United States Patent

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[31] **42/13,111**

[54] **LIGHT-SENSITIVE SILVER HALIDE COLOR-PHOTOGRAPHIC MATERIAL**
5 Claims, No Drawings

[52] **U.S. Cl.** **96/77,** 96/100, 96/114
[51] **Int. Cl.** **G03c 1/42**
[50] **Field of Search** 96/114, 95, 96, 77, 100

[56] **References Cited**

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ABSTRACT: Light-sensitive silver halide color-photographic material comprises a support and, coated thereon, a light-sensitive silver halide emulsion layer containing a color former, and a complex formed from (a) an alkali-soluble phenolic compound having a hydroxyl group on its benzene nucleus and capable of reducing silver halide and (b) a water-soluble polymeric vinyl compound capable of forming a complex with said phenolic compound, said complex being included in said emulsion and/or in a layer contiguous therewith.

LIGHT-SENSITIVE SILVER HALIDE COLOR-PHOTOGRAPHIC MATERIAL

This invention relates to a light-sensitive silver halide photographic material useful for color photography. This invention particularly is directed to a light-sensitive silver halide color-photographic material which comprises, as a developing aid, the combination of a certain phenolic compound with a certain polymeric compound in a light-sensitive silver halide emulsion layer and/or the layer contiguous therewith.

In color development, as is well known in the art, a color image is formed by the reaction of a color former with a color developer in its oxide form. Since conversion of the color developer into its oxide form occurs by the treatment of a latent silver image (silver ion) ion) with a developing solution containing said color developer, the formation of dye is somewhat restricted to around the reduced silver particles, thereby to cause graininess of the dye.

Various methods have been proposed heretofore to obtain improved graininess. For example, it is a common practice to use silver halide in the form of particles as fine as possible. However, this usually suffer from decrease in photographic sensitivity. In some instance, use of a color former having delayed coupling rate or a protected oil-soluble color former having a low rate of reaction with the oxide of a color developer is proposed thereby to have sufficient diffusion of the oxide with the less degradation of graininess. However, this method is disadvantageous because it makes difficult silver development to proceed and results in decrease in photographic speed and gradient. Use of a black-and-white developer and a color developer in a developing solution is also known to obtain their superadditive effect for color development. However, this procedure makes the maintenance of a developing bath considerably troublesome. Incorporation of a black-and-white developer in a light-sensitive layer is not recommendable because this causes undesired migration of said agent into other photographic layers. Further, said agent is likely to be dissolved out from the layer during development.

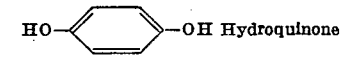
Accordingly, it is an object of the invention to provide a light-sensitive silver halide color-photographic material with improved graininess and free from color fog.

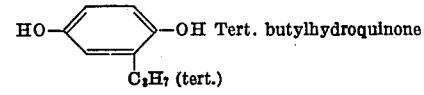
The above-mentioned object can be accomplished by the present invention. In accordance with the present invention, there is provided a light-sensitive silver halide color-photographic material which comprises a support and, coated thereon, a light-sensitive silver halide emulsion layer containing a color former, characterized by that the combination of (a) an alkali-soluble phenolic compound having a hydroxyl group on its benzene nucleus and capable of reducing silver halide and (b) an water-soluble polymeric vinyl compound capable of forming a complex with said phenolic compound exists in a light-sensitive silver halide emulsion layer and/or the layer contiguous therewith.

