United States Patent Office

3,520,694
Patented July 14, 1970

3,520,694

GELATIN-SILVER HALIDE COMPOSITIONS CONTAINING TRIHYDRIC ALCOHOLS

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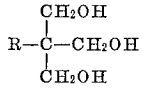
No Drawing. Filed Dec. 16, 1966, Ser. No. 602,150
Claims priority, application Japan, Dec. 17, 1965, 40/77,702
Int. Cl. G03c 1/02
U.S. Cl. 96—114.4 9 Claims

ABSTRACT OF THE DISCLOSURE

An improved photographic light-sensitive element is realized where at least one silver halide containing layer has incorporated therein a compound represented by the formula:



R is an alkyl group of 1–5 carbon atoms.

The present invention relates to a photographic gelatino silver halide light-sensitive element.

A gelatino silver halide emulsion coating on a natural or synthetic polymer support such as paper, a cellulose ester, or a polyester is usually reduced in flexibility and other physical properties under the conditions of low temperature and low humidity. Additionally, if a mechanical stress such as tortion, bending or friction is added thereto during manufacturing or during processing after manufacture before development, it is sometimes endowed with undesirable photographic properties such as desensitization, fogging and the like. Furthermore, it is commonly known that in the case of employing a so-called Festoon-drying system to dry a gelatino silver halide emulsion coating, an undesirable annular ring like pattern, so-called stick mark, appears at the portion which was dried unevenly, caused by being placed in an intermittent drying condition (cf. e.g., E. Zünd; "Zeitchrift fur Wissenchaftliche photographic photophysic und photochemie," vol. 49, pages 25–103).

As a method for improving these drawbacks, it has been reported to be effective to incorporate into the gelatin coating composition polyhydric alcohols such as glycerine, ethylene glycol or 1,6-hexane diol (U.S. Pat. 2,960,404) or a dialkyl phthalate (British Pat. 738,637).

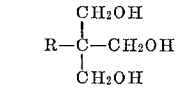
However, some of these materials have large faults in that although they may improve the physical properties of the coating material containing gelatin under conditions of low temperature and low humidity, they also may reduce the physical properties and the photographic properties of the coating under severe conditions of high temperature and high humidity. Even if they can prevent to some extent the lowering of photographic properties by a mechanical stress, they reduce the adhesive strength of the gelatin coating layer to the support at the same time, and give excessive stickiness to the surface of coating, which results in the adhesion of the coating to other surfaces.

Therefore, an object of the prevent invention is to provide a photographic gelatino silver halide light-sensitive material in which the physical properties and the adhesive property of the emulsion layer to the support are not reduced, the formations of darking, desensitization caused by strain, stick mark as mentioned above

are restrained, the stickiness of the gelatin coating to other surfaces is weak, and the preservation properties thereof are good.

As the result of investigation, it has been found that the above objects can be accomplished by incorporating in a photographic coating composition containing gelatin a trihydric alcohol having three hydroxyl groups bonded to the first carbon atom.

The above-mentioned trihydric alcohols used in the present invention are represented by the following general formula:



(I)

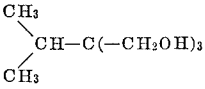
wherein R represents an alkyl group having from 1 to 5 carbon atoms. The compound may usually be prepared by the reaction of aliphatic aldehyde such as propionaldehyde or n-butylaldehyde with formaldehyde.

The typical examples of the trihydric alcohol are as follows:

(1) $CH_3-C(-CH_2OH)_3$

(2) $C_2H_5-C(-CH_2OH)_3$

(3)



and

(4) $CH_3-(CH_2)_4-C(CH_2OH)_3$

The amount of the compound added to the photographic material in this invention is not particularly limited but 1–30% by weight to the amount of gelatin is preferable. That is, if the amount is less than 1% by weight, a remarkable effect is not obtained, and if it is larger than 30% by weight, the coated layer becomes stickly. In particular, if the amount of the compound added is 5–20% by weight to the amount of gelatin, the desensitization and draking caused by strain of the gelatino silver halide layer containing the compound by mechanical stress and the formation of stick mark thereof by uneven drying are markedly restrained. Furthermore, the stickiness of the surface of the coating is remarkably improved as compared with the case of adding a known plasticizer.

