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ANTISTAIN AGENTS COMPRISING MIXTURES OF SECONDARY-ALKYLHYDROQUINONES

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ABSTRACT OF THE DISCLOSURE

Mixtures of at least two secondary-alkylhydroquinones in which there are from one to two secondary-alkyl substituents each having from 9 to 20 carbon atoms and, preferably, mixtures that contain secondary-alkylhydroquinone isomers that are eutectics with low eutectic points, i.e., near or below room temperature, are photographic antistain agents that are superior in chemical and physical properties to antistain agents described in the prior art. Dispersions of the immediate antistain agents in hydrophilic colloids can be held before coating at temperatures below room temperature without crystallizing while antistain agents outside the invention do crystallize.

This invention relates to color photography and particularly to materials 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. Pat. 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 and Godowsky U.S. Pat. 2,304,940, Dec. 15, 1942, and Jelley and Vittum U.S. Pat. 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 layers 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.

The incorporation of hydroquinone or certain of its derivations is well known in the prior are for the control of color fog or stain.

The alkyl and di-alkyl hydroquinones available in the prior art have certain disadvantages however. Many are

difficult to synthesize requiring two to four steps; others have low molecular weights which allow them to wander between layers in a multilayer color photographic material, thereby causing undesirable side effects; still others crystallize out during or after coating to give poor coating quality; and also some of the alkyl hydroquinones can be shown to undergo an oxidation reaction during coating operations, or during processing to give colored by-products.

It is an object of my invention, therefore, to provide novel antistain agents which are easily synthesized.

It is also an object of my invention to provide novel antistain agents which do not crystallize from dispersions in aqueous hydrophilic colloid coating compositions before, during or after coating.

Another object of my invention is to provide novel liquid antioxidants which are advantageously incorporated as dispersions in aqueous hydrophilic colloid coating compositions without the use of a solvent.

A further object is to provide novel antistain agents which are not oxidized to colored by-products in aqueous hydrophilic colloid coating compositions before, during coating, or during processing.

Another object is to provide novel photographic elements containing at least one hydrophilic colloid layer containing a dispersion of our antistain agents.

These and other objects of my invention will become apparent from the following description of my invention.

These and still other objects are accomplished according to my invention by the preparation of my antistain agents which are mixtures of at least two secondary-alkylhydroquinones in which the secondary alkyl substituents have from 9 to 20 carbon atoms, the preparation of dispersions of my antistain agents in hydrophilic colloids, and the use in multilayer multicolor photographic elements of coatings of hydrophilic colloid containing dispersions of my antistain agents.

My antistain agents are mixtures of at least two secondary-alkylhydroquinones which are monosubstituted and/or disubstituted hydroquinones in which the secondary-alkyl groups have from 9 to 20 carbon atoms, such as, a secondary nonyl group (e.g., 1-methyloctyl, 1-ethylheptyl, 1-propylhexyl, 1-butylamyl, etc.), a secondary decyl group (e.g., 1-methylnonyl, 1-ethyloctyl, 1-propylheptyl, 1-butylhexyl, etc.), a secondary-undecyl group (e.g., 1-methyldecyl, 1-ethylnonyl, 1-propyloctyl, 1-butylheptyl, 1-pentylhexyl, etc.) a secondary-dodecyl group (e.g., 1-methylundecyl, 1-ethyldecyl, 1-propylnonyl, 1-butyloctyl, 1-amylheptyl, etc.), a secondary-tridecyl group (e.g., 1-methyldodecyl, 1-ethylundecyl, 1-propyldecyl, 1-butylnonyl, 1-amyloctyl, 1-hexylheptyl, etc.), a secondary-tetradecyl group (e.g., 1-methyltridecyl, 1-ethyldodecyl, 1-propylundecyl, 1-butyldecyl, 1-amylnonyl, 1-hexyloctyl, etc.), a secondary-pentadecyl group (e.g., 1-methyltetradecyl, 1-ethyltridecyl, 1-propyldodecyl, 1-butylundecyl, 1-amyldecyl, 1-hexylnonyl, etc.), a secondary-hexadecyl group (e.g., 1-methylpentadecyl, 1-ethyltetradecyl, 1-propyltridecyl, 1-butyldodecyl, 1-amylundecyl, 1-hexyldecyl, 1-heptylnonyl, etc.), a secondary-heptadecyl group (e.g., 1-methylhexadecyl, 1-ethylpentadecyl, 1-propyltetradecyl, 1-butyltridecyl, 1-amyldodecyl, 1-hexylundecyl, 1-heptyldecyl, 1-octylnonyl, etc.), a secondary-octadecyl group (e.g., 1-methylheptadecyl, 1-ethylhexadecyl, 1-propylpentadecyl, 1-butyltetradecyl, 1-amyltridecyl, 1-hexyldodecyl, 1-heptylundecyl, 1-octyldecyl, etc.), a secondary-nonadecyl group (e.g., 1-methyloctadecyl, 1-ethylheptadecyl, 1-propylhexadecyl, 1-butylpentadecyl, 1-amyltetradecyl, 1-hexyltridecyl, 1-heptyldodecyl, 1-octylundecyl, 1-nonyldecyl, etc.) and a secondary-phytyl group (e.g., 1-methylnonadecyl, 1-ethyloctadecyl, 1-propylheptadecyl, 1-butylhexadecyl, 1-amylpentadecyl, 1-