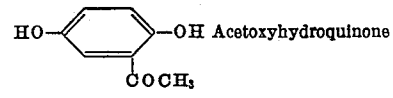
For the purpose of the present invention, it is essential to incorporate the combination of both of the phenolic compound (a) with the polymeric vinyl compound (b) into a light-sensitive silver halide emulsion layer and/or the layer contiguous therewith. It is presumed, without full exactness, that the above-referred combination of the phenolic compound (a) with the polymeric vinyl compound (b) is present in the form

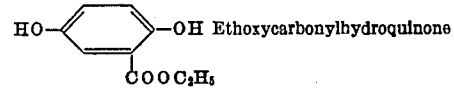
of a complex of the compounds (a) and (b), as such complex is understood as the result of the formation of a hydrogen bond between the hydroxyl group of the phenolic compound and the oxygen atom of the heterocyclic keto group of the polymeric vinyl compound when both of these compounds are brought into an aqueous or alcoholic medium. As well known for those skilled in the art, the present application is applicable to light-sensitive silver halide color-photographic films including monochromatic color films and tri-color films. Therefore, the combination of the compounds (a) and (b) can be incorporated in one or more light-sensitive silver halide emulsion layers. Similarly, it can be incorporated in other photographic layers contiguous to the light-sensitive emulsion layers, said other photographic layers being inter layer, protective layer, antihalation layer, subbing layer, and filter layer.

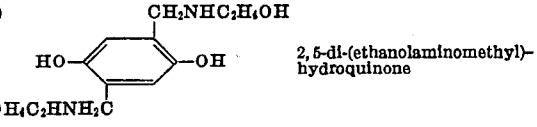
The essential requirements for the phenolic compound (a) outlined before are that it is soluble in alkali; it has on its benzene nucleus at least one hydroxyl group which serves to form a hydrogen bond; and it is capable of reducing silver halide to silver. Suitable phenolic compounds (a) as referred to may be obtained from a wide variety of conventionally known black-and-white developers. Hydroquinone, aminophenol and pyrogallol which are well known black-and-white developers are typical phenolic compounds useful in this invention. Nucleically substituted hydroquinones and N-substituted aminophenols are also useful. The following are typically suitable compounds for the purpose of this invention.

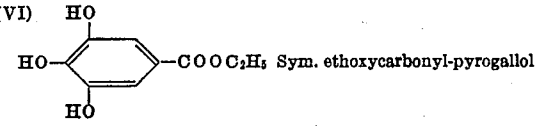
(I)  Hydroquinone

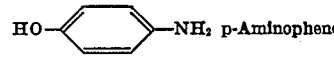
(II)  Tert. butylhydroquinone

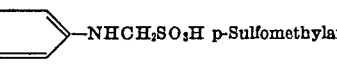
(III)  Acetoxyhydroquinone

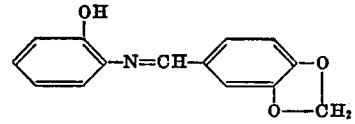
(IV)  Ethoxycarbonylhydroquinone

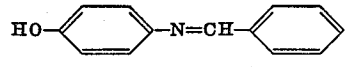
(V)  2,5-di-(ethanolaminomethyl)-hydroquinone

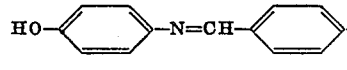
(VI)  Sym. ethoxycarbonyl-pyrogallol

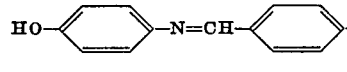
(VII)  p-Aminophenol

(VIII)  p-Sulfomethylaminophenol

(IX)  o-(3, 4-Methylenedioxy-benzalamino)-phenol

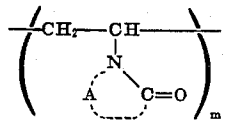
X)  p-Benzalaminophenol

XI)  p-(p-Chlorobenzalamino)-phenol

(XII)  p-(p-Methoxybenzalamino)-phenol

Almost all of the conventionally known black-and-white developers are usable in this invention, as far as said developers have a hydroxyl group to form a hydrogen bond. In the following description, therefore, the term "black-and-white developer" may be interpreted synonymous with the term "Phenolic compound (a)" as referred to above.

