United States Patent

Sato et al.

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[54] LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC EMULSIONS

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[58] **Field of Search**.....96/109, 107, 114

[56] **References Cited**

UNITED STATES PATENTS

3,173,790 3/1965 Dersch et al.....96/109

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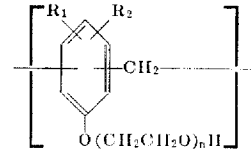
[57] **ABSTRACT**

An ethylene oxide addition polymer of an alkylphenol- formaldehyde condensate, said polymer consisting of the recurrent structural unit of the formula



wherein R_1 is an alkyl group; R_2 is an alkyl group or a hydrogen atom; and n is an integer of 1 to 100, and having an average polymerization degree in the range of 2 to 10, has been found effective as a sensitizer for a light-sensitive silver halide photographic emulsion, without causing any adverse effect on photographic properties.

5 Claims, No Drawings

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC EMULSIONS

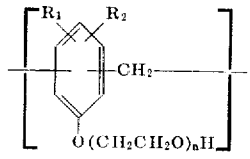
This invention relates to the enhancement in light sensitivity of light-sensitive silver halide photographic emulsions. More particularly, the invention pertains to light-sensitive silver halide photographic emulsions containing ethylene oxide addition polymers of alkylphenol-formaldehyde condensates.

Heretofore, there have been proposed many processes for enhancing the light sensitivity of light-sensitive silver halide emulsions. Typical as such processes are chemical sensitization processes using sulfur compounds capable of forming silver sulfide, or using suitable reducing substances or noble metal salts. Further, it is well known that the light sensitivity can be further increased by using a combination of said compounds. [Refer to, for example, "The Theory of The Photographic Process," 3rd Edition (1967), pages 113–117]. Another well known chemical sensitization process is the process using polyalkylene oxide compounds having a molecular weight of at least 300. However, all these known sensitizers are restricted in the amount to be added to emulsions and, in case the amounts thereof exceed a definite limit, there are brought about such drawbacks that photographic films prepared by use of such emulsions are greatly increased in fog and are low in stability during storage at high temperatures. Moreover, there are such difficulties that the fog is high in degree and cannot be controlled even when anti-fogging agents are incorporated into the emulsions.

In view of the above, the present inventors made various studies to find that when ethylene oxide addition polymers of alkylphenol-formaldehyde condensates are incorporated into photographic silver halide emulsion layers or into layers adjacent to said emulsion layers, the films can be increased in gamma, effective sensitivity and maximum density with good stability and without fogging even when the films have been stored at high temperatures.

The compounds employed in the present invention have such features that they do not increase fog of silver halide emulsions due to lapse of time, are scarcely increased in amount to be added and hence are easily usable, and can improve the characteristics of photographic emulsions. Particularly, they show such prominent effects that they can give marked increase in maximum density and gamma which cannot be attained by use of conventional polyalkylene oxide compounds.

The ethylene oxide addition polymers of alkylene-phenol-formaldehyde condensates employed in the present invention are formed by the polymerization of structural units represented by the formula,



wherein R_1 is an alkyl group; R_2 is an alkyl group or a hydrogen atom; and n is an integer of 1 to 100, and those in which said structural units have been polymerized to an average polymerization degree in the range of 2 to 10 are preferable. These polymers are such that all the alkyl groups represented by R_1 which are bonded to benzene nuclei of the structural units may be same or different. These compounds can be synthesized according to the methods disclosed in U.S. Pat. No. 2,454,541. Generally, the compounds are viscous paste-like, wax-like or semi-solid resins, and are soluble in water, acetone, alcohol, benzene and the like.

Typical as such compounds are set forth below, but compounds usable in the present invention are not limited to these.

Compound 1: Compound prepared by addition-polymerizing p-cresol-formaldehyde resin with 1.5 moles of ethylene oxide. n^{20}_D 15808.

Compound 2: Compound prepared by addition-polymerizing p-cresol-formaldehyde resin with 8 moles of ethylene oxide. n^{20}_D 15199.

Compound 3: Compound prepared by addition-polymerizing nonylphenol-formaldehyde resin with 16 moles of ethylene oxide. n^{20}_D 14928.

Compound 4: Compound prepared by addition-polymerizing octylphenol-formaldehyde resin with 15 moles of ethylene oxide. n^{20}_D 14917.