hexyltetradecyl, 1-heptyltridecyl, 1-octyldodecyl, 1-nonylundecyl, etc.

In the simplest mixtures containing two different secondary-alkylhydroquinones usually there is in the range from 1% to 99% of one compound and in the range from 99% to 1% of the second compound. A preferred range is from 5% to 95% of one compound and from 95% to 5% of the second compound. A large variety of mixtures of secondary-alkylhydroquinones are used to advantage according to my invention. For example, (1) mixtures of 2-secondary-alkylhydroquinones in which the compounds differ in the number and/or arrangement (position isomers) of carbon atoms in the alkyl group are used to advantage, (2) mixtures of 2,5-di-secondary-alkylhydroquinones in which the compounds differ in the number and/or arrangement of carbon atoms in the alkyl group on one or both, i.e., 2- and 5-position substituents are used to advantage, and mixtures of (1) and (2) are used to advantage. Preferred mixtures of my invention are mixtures of isomers of a 2-secondary-alkylhydroquinone, mixtures of isomers of a 2,5-di-secondary-alkylhydroquinone or mixtures of a 2-secondary-alkylhydroquinone (a single compound or mixture of two or more isomers) and a 2,5-di-secondary-alkylhydroquinone (a single compound or mixture of two or more isomers).

Such mixtures of isomers are advantageously made by reacting hydroquinone with the appropriate primary olefin(s) containing from 9 to 20 carbon atoms in the presence of a Lewis Acid at elevated temperatures over an extended period of time so that isomeric forms of the primary olefin are formed and react with hydroquinone to produce at least one isomeric compound of the monosubstituted secondary-alkylhydroquinone and at least one isomeric compound of the disubstituted secondary-alkylhydroquinone compound in a single reaction step. An inert solvent, preferably immiscible with water, such as, benzene, nitrobenzene, toluene, xylene, etc., is advantageously used for the reaction mixture. Lewis Acids are protons and sources of protons, such as acids, metal atoms which are able to form coordination systems with water or ammonia, sulfur from sulfur dioxide, sulfuric acid, sodium bisulfite, atoms and free radicals with incomplete electron shells, etc. Especially useful Lewis Acids are sulfuric acid, phosphoric acid, hydrochloric acid, sodium bisulfate, monosodium phosphate, zinc chloride, aluminum chloride, boron trifluoride, benzene sulfonic acid, silica-alumina, Amberlite IR–120 (Rohm and Haas Co. trade name for an acidic ion exchange resin), etc. It is advantageous to heat a solvent solution of hydroquinone together with the Lewis Acid to distill any moisture from the mixture as an azeotrope and then add the primary olefin or primary olefins while raising the temperature of the reaction mixture to a temperature in the range of from about 130° C. to about 240° C. over an extended period of time. The rate at which the olefin is added to the reaction mixture, the rate of heating and the reaction time are selected so as to produce the desired mixture of isomers in the final product. The most advantageous reaction conditions will depend upon the particular mixture of isomers desired and are readily determined. After the reaction is completed, the reaction mixture is cooled, added to a suitable organic solvent such as ligroine; the Lewis Acid is removed by filtration or other appropriate means; the unreacted olefin is removed by distillation at reduced pressure and then the mixture of my secondary-alkylhydroquinones is distilled off at reduced pressure or separated from the residual reaction mixture by other appropriate means. The hot mixture of my compounds is advantageously protected from air oxidation whenever possible during this procedure by keeping it under a nitrogen atmosphere.

The following mixtures of secondary-alkylhydroquinones are illustrative of those used to advantage as antistain agents according to my invention.