Suitable water-soluble polymeric vinyl compounds (b) are those containing the recurrent monomeric unit of the general formula



wherein A means an atomic grouping necessary to constitute, together with the adjacent nitrogen and carbon atoms, a five- to seven-membered ring. These polymeric vinyl compounds can be prepared by the homopolymerization or copolymerization of an appropriate monomer corresponding to the said general formula. Typically useable polymeric vinyl compounds (b) include, for instance, polyvinyl pyrrolidone, polyvinyl oxazolidone, polyvinyl piperidone, polyvinyl caprolactam, etc. If desired, these compounds may be modified by the introduction of any suitable substituent, e.g. a solubilizing group, so as to impart desired useful property to said compounds. The essential requirement for the polymeric vinyl compounds (b) is that they are soluble in water and capable of complexing with the above-mentioned phenolic compounds (a) (or the black-and-white developers) of the pH range of about 6.0 to about 8.0. Preferably, these polymeric vinyl compounds should have an average molecular weight as great as about 10,000 or more. If these polymers have too small molecular weight, the resulting combination products or complexes still tend to migrate in photographic layers or induce dissolution of color formers or dyes in developing solutions during color development. It is desirable that the polymeric vinyl compound can produce a complex having a sufficiently great molecular weight to prevent its migration in photographic layers.

The ratio of these polymers with the black-and-white developer to be combined may be defined as $m:n = 2:1-100:1$, wherein m means the polymerization degree of the polymer and n is the mole number of the black-and-white developer. Depending on the types of the polymer and black-and-white developer, the higher or lower ratio (m/n) may be used. The black-and-white developer may be used singly or in combination to form one or more complexes.

The polymer and the black-and-white developer may be added separately to a coating liquid to form a complex in situ. Alternatively, a complex is formed in water or alcohol by the reaction of the polymer with the black-and-white developer and then added to a photographic coating liquid. The amount used may be 1–30 percent based on the amount of a film-forming binder such as gelatine, but this can be varied depending on the type of the complex, the silver halide content of the emulsion layer, the silver content of the filter layer, the hardness of the binder layer, etc. X

This invention is applicable to any light-sensitive silver halide color-photographic material containing a color former which may be alkali-soluble coupler having a nondiffuse group, oil-soluble incorporated coupler, etc. or colorless coupler, colored coupler, etc. Similarly, any color developer which is conventionally known is also usable for color development of the color-photographic material of this invention.

As explained hereinabove, the present invention can exhibit the superadditive effect of the color developer and the black-and-white developer in Redox system during color development, thereby to obtain improved graininess of dyes and decrease of fogging, without sacrificing photographic speed and gradient.

The following examples describe certain ways in which the principle of the invention has been applied, but are not to be construed as limiting its scope.

EXAMPLE 1

A high speed green-sensitive photographic emulsion is prepared which contains 100 g. of gelatin and 0.35 moles of silver bromoiodide containing 5 mole percent silver iodide. This emulsion is divided to 12 equal portions. Six portions are added with each one of the before-indicated phenolic compounds (II), (IV), (VI), (VIII) and (X) and poly-N-vinyl-2-pyrrolidone having an average molecular weight of 350,000 (this is referred to as the compound (P), hereinafter). Five portions are added with each one of the compounds (II), (IV), (VIII) and (X), respectively, combined with the compound (P) in methanolic solution. The remaining one portion is used as a control sample by adding thereto methanol only. Each of these emulsions are added with a magenta color former, 1-[4-(4-tert.butylphenoxy)-3-sulfophenyl]-3(3-palmitamidobenzamido)-5-pyrazolone, in the proportion of 3 mole percent based on the molar content of the silver halide and then adjusted at pH 6.8. These emulsions are coated on cellulose triacetate film based and dried. The resulting film strips are subjected to exposure to light in a sensitometer. After the light exposure, these film strips are treated at 20° C. for 10 minute with a developing solution of the following formulation.

