 3μ. (Material A_1.)

A comparison material B_1 differed from material A_1 in that 19 g. of 2-m(m-hydroxylaminophenyl)-1-octadecyl-benzimidazole-5-sulfonic acid per mol of silver halide were added in the form of a 5% by weight solution in 0.1 N NaOH, and the pH then adjusted to 7.0 with citric acid.

Samples of materials A_1 and B_1 were stored for 7 days at 40° C. and 85% relative humidity. The samples of A_1 and B_1 stored in this way, together with samples of A_1 and B_1 stored cold at +3° C. for the same period, were exposed behind a step wedge and developed for 8 minutes in a color-forming developer of the following composition:

	Grams
Sodium hexametaphosphate	2.0
p-Diethylaminoaniline sulfate	2.75
Sodium sulfite (anhydrous)	2.0
Potassium bromide	1.5
Potassium carbonate	75.0

Water, 1 liter.

The developed materials were washed, bleached in a potassium ferricyanide bleaching bath and then fixed and washed according to common practice. Sensitometric analysis of the following maximum color densities:

	Material A_1	Material B_1
Cold-stored	1.0	1.02
After storage at 40° C	0.30	1.04

The stabilizing effect of the hydroxylamine derivative is readily apparent.

EXAMPLE 2

Two photographic materials (samples A_2 and B_2) were prepared as described in Example 1. Material B_2 contained an equimolar quantity of compound II, instead of the hydroxylamine derivative referred to in Example 1. After storage, exposure and color-forming development as in Example 1, the following maximum color densities were otbained

	Material A_2	Material B_2
Cold-stored	1.0	1.01
After storage at 40° C	0.32	1.03

EXAMPLE 3

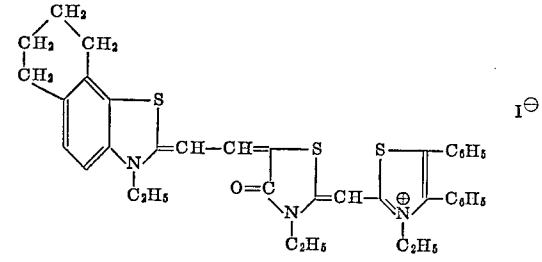
A photographic material similar to that described in Example 1 was prepared (A_3). Comparison sample B_3 contained in place of the hydroxylamino compound of sample B_1 an equimolar quantity of compound III. After storage for 7 days at 40° C. and 85% humidity, both the materials were exposed in a sensitometer and processed as described in Example 1 of British patent specification 916,657. Sample A_3 suffered a loss in yellow density of D=0.68 as compared with sample B_3.

EXAMPLE 4

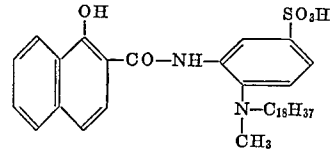
Layers containing the direct positive dihydrazone color component stabilized with an organic hydroxyl amine derivative according to the invention can also be used in multi-layer color photographic materials to correct the undesirable absorption of subtractive color couplers, in particular the undesirable absorption of magenta color couplers.

Such a multilayer material can be composed as follows: on a transparent support, for example, of cellulose acetate or polyethylene glycol terephthalate having a subbing layer coated thereon are applied the following layers:

(a) A red-sensitive silver bromide gelatin emulsion which contains 6 mol percent of silver iodide and which further contains per liter emulsion 30 ml. of a 1% aqueous solution of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, 40 ml. of a 0.1% methanolic solution of the red-sensitizer of the following formula:



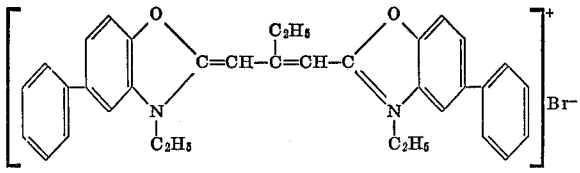
250 ml. of a 6% aqueous solution of the sodium salt of the cyanine coupler of the following formula:



40 ml. of a 7.5% aqueous solution of saponin and 9 ml. of a 5% methanolic solution of tris(acryloyl)-perhydrotriazine. The dried layer contains 0.85 g. of silver in the form of silver halide per square meter.

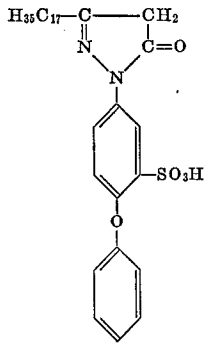
(b) One of the emulsions described in Examples 1–3 sensitized to the green region of the spectrum by adding

per liter of emulsion 50 ml. of 1% methanolic solution of the following sensitizing dye:



(c) An intermediate layer of gelatin,

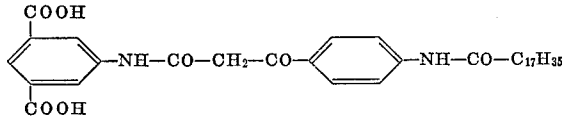
(d) A bromsilver gelatin emulsion containing 6 mol percent of silver iodide per liter of the emulsion, 20 ml. of a 1% aqueous solution of 1-(p-sulfonic acid-phenyl-amino)-2-methyl-mercapto-1,3,4-triazol, 40 ml. of 0.1% methanolic solution of the above green sensitizing dye, 500 ml. of a 2.5% aqueous solution of the sodium salt of the following magenta coupler