Mixture 1

2-(1-methyloctyl)hydroquinone
2,5-di(1-methyloctyl)hydroquinone
2,5-di(1-ethylheptyl)hydroquinone
2,5-di(1-propylhexyl)hydroquinone and
2,5-di(1-butylamyl)hydroquinone

Mixture 2

2-(1-methylundecyl)hydroquinone
2-(1-ethyldecyl)hydroquinone
2-(1-butyloctyl)hydroquinone
2-(1-amylheptyl)hydroquinone
2,5-di(1-methylundecyl)hydroquinone
2,5-di(1-ethyldecyl)hydroquinone
2,5-di(1-butyloctyl)hydroquinone
2,5-di(1-propylnonyl)hydroquinone
2,5-di(1-amylheptyl)hydroquinone
2-(1-methylundecyl)-5-(1-propylnonyl)hydroquinone
2-(1-methylundecyl)-5-(1-ethyldecyl)hydroquinone
2-(1-methylundecyl)-5-(1-butyloctyl)hydroquinone
2-(1-methylundecyl)-5-(1-amylheptyl)hydroquinone
2-(1-ethyldecyl)-5-(1-butyloctyl)hydroquinone
2-(1-butyloctyl)-5-(1-amylheptyl)hydroquinone and
2-(1-propylnonyl)-5-(1-amylheptyl)hydroquinone

Mixture 3

Is like Mixture 2, but includes the following additional compounds:

2-(1-propylnonyl)hydroquinone
2-(1-ethyldecyl)-5-(1-propylnonyl)hydroquinone
2-(1-ethyldecyl)-5-(1-amylheptyl)hydroquinone, and
2-(1-propylnonyl)-5-(1-butyloctyl)hydroquinone

Mixture 4

Is like Mixture 2, but contains 2-(1-propylnonyl)hydroquinone in place of 2-(1-amylheptyl)hydroquinone and contains 2-(1-ethyldecyl)-5-(1-propylnonyl)hydroquinone, 2-(1-ethyldecyl) - 5 - (1-amylheptyl)hydroquinone, and 2-(1-propylnonyl)-5-(1 - butyloctyl)hydroquinone in place of 2-(1-propylnonyl)-5-(1-amylheptyl)hydroquinone and 2-(1-butyloctyl)-5-(1-amylheptyl)hydroquinone.

Mixture 5

2-(1-methylundecyl)hydroquinone and
2,5-di-(1-methylundecyl)hydroquinone

Mixture 6

2-(1-methylundecyl)hydroquinone
2,5-di(1-methylundecyl)hydroquinone
2,5-di(1-ethyldecyl)hydroquinone, and
2-(1-methylundecyl)-5-(1-ethyldecyl)hydroquinone

Mixture 7

2-(1-methyldecyl)hydroquinone and
2,5-di(1-methyldecyl)hydroquinone

Mixture 8

2-(1-methyldodecyl)hydroquinone and
2,5-di(1-methyldodecyl)hydroquinone

Mixture 9

2-(1-methyldodecyl)hydroquinone
2-(1-ethylundecyl)hydroquinone
2,5-di(1-methyldodecyl)hydroquinone
2,5-di(1-ethylundecyl)hydroquinone
2,5-di(1-propyldecyl)hydroquinone, and
2-(1-methyldodecyl)-5-(1-ethylundecyl)hydroquinone

Mixture 10

2-(1-methyltridecyl)hydroquinone and
2,5-di(1-methyltridecyl)hydroquinone

Mixture 11

2-(1-methylpentadecyl)hydroquinone and
2,5-di(1-methylpentadecyl)hydroquinone

Mixture 12

2-(1-methylnonadecyl)hydroquinone and
2,5-di(1-methylnonadecyl)hydroquinone

In addition to the specific compounds shown in Mixture Nos. 5, 7, 8, 10, 11 and 12, one or more isomers are advantageously included of either or both the mono- or di-substituted secondary-alkylhydroquinone. Mixtures like Mixture 10, for example, can have as many as seven isomers of the monosubstituted secondary-alkylhydroquinone and as many as 27 isomers of the disubstituted secondary-alkylhydroquinone. Mixtures like Mixture 12, for example, can have as many as nine isomers of the monosubstituted secondary-alkylhydroquinone and forty-five isomers of the disubstituted secondary-alkylhydroquinone.

My mixtures are eutectic mixtures (or nearly eutectic mixtures) in which the components produce minimum eutectic points, preferably below room temperature.