4-Amino-N-ethyl-N-[β-methanesulfonamidoethyl] -m-toluidine sesquisulfate monohydrate	5 g.
Anhydrous sodium sulfite	4 g.
Sodium carbonate monohydrate	50 g.
Hydroxylamine semi-sulfate	0.6 g.
Potassium bromide	2 g.
Water to make up 1 l.	

After development, the film strips are washed with water for 5 seconds and treated with a magnesium sulfate solution at 20° C. for 10 minutes. Then, they are rinsed, bleached, rinsed, fixed, rinsed and dried in the manner known per se.

Complementary color density of the color-developed film strips is measured. Fog., relative speed at the density of 0.1 above fog., gamma value averaging those of from the point at which the photographic speed is obtained to the point at which an exposure amount as much as 10 times is given are obtained. The color-developed film negatives thus obtained are printed by enlargement (x10) on Sakura color photographic paper. These color prints are visually compared with the control color print by 10 persons with reference to a series of standard color image samples which represent 10 discriminating grades of graininess. Rating of graininess of the tested color prints is determined. For example, +2 means that the color print in question is better in graininess by two grades than the control color print. The results are set forth in table 1, wherein the amount is expressed by percent weight based on the gelatine amount. The complex is expressed as by [P]m [II] n, wherein m and n are the molar ratio of the individual components.

TABLE 1

Film strip		Photographic properites			Difference of grade in graininess
Compound	Amount percent	Fog	Relative speed	Gamma	
Control		0.20	100	0.65	
[P]	10	0.18	90	0.63	+2
[II]	1.50	0.17	95	0.67	−1
[IV]	1.64	0.19	100	0.65	0
[VI]	3.56	0.22	95	0.64	+1
[VIII]	3.66	0.18	95	0.63	+1
[X]	0.25	0.16	96	0.62	+2
[P] 10[II] 1	(10) (1.50)	0.15	100	0.63	+5
[P] 10 [IV] 1	(10) (1.64)	0.13	98	0.66	+6
[P] 5[VI] 1	(10) (3.56)	0.14	96	0.67	+4
[P] 5[VIII] 1	(10) (3.66)	0.18	110	0.64	+4
[P] 70[X] 1	(10) (0.25)	0.17	105	0.62	+7

As apparent from table 1, the complex compound of the polymer with the black-and-white developer according to this invention (which compound is expressed as by [P] 10 [II]1)

can show remarkably improved graininess of dyes without decrease in photographic speed and gradient, in comparison with the control, the polymer alone and the black-and-white developer alone. cEXAMPLE 2

A high speed red-sensitive photographic emulsion is prepared which contains 80 g. of gelatine and 0.35 moles of silver bromoiodide containing 4 mole percent silver iodide. The emulsion thus prepared is divided to six equal portions, one of which is used as a control emulsion and the remaining five are added with each one of the compound (III), poly-N-vinyl-5-methyl-2-oxazolidinone having an average molecular weight of 250,000 (this is referred to as the compound [0] hereinafter), copolymer of poly-N-vinyl-2-pyrrolidone having an average molecular weight of 160,000 with sodium polymethacrylate having an average molecular weight of 32,000 (this copolymer is referred to as the compound (PM) hereinafter), a complex of (III) with (0) and a complex of (III) with (PM). The thus prepared emulsions are added with a cyan color former, 1-hydroxy-2-naphthoyl-N-octadecylamido-4-sulfonic acid, in the amount of 6 mole percent based on the silver halide content. The emulsions are adjusted pH 6.8. These are coated on cellulose triacetate film bases and dried. The each samples obtained are exposed to light in a sensitometer. The same measurement as in example 1 is conducted. The results are set forth in table 2.