Compound 5: Compound prepared by addition-polymerizing p-octadecylphenol-formaldehyde resin with 100 moles of ethylene oxide. m.p. 58°–59° C.

Compound 6: Compound prepared by addition-polymerizing nonylphenol-p-cresol-formaldehyde resin with 15 moles of ethylene oxide. n^{20}_D 14904.

Compound 7: Compound prepared by addition-polymerizing p-nonylphenol-dinonylphenol-formaldehyde resin with 30 moles of ethylene oxide. n^{20}_D 14896.

The compounds employed in the present invention may be added at any time during the second ripening step. Ordinarily, however, it is preferable to add after completion of the second ripening. In adding the compounds, they are dissolved in water or in a water-miscible organic solvent such as methanol or ethanol and are added to photographic emulsion layers or layers adjacent thereto. The amounts of the compounds to be added vary depending on the kind of the compounds or light-sensitive materials employed, but are ordinarily within the range of 0.01 g. — 3 g. per kg. of silver halide emulsion.

The compounds employed in the present invention can be applied to any type of silver halide emulsions such as silver chlorobromide, silver iodobromide and the like emulsions. These emulsions may have been subjected to gold sensitization, chemical sensitization, or spectral sensitization or supersenitization by use of spectral sensitizing dyes. Further, they may have been incorporated with various types of stabilizers, hardeners and surface active agents.

The compounds employed in the present invention are applicable not only to black and white photographic emulsions but also to color photographic emulsions containing couplers.

The present invention will be illustrated in detail below with reference to examples.

EXAMPLE 1

An emulsion for neutral process negative comprising 5 mole percent of silver iodide and 95 mole percent of silver bromide was subjected to second ripening to attain the maximum sensitivity by means of a sulfur sensitizer and a gold sensitizer. Thereafter, the emulsion was divided into portions of 100 g. each in weight. To each of the divided emulsions were individually added the present compounds shown in Table 1. After adding a suitable amount of saponin as a coating aid, each emulsion was uniformly coated under the same conditions onto a cellulose triacetate film base to prepare a sample. The sample was exposed to light by means of a sensitometer KS-1 (Manufactured and sold by Konishiroku Photo Industry Co., Ltd.) at 160 Lux, 5,400° K and was then developed at 20° C. for 5 minutes with a developer of the following composition:

Metol	3 g.
Anhydrous sodium sulfite	50 g.
Hydroquinone	6 g.
Sodium carbonate (monohydrate)	29.5 g.
Potassium bromide	1 g.
Water to make	1,000 cc.
(In application, the developer was diluted with water to 1 : 1).	

Thereafter, each sample was subjected to sensitometry to obtain the results set forth in Table 1.

TABLE 1

Sample No.	Compound added	Amount mg/100 g. emulsion	Sensitivity	Gamma	Maximum density	Fog

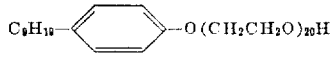
1	Compound 2	60	107	0.90	2.10	0.06
2	Compound 4	60	120	1.00	2.29	0.06
3	Compound 6	60	124	1.10	2.31	0.07
4	Non-addition	0	100	0.80	2.02	0.06

In the table, the sensitivity was represented by a relative sensitivity measured in the case where the sensitivity of non-addition compound (Sample No. 4) was regarded as 100.

As is clear from Table 1, it is understood that in accordance with the present invention, light-sensitive photographic materials improved in sensitivity, gamma and maximum density can be obtained.

EXAMPLE 2

The same high sensitivity emulsion as in Example 1 was divided, after completion of the second ripening, into portions of 100 g. each in weight. To each portion were individually added the present compounds as set forth in Table 2. Subsequently, 20 mg. per 100 g. of emulsion of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as a stabilizer was added, and then suitable amounts of a hardener and a coating aid were added to prepare an emulsion. This emulsion was uniformly coated on a cellulose triacetate film base and was then dried. Samples obtained in the above manner were subjected to incubation test at high temperature and humidity to obtain the results as set forth in Table 2. For comparison, a compound of the formula



(disclosed in British Pat. No. 805,826) was used to prepare a control sample.

The samples in accordance with the present invention give excellent light-sensitive photographic materials which are less in formation of fog due to lapse of time and free from degradation in sensitivity even when stored under severe conditions.