My mixtures of secondary-alkylhydroquinones are advantageously dispersed in any of the well-known photographic hydrophilic colloids, including gelatin, albumen, collodion, gum arabic, agar-agar, cellulose derivatives, e.g., alkyl esters of carboxylated cellulose, hydroxyethyl cellulose, synthetic resins, e.g., the amphoteric copolymers described by Claver et al. in U.S. Pat. 2,949,442, polyvinyl alcohol, polyvinyl pyrrolidone, copolymers of an alkyl acrylate, an alkylcarbonylacetoxyalkylacrylate and either a sulfoalkylacrylate or acrylic acid, e.g., are described by Smith in U.S. Pat. 3,488,708, issued Jan. 6, 1970, particularly from line 28 in column 5 to line 8 in column 6, and others well known in the art. My mixtures that are liquid at room temperature are readily dispersed without the need of a solvent. My mixtures that are not liquid at room temperature are advantageously dispersed as a solution in (1) a high-boiling organic crystalloidal solvent, such as alkyl esters of phthalic acid, e.g., methyl phthalate, ethyl phthalate, propyl phthalate, n-butyl phthalate, di-n-butyl phthalate, n-amyl phthalate, isoamyl phthalate and dioctyl phthalate, and esters of phosphoric acid, e.g., triphenyl phosphate, tricresyl phosphate, diphenyl mono-p-tert, butyl phenyl phosphate or (2) low-boiling organic solvents, such as, lower alkyl acetates, ethyl propionate, sec.-butyl alcohol, methyl isobutyl ketone, β-ethoxyethyl acetate, methyl Cellosolve acetate, acetonyl acetone, etc.

Dispersions in hydrophilic colloids of my antistain agents(my mixtures) are characterized by not crystallizing when held at temperatures below room temperature before, during and after coating as a layer in a multilayer photographic element. This represents a valuable technical advance over the prior art antistain agents which do crystallize from dispersions in hydrophilic colloids while being held below room temperature prior to coating.

Dispersions of my antistain agents are further characterized by not producing discolorations that certain prior art antistain agents produce.

Dispersions of my antistain agents in hydrophilic colloids are advantageously coated in any of the layers of any of the multilayer multicolor photographic elements where antistain agents are used. For example, they are advantageously added to one or more of the light-sensitive layers and/or in nonlight-sensitive layers coated over or between the light-sensitive layers. They are used in photographic elements that contain incorporated color-forming couplers in the light-sensitive emulsion layers or in multilayer multicolor photographic elements that do not contain incorporated color-forming couplers. The photographic elements are either of camera speed or elements such as are used for reflection color prints. The elements are coated on any of the usual support materials such as paper, other fibrous support, cellulose acetate or any of the synthetic polymers used for photographic film supports. My antistain agents are dispersed in hydrophilic colloids in the range of from about .01% to about 90%, by weight, of dry hydrophilic colloid and, preferably, in

the range from about 1% to about 85%. The optimum concentration will depend upon the particular photographic element in which my antistain agents are to be used and is easily determined by methods well known in the art.

My antistain agents actively reduce the oxidized form of any of the primary aromatic amine color-developing agents (used in color processes) back to the developing agent or to a form that will not couple with color-forming coupler. Hydrophilic colloid layers of my antistain agents coated between two light-sensitive layers are very effective in preventing oxidized color developing agent formed by development in one light-sensitive layer from wandering into the second layer and forming unwanted dye in the second layer.

In the prior art, the pure compounds used as antistain agents, such as 2,5-di-n-dodecylhydroquinone required four steps in its synthesis and the pure 2-n-dodecylhydroquinone required two steps. By use of my invention, only a one-step synthesis is required, and an antistain agent is obtained which is superior in its chemical and physical properties to any described in the prior art.

The following examples are included for a further understanding of my invention.

EXAMPLE 1

(A) Pure 2,5-di-n-dodecylhydroquinone (not of my invention), designated as Antistain Agent X, is prepared as described in lines 48–68, column 8 of U.S. Pat. 2,728,659, Loria et al., using four reaction steps (M.P. 108–110° C.)