TABLE 2

Film strip		Photographic properites			Difference of grade in graininess
Compound	Amount percent	Fog	Relative speed	Gamma	
Control		0.11	100	0.64	
[O]	15	0.08	95	0.63	+2
[PM]	7.9	0.09	100	0.64	+1
[III]	1.80	0.08	89	0.66	−1
[O] 10[III] 1	(15) (1.80)	0.04	105	0.65	+5
[PM] 5[III] 1	(7.9) (1.80)	0.05	97	0.63	+4

As apparent from table 2, use of the complexes according to the invention is effective to improve graininess of dyes and decrease fog, without any adverse influence on photographic speed and gamma.

EXAMPLE 3

A colloidal silver suspension containing 100 g. of gelatine and 5.2 g. of blue colloidal silver is prepared. This suspension is for use in the preparation of antihalation layer. This is divided to five equal portions, one of which is used as a sample and the remaining four are added with each of the compound (IV), the compound (XII), poly-N-vinyl-2-pyrrolidone having an average molecular weight of 350,000 (this is referred to (P), hereinafter), the complex of (IV) with (P) and the complex of (XII) with (P). The emulsions are adjusted at pH 6.8 and then coated on cellulose triacetate film bases. The high speed red-sensitive color photographic emulsion containing a cyan color former which emulsion is used in example 2 is overcoated and dried. Each film samples thus prepared are exposed to light in a sensitometer and then treated with a developing solution of the following formulation:

N,N-diethyl-p-phenylenediamine monohydrochloride	2.5 g.
Anhydrous sodium sulfite	4 g.
Sodium carbonate monohydrate	50 g.
Hydroxylamine semi-sulfate	0.6 g.
Potassium bromide	2 g.
Water to make up 1 *l.*	

After development, these film samples are worked up in the same manner as in example 1. The results of measurement are set forth in table 3. It is to be noted that the control (I) appearing in table 1 is the same as the control of example 2 and has no antihalation layer, and the control (II) is the control sample with antihalation layer.

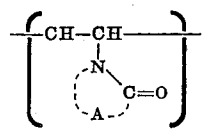
TABLE 3

Film strip			Photographic properties			Difference of grade in graininess
Compound	Amount (percent)		Fog	Relative speed	Gamma	
Control	[I]		0.16	94	0.67	0
Control	[II]		0.28	100	0.68	
[P]	15		0.21	102	0.67	0
[IV] plus [XII] [P] 70 [IV] 7 [XII] 1	(2.46) (0.45)	(15) (2.46) (0.45)	0.25	95	0.68	+1
			0.17	100	0.66	+3

As apparent from table 3, the present invention is useful to improve graininess remarkably and decrease fog., without any adverse influence on photographic speed and gamma.

What we claim is:

1. A light-sensitive silver halide color-photographic material which comprises a support and, coated thereon, a light-sensitive silver halide emulsion layer containing a color coupler, characterized in this that the combination of an alkali-soluble phenolic compound having at least one hydroxyl group on its benzene nucleus and capable of reducing silver halide with a water-soluble polymeric vinyl compound containing the recurrent unit of the general formula



wherein A means an atomic grouping necessary to constitute, together with the adjacent nitrogen and carbon atoms, a five- to seven-membered oxygen-containing heterocyclic ring, and capable of forming a complex with said phenolic compound through a hydrogen bond, is present in said light-sensitive silver halide emulsion layer and/or the layer contiguous therewith.

2. A light-sensitive silver halide color-photographic material as claimed in claim 1, wherein said material is a monochromatic color or tri-color photographic film.

3. A light-sensitive silver halide color-photographic material as claimed in claim 1, wherein said combination is present in at least one layer selected from light-sensitive emulsion layer, interlayer, protective layer, antihalation layer, filter layer and sublayer.

4. A light-sensitive silver halide color-photographic material as claimed in claim 1, wherein said phenolic compound is one member selected from black-and-white developers having at least one phenolic hydroxyl group.

5. A light-sensitive silver halide color-photographic material as claimed in claim 1, wherein said polymeric vinyl compound is one member selected from polyvinyl pyrrolidone, polyvinyl oxazolidone, polyvinyl piperidone and polyvinyl caprolactam.

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