TABLE 2

Sample No.	Compound added	Amount (mg./100 g. emulsion)	Allowed to stand for 3 days under environmental conditions: Sensitivity	Maximum Density	Fog	Allowed to stand at 55° C. for 3 days: Sensitivity	Maximum density	Fog	Allowed to stand at 50° C. and R.H. of 80% for 3 days: Sensitivity	Maximum density	Fog
5	Compound 1	120	105	1.97	0.05	110	2.00	0.06	105	2.00	0.06
6	Compound 5	60	130	2.20	0.06	130	2.27	0.07	135	2.23	0.06
7	Compound 7	100	120	2.10	0.05	125	2.13	0.06	120	2.12	0.05
8	Control	60	110	1.92	0.06	105	1.90	0.07	110	1.87	0.06
8'	Non-addition	100	100	1.90	0.05	105	1.95	0.06	100	1.90	0.06

NOTE.—In the table, the sensitivity is a relative sensitivity measured by assuming that the sensitivity of non-addition sample (Sample No. 8) was 100.

EXAMPLE 3

A silver iodobromide color photographic emulsion containing 4 mole percent of silver iodide was subjected to gold sensitization and sulfur sensitization to effect second ripening. Immediately before completion of the ripening, the emulsion was divided into portions of 100 g. each in weight, and the present compounds as shown in Table 3 were individually added to each of the divided emulsions. After completion of the ripening, each emulsion was charged with a solution prepared by dissolving at an elevated temperature 1-hydroxy-2-N[δ(2,4-di-tert-amylphenoxy)butyl] naphthoamide as an internal cyan coupler in a mixture of di-N-butyl phthalate and ethyl acetate, and was emulsified and dispersed by use of sodium alkylbenzenesulfonate in a gelatine solution. Subsequently, the emulsion was incorporated with a hardener, and was then uniformly coated on a cellulose triacetate film support, followed by drying, to prepare a sample. Each sample thus prepared was exposed in the same manner as in Example 1 and was then developed at 20° C. for 10 minutes with a color developer of the following composition:

N-Ethyl-N-β-methanesulfonamido-ethyl-3-methylaminoaniline sulfate	5.0 g.
Sodium sulfite (anhydrous)	2.0 g.
Sodium carbonate (monohydrate)	50 g.
Potassium bromide	1.0 g.
Benzyl alcohol	3.8 g.
Sodium hydroxide	5.5 g.
Water to make	1,000 cc.

Thereafter, each sample was subjected to ordinary stopping, fixing, water-washing and bleaching treatments, was washed with flowing water for 20 minutes and was then dried to obtain a cyan image. The thus obtained cyan image was subjected to sensitometry to obtain the results as set forth in Table 3.

TABLE 3

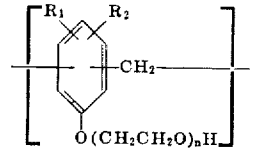
Sample No.	Compound added	Amount (mg/100 g emulsion)	Sensitivity	Gamma	Fog
9	Compound 3	100	120	0.92	0.03
10	Compound 3	50	115	0.90	0.03
11	Non-addition	—	100	0.70	0.03

In the table, the sensitivity is a relative sensitivity measured by assuming that the sample prepared without the addition of the present compound was 100.

From the table, it is understood that the present compounds are effectively applied also to coupler-containing emulsions.

What we claim is:

1. A light-sensitive silver halide photographic emulsion which contains a sensitizing amount of an ethylene oxide addition polymer of an alkylphenol-formaldehyde condensate, said polymer consisting of the recurrent structural unit of the formula



wherein R_1 is an alkyl group; R_2 is an alkyl group or a hydrogen atom; and n is an integer of 1 to 100, and having an average polymerization degree in the range of 2 to 10.

2. A light-sensitive silver halide photographic emulsion as claimed in claim 1, further comprising a color coupler.

3. A light-sensitive silver halide photographic emulsion as claimed in claim 1, wherein said emulsion has been sensitized by way of noble metal sensitizers, sulfur sensitizers, reduction sensitizers or polyalkylene oxide type sensitizers.

4. A light-sensitive silver halide photographic emulsion as claimed in claim 1, further including stabilizers, surface active agents, coating aids or hardeners.

5. A light-sensitive silver halide color photographic material which comprises a film support and, coated thereon, a layer of the emulsion as claimed in claim 2.

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