(B) The mixed isomers of secondary-dodecylhydroquinone are prepared using my invention as follows: In a 500-ml. 4-necked flask, in an oil bath, equipped with a stirrer, distillation head, dropping funnel and thermometer, are placed 55 g. (0.5 mole) of hydroquinone, 18 g. of a silica-alumina catalyst, and 100 ml. of toluene. While stirring, the reaction mixture is heated in the oil bath, and the toluene-water azeotrope is removed. When about 75 ml. is collected, the pot temperature is about 130° C. To the hot reaction mixture is added 150 ml. (123 g., 0.675 mole) of 1-dodecene. The oil bath temperature is raised to 230° C., and the reaction temperature rises to 220° C. over a two-hour period. After the temperature of 220–225° C. has been maintained for one hour, an additional 100 ml. (75 g., 0.446 mole) of 1-dodecene is added dropwise at such a rate that the reaction mixture temperature is not lowered. After stirring at this temperature for an additional three hours, the stirring is stopped and the flask is removed from the oil bath. From now on the crude product is kept under a nitrogen atmosphere whenever possible to prevent oxidation. When this reaction mixture has cooled to 120° C., it is cautiously poured into 500 ml. of ligroine. The silica-alumina catalyst is removed by filtration and washed with ligroine. The ligroine is distilled from the product at atmospheric pressure. The unreacted dodecene is removed by distillation at reduced pressure, collecting the fraction which boils at 78–110°/10 mm. The product is distilled at oil pump vacuum, collecting the fraction which boils at 210–250°/0.15 mm. The yield is 185 g. which is 83% of the theoretical amount of 226 g. based on the amount of hydroquinone used. This mixture of isomers, identified as Antistain Agent A, is a liquid at room temperature. Gas chromatography shows that it is a mixture of twelve of the fifteen possible disubstituted isomers (95% by weight) and four of the five possible mono-substituted isomers (5% by weight).

(C) Dispersions are made of Antistain Agents A and X with the following compositions:

50 g. antistain agent
25 g. tricresyl phosphate
60 g. gelatin dissolved in 600 ml. water

The melts containing A and X, respectively, are coated immediately at rates of 600 mg./ft.^{2} of gelatin. Compound

X is seen to crystallize immediately when the coating is examined in cross-section photomicrographs. The dispersions containing Antistain Agents A and X are held for two hours at 105° F. as melts and then examined for crystals. Only the dispersion containing Antistain Agent X crystallizes. Also upon holding, the dispersion of Antistain Agent X turns blue due to oxidation of the hydroquinone to a colored quinhydrone. In U.S. Pat. 2,728,659 cited herein, Antistain Agent X is described as being an improvement over the prior art in its resistance to oxidation. This example demonstrates that a mixture of isomers of similar structure is superior to Antistain Agent X in its resistance to oxidation.

EXAMPLE 2

Antistain Agent Y, i.e., 2,5-di-tertiaryoctylhydroquinone (outside my invention) is compared with Antistain Agent A prepared in Example 1(B). Two dispersions are made as follows:

(1) A solution is made of 40 g. of Antistain Agent Y in 20 g. of tri-cresyl phosphate and this is dispersed in 1 l. of aqueous gelatin containing 8% gelatin;

(2) A solution is made of 40 g. of Antistain Agent A in 20 g. of tri-cresyl phosphate and this is dispersed in 1 l. of aqueous gelatin containing 8% gelatin.

These dispersions are kept at 25° F. and 45% RH for two weeks. The dispersion containing Antistain Agent Y crystallizes. To demonstrate the inferior quality of dispersion of Antistain Agent Y, the dispersion is melted and filtered and a quantity of crystallized Antistain Agent Y remains on the filter. This results in the final melt having an incorrect composition. A melt containing a fresh dispersion of Antistain Agent Y is added to the melt containing the crystalline dispersion of Antistain Agent Y. It is observed that the total melt crystallizes during holding. The crystals seed the good melt and crystals formed throughout the good dispersion. No crystals form in the dispersion of Antistain Agent A (using my invention) and the melt passes completely through the filter.

EXAMPLE 3

Three paper-supported multilayer gelatinous silver halide coatings of the compositions illustrated below are exposed to a graduated-density test object, color developed, bleached, fixed, washed and dried.

Coating No. 1

Layer 3: Gelatin 100 mg./ft.^{2}, cyan-dye-forming coupler 50 mg./ft.^{2}, dibutyl phthalate 50 mg./ft.^{2}
Layer 2: Gelatin 100 mg./ft.^{2}
Layer 1: Gelatin 300 mg./ft. silver halide, 200 mg./ft.^{2}, yellow-dye-forming coupler, 100 mg./ft.^{2} of dibutyl phthalate
Support: Paper

Coating No. 2

Like Coating No. 1, but 26 mg./ft.^{2} of Antistain Agent X in Layer #2 dispersed as in Example 2.

Coating No. 3

Like Coating No. 1, but 26 mg./ft.^{2} of Antistain Agent A in Layer #2 dispersed as in Example 2.

