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3,457,079

**PHOTOGRAPHIC SILVER HALIDE EMULSIONS
STABILIZED WITH GALLIC ACID OR AN ALKYL
ESTER THEREOF**

Kenichi Koda, Shui Sato, Masayuki Shoono, and Haruo Hori, Tokyo, Japan, assignors to Konishiroku Photo Industry Co., Ltd., Tokyo, Japan, a corporation of Japan

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5 Claims

This invention relates to stabilized photographic compositions, and more particularly, it concerns with a photographic element, e.g., photographic film, paper or plate, bearing on a support a photosensitive layer containing gallic acid or its alkyl esters which may be generically referred to "a gallic compound" hereinafter.

In the art it is well known that photographic compositions, when stored for a long period after their preparation, suffer from decrease in speed and formation of undesired fog. In order to prevent these adverse effects, a variety of stabilizers also have been proposed. Incorporation of the known stabilizers (e.g., azaindolizine), however, is disadvantageous because it often causes decrease in speed, and the demand in the art has been directed to develop a stabilizer which will permit to prevent fog without any adverse influence on photosensitivity.

It is accordingly one object of the present invention to provide a photographic composition which can resist to any undesired effect caused by storage over a long period of time.

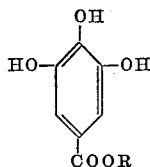
Another object of the present invention is to provide a photographic element which is entirely safe from formation of fog.

Other objects, features, capabilities and advantages which are comprehended by the invention will be apparent from the specification and claims which follow.

The above-mentioned and other objects can be attained by incorporating a gallic compound as a stabilizer into a photographic composition.

We have now found that if the gallic compound is present in a photographic composition of the present invention, the said composition can be safely stored over a long period of time, without suffering from decrease in speed or formation of fog. In a typical embodiment of the present invention, the gallic compound may be incorporated into at least one of the gelatine-containing layers of a photographic element, such layers including emulsion layers, sublayers, internal layers, protective layers and backing layers. Another advantage of the present invention is that where the gallic compound is added to a photographic emulsion during its digestion or ripening, it is possible to prevent fog formation and consequently to facilitate an increase of speed due to the digestion or ripening.

Suitable gallic compounds can be represented by the general formula



wherein R represents hydrogen atom or a straight or branched alkyl radical containing 1 to 18 carbon atoms.

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Typical compounds are gallic acid (M.P. 235° C. (decomp.)), methyl gallate (M.P. 200° C.), ethyl gallate (M.P. 155° C.), n-propyl gallate (M.P. 148° C.), isopropyl gallate (M.P. 124° C.), n-butyl gallate (M.P. 134° C.), isoamyl gallate (M.P. 146° C.), n-amyl gallate (M.P. 109° C.), n-hexyl gallate (M.P. 93° C.), n-heptyl gallate (M.P. 96° C.), n-octyl gallate (M.P. 96° C.), n-nonyl gallate (M.P. 97° C.), n-decyl gallate (M.P. 95° C.), n-hendecyl gallate (M.P. 97° C.), n-dodecyl gallate (M.P. 97° C.), n-tetradecyl gallate (M.P. 97° C.), n-hexadecyl gallate (M.P. 100° C.) and n-octadecyl gallate (M.P. 104° C.). Among these compounds, lower alkyl gallates can be readily prepared by the conventional techniques known by those skilled in the art, and higher alkyl gallates, for example, having more than ten carbon atoms can be prepared by the method described in Rec. Trav. Chim., 70, 277-284 (1951).

Incorporation of the gallic compound into a layer or layers of the photographic element of the present invention can be made in the manner heretofore known per se in the art. For example, if the gallic compound is to be present in an emulsion layer of the said element, it is possible to add the said compound into the emulsion at any time just before, during or after the second ripening of the said emulsion. Addition of the gallic compound at the stage after the second ripening of the emulsion is most preferred. Alternatively, the gallic compound may be added to a starting material for preparation of the emulsion, for example, gelatine. The amount added will vary depending on the type of emulsions, the degree of stabilization desired and the type of a layer to which the gallic compound is added, but it usually is within the range of from 0.003 g. to 3.0 g. per liter of the emulsion or coating solution. It is desirable to add this compound in solution dissolved in a suitable solvent, e.g., water, methanol, ethanol, etc., if the addition is made to an emulsion.

Use of the gallic compound as a stabilizer does not adversely influence on sensitization of a photographic emulsion concerned. Thus, the photographic emulsion sensitized by way of gold-, sulfur- or other chemical sensitization or optical sensitization can be successfully stabilized with the gallic compound. Any hardener, coating aid or other known photographic additives may be optionally used in combination with the gallic compound, without a significant loss of its stabilizing effect. Furthermore, it sometimes can provide desirable effect to facilitate an increase of speed because the said compound will prevent increased fog which frequently occurs accompanying to the sensitization. It is, of course, true that decrease of speed and increase of fog during storage of the emulsion also can be prevented by using the gallic compound.

Still another advantage of the present invention is that fog and desensitization both which frequently occur during the storage of a color photographic material containing color formers in the emulsion can be effectively prevented by using the gallic compound.

The emulsion to which the gallic compound has been added can be applied to a suitable support in the manner heretofore known per se in the art, e.g., coating or pouring. Suitable supports include films, papers and glass plates. For example, films of the types, such as cellulose esters, e.g., cellulose triacetate; polyesters obtained by the polycondensation of phthalic, isophthalic or terephthalic acid with a dihydric alcohol, e.g., polyethylene terephthalate, poly[cyclohexane - 1,4 dimethylol]terephthalate, etc.; and polycarbonates including those obtained by the polycondensation of bis-phenol A with carbonic acid, are suitable.