The compound of this invention may be dissolved in a solvent which has no detrimental effect on the photographic silver halide emulsion; such a solvent might be water, lower alcohol such as methanol ethanol and the like, or ketone such as acetone. The compound may then be added to the photographic gelatin silver halide emulsion at any stage before coating. However, it is most preferable to add after second ripening and before coating.

The above explanation is only the case of incorporating the trihydric alcohol in a photographic gelatino silver halide emulsion, but the trihydric alcohols of this invention may be incorporated in other gelatin-coating composition, for example, a protective layer and intermediate layer of a photographic light-sensitive material, and also may be incorporated in a photographic gelatino silver halide emulsion and other gelatin-containing coating composition simultaneously.

The photographic gelatino silver halide emulsions to be employed in this invention may be emulsions for black and white positive or negative photographic light-sensitive material and/or light-sensitive graphic art material, emulsions for photographic X-ray film, and coupler-in-emulsion type color photographic emulsion wherein a color coupler is incorporated in the emulsion, and coupler-in-developer type color photographic emulsion wherein a color coupler is incorporated in a developer.

Further, the compound of this invention may be incorporated with a good result in various silver halide emulsions, such as, a silver chloride emulsion, and silver bromide emulsion, and silver bromo-chloride emulsion and a silver bromo-iodide emulsion, and the like.

The silver halide emulsion to be used in this invention may be chemically sensitized by a conventional method, for example, with a compound containing unstable sulfur, such as ammonium thiosulfate or allylthiourea (for example, P. Glafkides; "Chimie photographique"; 2 eme edition, publication photocinema, Paul Montel Peris, pages 297–299, 1957), a complex salts of mono-valent gold and thiocyanic acid (cf. ibid., page 301), a polyalkylene oxide derivative, or a combination thereof. The silver halide emulsion may be optically sensitized by the addition of sensitizers such as a cyanine dye or a merocyanine dye (Shinichi Kikuchi; Kagaku Shashin Binran (II), pages 13–24, 1959). Furthermore, the silver halide emulsion may be stabilized with various well-known antifoggants (cf., ibid., pages 32–47) and may be hardened by various well-known gelatin hardening agents, such as aldehyde compounds (cf. ibid., 30–32), polyfunctional ethylene-imine compounds (e.g. Japanese Pat. 309,487), epoxy compounds (e.g. Japanese Patent 257,564), active halogen compounds (e.g. French Pat. 1,379,255) and active vinyl compounds (e.g. German Pat. 872,153).

The silver halide emulsion or other gelatin-containing coating composition to be employed in this invention may further contain a well-known wetting agent, such as nonionic, anionic and amphoteric surface active agents (e.g. polyoxyethylene nonylphenyl ether, sodium alkylbenzene sulfonate, or N-methylalkyl tauride), and anionic surface active agents containing an ethylene oxide chain as described in Belgian Pat. 650,004.

The following examples illustrate some of the present invention.

EXAMPLE 1

An aqueous 20% solution of trimethylolethane (Compound 1) or trimethylolpropane (Compound 2) was added in a negative high-sensitive silver bromo-iodide emulsion containing 7% by weight of gelatin which had been sensitized with sulfur and gold. The resulting emulsion was applied to a cellulose triacetate base so that the dried thickness of the coating after drying was 10±1 microns. Then, the coated layer was set by supplying the clear air of 7° C. and then dried for about 50 minutes by passing the thus coated film through a drying chamber in which the drying temperature was so controlled that it was raised gradually from 18° C. to 45° C. A sample of 5 cm. x 12 cm. was cut from the thus obtained film and placed in for 48 hours at 23° C. in the atmosphere of 65% in relative huimidity. Then opposite ends of this film were combined such that the emulsion layer was positioned at the inside thereof, and a stress was applied to the thus folded film by passing through a slit of 3 mm. in width from the side of the combined ends. Thereafter, the film was developed for 5 minutes at 20° C. in the developer having the following composition.

	G.
N-methyl-p-aminophenol sulfate	1.0
Sodium sulfite (anhydrous)	75.0
Hydroquinone	9.0
Sodium carbonate mono-hydrate	30.0
Potassium bromide	5.0

Water to make 1 liter.

The developed coatings were fixed, water-washed and dried as usual, and then the density of the portion blackened by the pressure was measured.

Apart from this, the above-prepared film was placed for 48 hours in an atmosphere of 85% in relative humidity at 35° C. Then, the film was folded so that the emulsion layers were in contact with each other; it was allowed to stand for 24 hours in the same atmosphere while adding the static pressure of 50 g./sq. cm., and then the sticked areas of the emulsion layer were measured.