The effectiveness of Antistain Agents A and X are determined by measuring the amount of cyan dye formed in Layer 3 resulting from the interaction of oxidized color developer from Layer 1 with the coupler in Layer 3. The results are as follows:

Coating number	Antistain agent	Cyan dye density
1	None	.95
2	X	.64
3	A	.42

This shows that Antistain Agent A of my invention is substantially superior to Antistain Agent X of the prior art in its antistain properties. The cyan-dye-forming coupler used in Layer 3 of Coating Nos. 1, 2 and 3 is a coupler of the type described in lines 39 through 54 in column 2 of Fierke et al., U.S. Pat. 2,801,171, issued July 30, 1957. The yellow-dye-forming coupler used in Layer 1 of Coating Nos. 1, 2 and 3 is an α-pivalyl acetanilide coupler of the type described in column 5, line 20, all of column 6 and column 7 through line 4 of Weissberger and Kibler, U.S. Pat. 3,265,506, issued Aug. 9, 1966. The silver halide emulsion used in Coating Nos. 1, 2 and 3 is a silver bromoiodide emulsion. The color developer, bleach and fix solutions used in the immediate example have the composition indicated below:

Color developer solution

Benzyl alcohol	ml	12.6
Sodium hexametaphosphate (Calgon)	g	2.0
Sodium sulfite, anhydrous	g	2.1
Sodium carbonate monohydrate	g	26.8
Sodium bicarbonate	g	2.9
Potassium bromide	g	0.48
Sodium chloride	g	0.7
Hydroxylamine sulfate	g	2.1
Color developer *	g	4.2
pH at 75° F.		9.96

Water to 1 l.

*4 - amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.

Bleach solution

	G.
Sodium nitrate	45.0
Potassium ferricyanide	22.5
Potassium bromide	8.2
Boric acid	7.5
Borax	0.97

Water to 1.0 l.

Fix solution

	G.
Sodium thiosulfate	223.0
Sodium bisulfite	12.0
Sodium acetate, anhydrous	14.0
Sodium citrate	1.7
Boric acid	5.0
Potassium alum, granular	24.0

Water to 1.0 l.

EXAMPLE 4

A dispersion is made by passing a mixture of 50 g. of Antistain Agent A and 60 g. of gelatin in 600 ml. of water through a colloid mill three times. This, when compared to dispersions of Example 1, is about 19% lighter in weight. The liquid antistain agent requires no additional solvent to make a good dispersion. In photographic tests, this dispersion is shown to be substantially identical to a similar dispersion in solvent.

Example 1(C) is repeated using equivalent amounts of collodion, agar-agar, hydroxyethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone and copoly(methylacrylate-sodium - 3 - acryloyloxy-1-methylpropane-1-sulfonate-2-acetoacetoxyethyl acrylate) in place of gelatin. The superior characteristics of my Antistain Agent A over Antistain Agent X are again demonstrated.

EXAMPLE 5

Two multilayer color Elements X and A having a support coated in succession with a red-sensitized, gelatinous silver bromoiodide emulsion layer, a gelatin layer, a green-sensitized, gelatinous silver bromoiodide emulsion layer, a gelatin layer containing a bleachable yellow-colored dye and a blue-sensitive, gelatinous silver bromoiodide emulsion layer are made like the elements described in FIG. 2 in the drawing and in the specification on pages 1 and 2 of Mannes et al., U.S. Pat. 2,252,718, issued Aug. 19, 1941, except that the gelatin layers between the light-sensitive layers contain a dispersion of an antistain agent. The antistain agent containing layers of Element X (outside my invention) are coated with the dispersion of Antistain Agent X described in immediate Examples 1(A) and 1(C). Antistain Agent X is found to crystallize in the dispersion before coating, during the coating operation and after coating, resulting in coating imperfections and some product that is unusable. The antistain agent containing layers of Element A or my invention are coated with the dispersion of Antistain Agent A described in immediate Examples 1(B) and 1(C). Antistain Agent A is found not to crystallize before, during or after coating Element A. Element A is free of coating defects and is a product that is superior to Element X. Pieces of Element X and Element A are image exposed and processed as described in U.S. Pat. 2,252,718 from page 1, column 2, line 48 through page 2, line 73. Although processed Element X has cyan dye stain in the magenta image layer, Element A is free of cyan dye stain.