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 silver bromo-iodide emulsion useful for high speed negatives and containing 3 mol percent of silver iodide is prepared according to neutral process. This emulsion is added with a gold-sensitizer and then subjected to second ripening at a temperature of 60° C. for 75 minutes. After the said ripening, the emulsion is divided to eleven portions, one of which is used for preparation of control film without any stabilizer and the other nine used after the addition of the gallic compounds specified in the respective columns of Table I. The remaining one por-

ripening, the emulsion is optically sensitized by addition of 9-methyl-3,3'-diethyl seleno carbocyanine bromide in the amount of 50 mg. per liter of the emulsion. The emulsion is divided to nine portions, one of which is used for preparation of control film without any stabilizer and the other seven used after the addition of the gallic compounds specified in the respective columns of Table II. The remaining one portion is added with the same known stabilizer as in Example 1. Each portions are prepared to form films. Test pieces cut from the films are then subjected to a comparative test in the same manner as in Example 1. The results obtained are set forth in Table II.

TABLE II

Compound	Amount used (mg./l.)	Just after preparation of the film		Incubated at 55° C. for 2 days after preparation		Incubated at 50° C. and 80% RH for 2 days after preparation	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
Control.....	0	100	0.09	67	0.34	90	0.12
Gallic acid.....	135	101	0.10	93	0.12	99	0.10
Ethyl gallate.....	160	96	0.09	90	0.12	100	0.09
n-Propyl gallate.....	170	100	0.09	90	0.08	101	0.10
n-Butyl gallate.....	180	100	0.09	96	0.11	100	0.10
n-Heptyl gallate.....	210	100	0.09	89	0.10	110	0.11
n-Dodecyl gallate.....	270	102	0.10	98	0.11	100	0.11
n-Hexadecyl gallate.....	310	103	0.10	99	0.12	103	0.11
Known stabilizer.....	150	96	0.09	84	0.08	73	0.08

tion is added with 5-methyl-7-hydroxy-1,3,4-triazaindoline which is the known stabilizer. Each portions are prepared to form films. Each films are cut into three pieces, one of which is immediately subjected to the later specified sensitometric test, and the second and third pieces are stored at 55° C. for 2 days or at 50° C. under a relative humidity of 80% for 2 days before the same test. Samples of these film coatings were then exposed in an intensity-scale type sensitometer and developed for five minutes in a developer of the following formulation:

	Grams
Metol (monomethyl-p-aminophenol sulfate)	1.5
Sodium sulfite (anhydrous)	25.0
Hydroquinon	3.0
Sodium carbonate (monohydrate)	15.0
Potassium bromide	0.5
Water to make 1.0 liter.	

The developed samples were stopped with dilute acetic acid and then fixed, washed and dried. The results are set forth in Table I.

TABLE I

Compound	Amount used (mg./l.)	Just after preparation of the film		Incubated at 55° C. for 2 days after preparation		Incubated at 55° C. and 80% RH for 2 days after preparation	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
Control.....	0	100	0.14	74	0.43	142	0.22
Gallic acid.....	135	98	0.12	98	0.18	115	0.11
Ethyl gallate.....	160	100	0.10	100	0.16	109	0.10
n-Propyl gallate.....	170	95	0.10	92	0.15	107	0.10
Isoamyl gallate.....	190	99	0.12	95	0.17	110	0.10
n-Hexyl gallate.....	200	100	0.12	96	0.16	115	0.12
n-Octyl gallate.....	220	98	0.11	92	0.16	115	0.11
n-Decyl gallate.....	250	100	0.12	96	0.17	120	0.10
n-Tetradecyl gallate.....	290	100	0.12	97	0.16	115	0.11
n-Octadecyl gallate.....	330	98	0.13	99	0.18	112	0.11
Known stabilizer.....	150	80	0.13	76	0.12	61	0.09

In this test, photographic speed which is a reciprocal of the exposure to give an optical density of 0.5 above fog density, is expressed as relative speed to that of unstored control film, which is rated as 100. The data of Table I clearly indicates that alkyl gallates are useful for prevention of undesired fog formation during incubation.

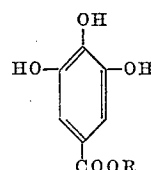
EXAMPLE 2

The photographic emulsion used in Example 1 is subjected to second ripening in the same manner as in Example 1. Five minutes before completion of the second

The data of Tables I and II clearly indicates that the photographic emulsions having been sensitized could be safely stabilized by addition of alkyl gallate. It is also noted that the gallic compounds do not cause substantial decrease in sensitivity in comparison with the known stabilizer.

What we claim is:

1. A light-sensitive, photographic silver halide emulsion comprising gelatin having light-sensitive silver halide dispersed therein and containing a stabilizing amount of a compound of the general formula



wherein R represents hydrogen atom or a straight or branched alkyl radical having 1 to 18 carbon atoms.

2. A light-sensitive, photographic silver halide emulsion as claimed in claim 1; further comprising a chemical sensitizer.

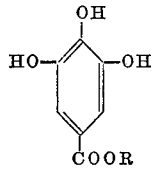
3. A light-sensitive, photographic silver halide emulsion as claimed in claim 1; further comprising an optical sensitizer.

4. A light-sensitive, photographic silver halide emulsion as claimed in claim 1; further comprising a color former.

5. A photographic element comprising a support bearing thereon layers at least one of which contains a photographic silver halide emulsion, at least one of said layers

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having incorporated therein a stabilizing compound of the formula



wherein R represents hydrogen atom or a straight or branched alkyl radical having 1 to 18 carbon atoms, the amount of said stabilizing compound being equal to 0.0003

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to 3.0 g. per liter of the emulsion in the coating solution used in the preparation of the emulsion layer.

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NORMAN G. TORCHIN, Primary Examiner
R. E. FICHTER, Assistant Examiner