40 ml. of a 7% aqueous solution of saponine and 12 ml. of a 5% methanolic solution of tris(acryloyl)perhydro-triazine. The dried layer contains 0.75 g. silver in the form of silver halide per square meter,

(e) A yellow filter layer consisting of colloidal distributed silver dispersed in gelatin,

(f) A blue-sensitive silver iodobromide gelatin emulsion layer the silver halide of which contains 6 mol percent of silver iodide. The emulsion further contains per liter of casting solution 30 ml. of a 1% aqueous solution of 4-hydroxy-6-methyl-1,3,3a-7-tetraazaindene, 200 ml. of a 10% aqueous solution of the sodium salt of the yellow color coupler



15 ml. of a 5% methanolic solution of tris-(acroloyl)-perhydrotriazine and 50 ml. of a 7.5% aqueous solution of saponine.

The dried layer contains per square meter 1.43 g. silver in the form of silver halide,

(g) A protecting layer of hardened gelatin.

The above material is exposed to a color original and processed according to common practice by developing and bleach-fixing the exposed material. A colored image of the original in true colors is obtained. An image of the same quality is obtained after storing the above material for several days at 40° C. and high humidity.

What is claimed is:

1. In a photographic light-sensitive silver halide emulsion containing an aromatic 1,2-hydrazone of an alpha dicarbonyl compound and forming a direct positive dye image upon exposure, color development and silver bleaching, the improvement according to which the emulsion also contains an alkyl or aryl hydroxylamine in an amount that stabilizes the unprocessed emulsion against the loss of final color intensity resulting from storage at elevated temperatures.

2. The combination of claim 1 in which the hydroxylamine is an alkyl hydroxylamine having up to 20 carbons.

3. The combination of claim 1 in which the hydroxylamine is a phenyl or naphthyl hydroxylamine.

4. The combination of claim 1 in which the hydroxylamine contains a carboxy or sulfo group.

5. The combination of claim 1 in which the hydroxylamine contains an alkyl group having from 7 to 20 carbons.

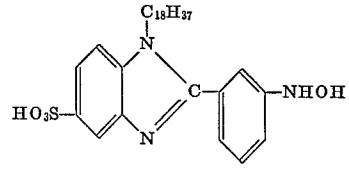
6. The combination of claim 1 in which the hydroxylamine contains a carboxy or sulfo group and in addition an alkyl group having from 7 to 20 carbons.

7. The combination of claim 1, wherein the hydroxylamine is a phenylhydroxylamine, the phenyl ring of which carries an alkyl group having between 7 and 20 carbon atoms, and a water-solubilizing group.

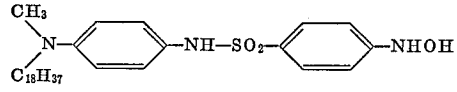
8. The combination of claim 1 in which the hydroxylamine has the formula R—NHOH wherein R represents alkyl having up to 20 carbon atoms, phenyl-substituted alkyl having up to 20 carbon atoms in the alkyl, carboxy substituted alkyl having up to 20 carbon atoms in the alkyl, sulfo substituted alkyl having up to 20 carbon atoms in the alkyl, naphthyl, phenyl, or substitution products of naphthyl or phenyl wherein the substituents are halogen, alkoxy having up to 18 carbon atoms, hydroxy, carboxy, esterified carboxy having up to 21 carbon atoms, sulfo, amino, acylamino having up to 20 carbon atoms, phenylsulfoamino, alkylamino having up to 20 carbon atoms, sulfamido, acylsulfamide having up to 20 carbon atoms, phenylsulfamido, alkylsulfamido having up to 20 carbon atoms or alkyl having up to 20 carbon atoms.

9. The combination of claim 7 wherein the alkyl group is linked to the phenyl ring via a phenyl sulfonamide grouping.

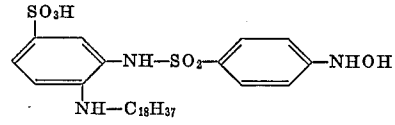
10. The combination of claim 1 wherein the hydroxylamine is



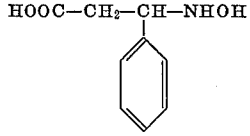
11. The combination of claim 1 wherein the hydroxylamine is



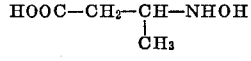
12. The combination of claim 1 wherein the hydroxylamine is



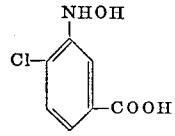
13. The combination of claim 1 wherein the hydroxylamine is



14. The combination of claim 1 wherein the hydroxylamine is



15. The combination of claim 1 wherein the hydroxylamine is



References Cited

UNITED STATES PATENTS

2,419,975 5/1947 Trivelli et al. ---------- 96—66

2,835,575 4/1955 Cowden et al. ---------- 96—28
2,419,975 5/1947 Trivelli et al. ---------- 96—95
2,835,575 5/1958 Cowden et al. ---------- 96—95
3,293,034 12/1966 Green et al. ---------- 96—95

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U.S. Cl. X.R.

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