EXAMPLE 6

Two multilayer color Elements Z and B like the element described in Example 2, column 7, line 56 through line 28 in column 8 of a Van Campen, U.S. Pat. 2,956,879, issued Oct. 18, 1960, having a support coated in succession with (1) a blue-sensitive gelatino-silver chlorobromide emulsion layer containing a yellow-dye-forming coupler and an antistain agent, (2) a gelatin layer, (3) a green-sensitized gelatino-silver chlorobromide emulsion layer containing an antistain agent, (4) a gelatin layer containing an ultraviolet-absorbing compound and an antistain agent and (5) a red-sensitized gelatino-silver bromoiodide emulsion layer containing an antistain agent. These elements are identical to those described in Example 2 of the cited reference, except that in Element Z a dispersion of Antistain Agent X, as described in immediate Examples 1(A) and 1(C), is used as the antistain agent in each of the layers containing an antistain agent. Crystallization of Antistain Agent X from the dispersion before, during and after coating Element Z results in coating defects and some product that cannot be used. Element B is like Element Z, except that a dispersion of Antistain Agent A, described in Examples 1(B) and 1(C) of this application, is used as the antistain agent in place of the dispersion of Antistain Agent X in each of the layers containing an antistain agent. No crystallization of Antistain Agent A is noticed in the coating compositions before, during or after coating Element B. Pieces of Elements Z and B are image exposed and color processed with color development, stop, fix, bleach, hardener fix, etc. as described in column 5, lines 35 through 44 in column 6 of U.S. Pat. 2,956,879 cited herein earlier. Element B of my invention gives quality that is superior to Element Z outside my invention.

Similarly, it can be shown that other multilayer multicolor elements coated with dispersions of my antistain agents are superior to elements coated with antistain agents outside my invention.

Examples 2, 3, 5 and 6 are repeated using equivalent amounts of collodion, agar-agar, hydroxyethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone and copoly(methyl acrylate-sodium 3-acryloyloxy-1-methylpropane-1-sulfonate-2-acetoacetoxyethyl acrylate) in place of gelatin. Results similar to those shown in Examples 2, 3, 5 and 6, respectively, are obtained.

Antistain Agent B of my invention is a mixture of isomers of 2-secondary-nonylhydroquinone and of 2,5-di-secondary-nonylhydroquinone prepared by a procedure like that used to prepare Antistain Agent A described in Example 1(B), but by substituting an equimolar amount of 1-nonene in place of 1-dodecene, and by using nitrobenzene as the solvent in place of toluene.

Antistain Agent C of my invention is a mixture of isomers of 2-secondary-hexadecylhydroquinone and of 2,5-di-secondary-hexadecylhydroquinone prepared by a procedure like that used to produce Antistain Agent A in Example 1(B) but by substituting an equimolar amount of 1-hexadecene in place of 1-dodecene.

A comparison of Antistain Agents B and C of my invention against Antistain Agent X when dispersed in gelatin as described in Example 1(C) again shows the superiority of my antistain agents over prior art Antistain Agent X. Similarly, it can be shown that Antistain Agent B is substantially superior to pure 2-secondary-nonylhydroquinone and substantially superior to pure 2,5-di-secondary-nonylhydroquinone. It can also be shown that Antistain Agent C is substantially superior to pure 2-secondary-hexadecylhydroquinone and is substantially superior to pure 2,5-di-secondary-hexadecylhydroquinone.

My antistain agents are valuable for incorporation in photographic hydrophilic colloid compositions because they are superior to antistain agents outside my invention. For example, dispersions of my antistain agents in hydrophilic colloid can be held prior to coating without crystallizing as do antistain agents outside my invention. My antistain agents are eutectic mixtures (or nearly eutectic mixtures) which have low eutectic points, preferably below room temperature. Solutions of my antistain agents in conventional high-boiling solvents or conventional low-boiling solvents are advantageously dispersed in an aqueous hydrophilic colloid. My liquid antistain agents, however, are advantageously dispersed without solvent in an aqueous hydrophilic colloid. My antistain agents do not form quinhydrone type dyes that some antistain agents outside my invention form. The antistain agents of my invention are used very effectively in photographic elements to prevent the wandering of oxidized color developing agents into layers where they cause unwanted dye formation (from coupling reactions). My antistain agents are easily made by a one-step chemical reaction, instead of the two- or four-step reaction required by prior art compounds.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A dispersion in a hydrophilic colloid of a photographic antistain agent that is a mixture of at least two secondary-alkylhydroquinones in which the secondary-alkyl substituents have from 9 to 20 carbon atoms, such that said dispersed antistain agent does not crystallize when held at temperatures below room temperature.

2. A dispersion of claim **1** in which said hydroquinones have from one to two secondary-alkyl substituents.

3. A dispersion of claim **1** in which said hydrophilic colloid is gelatin.

4. A dispersion in a hydrophilic colloid of a photographic antistain agent that is a mixture of at least two secondary-alkylhydroquinone isomers in which the secondary-alkyl substituents have from 9 to 20 carbon atoms, such that said dispersed antistain agent does not crystallize when held at temperatures below room temperature.

5. A dispersion in a hydrophilic colloid of a nondiffusible photographic antistain agent that is a mixture of at least two secondary-dodecylhydroquinones, such that said dispersed antistain agent does not crystallize when held at temperatures below room temperature.

6. A dispersion of claim **5** in which the hydrophilic colloid is gelatin.

7. A dispersion in a hydrophilic colloid of a nondiffusible photographic antistain agent that is a mixture of secondary-dodecylhydroquinone isomers that does not crystallize when held at temperatures below room temperature.

8. A dispersion in a hydrophilic colloid of a nondiffusible photographic antistain agent that is a mixture of secondary-alkylhydroquinones containing:

(1) at least one mono-secondary-dodecylhydroquinone with secondary-dodecyl substituents selected from the class consisting of 1-methylundecyl, 1-ethyldecyl, 1-propylnonyl, 1-butyloctyl and 1-amylheptyl; and

(2) at least one 2,5-secondary-dodecylhydroquinone with secondary-dodecyl substituents selected from

the class consisting of 1-methylundecyl, 1-ethyldecyl, 1-propylnonyl, 1-butyloctyl and 1-amylheptyl.

9. A dispersion in gelatin of a nondiffusible, photographic antistain agent that is a mixture containing:

(1) four mono-secondary-dodecylhydroquinone isomers with substituents selected from the class consisting of 1-methylundecyl, 1-ethyldecyl, 1-propylnonyl, 1-butyloctyl and 1-amylheptyl; and

(2) twelve 2,5 - di-secondary - dodecylhydroquinone isomers with substituents selected from the class consisting of 1-methylundecyl, 1-ethyldecyl, 1-propylnonyl, 1-butyloctyl and 1-amylheptyl.

10. In a multilayer color photographic element containing hydrophilic colloid layers containing differently sensitized silver halide emulsions in which the color images are formed during color processing by the reaction of an oxidized primary aromatic amine color developing agent with color-forming couplers, said element containing at least one hydrophilic colloid layer containing a dispersion of a non-diffusible antistain agent, the improvement comprising the use of a nondiffusible antistain agent that is a mixture of at least two secondary-alkylhydroquinones in which the secondary-alkyl substituents have from 9 to 20 carbon atoms.

11. In a multilayer color photographic element containing hydrophilic colloid layers containing differently sensitized silver halide emulsions in which the color images are formed during color processing by the reaction of an oxidized primary aromatic amine color developing agent with color-forming couplers, said element containing at least one hydrophilic colloid layer containing a dispersion of a nondiffusible antitstain agent, the improvement comprising the use of a nondiffusible antistain agent that is a mixture of at least two secondary-alkylhydroquinone isomers in which the secondary-alkyl substituents have from 9 to 20 carbon atoms.

12. In a multilayer color photographic element containing hydrophilic colloid layers containing differently sensitized silver halide emulsions in which the color images are formed during color processing by the reaction of an oxidized primary aromatic amine color developing agent with color-forming couplers, said element containing at least one hydrophilic colloid layer containing a dispersion of a nondiffusible antistain agent, the improvement comprising the use of a nondiffusible antistain agent that is a mixture of at least two secondary-dedocylhydroquinones.

13. In a multilayer color photographic element containing hydrophilic colloid layers containing differently sensitized silver halide emulsions in which the color images are formed during color processing by the reaction of an oxidized primary aromatic amine color developing agent with color-forming couplers, said element containing at least one hydrophilic colloid layer containing a dispersion of a nondiffusible antistain agent the improvement comprising the use of a nondiffusible antistain agent that is a mixture of secondary-dodecylhydroquinones containing:

(1) at least two mono-secondary-dodecylhydroquinone isomers with secondary-dodecyl substituents selected from the class consisting of 1-methylundecyl, 1-ethyldecyl, 1-propylnonyl, 1-butyloctyl and 1-amylheptyl; and

(2) at least two di-secondary-dodecylhydroquinone isomers with secondary-dodecyl substituents selected from the class consisting of 1-methylundecyl, 1-ethyldecyl, 1-propylnonyl, 1-butyloctyl and 1-amylheptyl.

14. A dispersion of claim **4** in which the hydrophilic colloid is gelatin.

15. A dispersion of claim **7** in which the hydrophilic colloid is gelatin.

16. In a multilayer color photographic element containing hydrophilic colloid layers containing differently sensitized silver halide emulsions in which the color images are formed during color processing by the reaction of an oxidized primary aromatic amine color developing agent with color-forming couplers, said element containing at least one hydrophilic colloid layer containing a dispersion of a nondiffusible antistain agent, the improvement comprising the use of a nondiffusible antistain agent that is a isomeric mixture of at least two secondary-dodecylhydroquinones.

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