The results obtained are shown in the following table together with the comparative results of adding no compound of this invention (other conditions are the same) and of adding glycerine instead of the compound of this invention (other conditions are the same), and it will be apparent from the table that the formation of fog by pressure was almost completely prevented and the stickiness of the coated surface was less in the case of adding the compound of this invention.

Compound	Quantity (g./100 g. gelatin)	Blackened density	Sticked areas, percent
Compound 1	7	0.13	50
Compound 1	14	0.06	55
Compound 2	7	0.15	45
Compound 2	14	0.08	50
Glycerine	7	0.20	75
Do	14	0.16	85
None		0.25	45

EXAMPLE 2

An aqueous 20% solution of trimethylol propane (Compound 2) or trimethylol isobutane (Compound 3) was added into a silver bromo-chloride emulsion for graphic arts containing 6% by weight of gelatin that has been sensitized by sulfur. The resulting emulsion was applied onto a polyethylene terephthalate base so that the dried thickness of the coating was 6.5±1 microns. Then, the coated layer was set by supplying clear air of 7° C., and dried for about 40 minutes by passing the thus coated film through a drying chamber in which the drying temperature was so controlled that it was raised gradually from 18° C. to 35° C. A sample was cut off from the film, subjected to above conditioned atmosphere, folded and pressed as in Example 1.

Thereafter, the sample was exposed such that the optical density thereof after development would become about 1.0, developed for 3 minutes at 20° C. in the developer having the following composition:

	G.
Sodium sulfite (anhydrous)	90.0
Hydroquinone	45.0
Sodium hydroxide	37.5
Potassium bromide	30.0

Water to make 1 liter.

The sample was then subjected to fixing, water-washing and drying as usual, and the difference between the density of the portion of which the sensitivity was reduced by the pressure and the density of the non-pressed portion was measured. Apart from this, the film was also treated by the process as in Example 1 and the sticked areas were measured.

Thus obtained results are shown in the following table together with the case of adding no compound of this invention (other conditions are the same) and the case of adding 1,6-hexane diol instead of the compound of this invention (other conditions are the same), and as clear from the table the extent of desensitization by pressure was extremely suppressed and the stickiness of the surface of the coating was less in the case of adding the compound of this invention.

Compound	Quantity (g./100 g. gelatin)	Density difference	Sticked area, percent
Compound 2	6.5	0.30	45
Do	13.0	0.15	50
Compound 3	6.5	0.35	40
Do	13.0	0.15	50
1,6-hexanediol	6.5	0.40	700
Do	13.0	0.25	80
None		0.60	40

EXAMPLE 3

A 20% aqueous solution containing trimethylol propane (Compound 2) or trimethylol hexane (Compound 4) was added into a silver bromo-iodide negative emul-

sion of a high ratio of silver to gelatin containing 7% by weight of gelatin, which had been sensitized with sulfur and gold, and the resulting emulsion was applied to a polyethylene terephthalate base so that the dried thickness of the coating was 10±1 microns. Then, the coated layer was set by supplying clear air of 7° C. A sample of 20 cm. x 20 cm. in area was cut off from the film and placed on a horizontally placed flat plate such that the uncoated side of the film was in contact with the plate. Then, air of about 23–25° C. was uniformly supplied onto the surface to dry it so that the water-content became 55±5%, and thereafter air of 35° C. in temperature and 50±5% in relative humidity was supplied to the film for 30 seconds through a nozzle having an inside diameter of 1.5 cm. placed above the sample at a distance of 20 cm. Subsequently the air supply was interrupted for 1 minute, and was repeated until the whole surface of the coated layer was dried. Then, the sample was developed in the developer having the following composition for 6 minutes at 20° C.

	G.
N-methyl-p-aminophenol	2.5
Sodium sulfite (anhydrous)	30.0
Hydroquinone	2.5
Sodium metaborate ($4H_2O$)	10.0
Potassium bromide	0.5

Water to make 1 liter.

and was subjected to fixing, water-washing and drying as usual.

The density difference between a high density portion and a low density portion of the drying uneveness of thus formed annular ring-like pattern, was measured. Apart from this, a film sample was dried uniformly as in Example 1, and the sticked areas were measured.

Thus obtained results are shown in the following table together with the case of adding no compound of this invention (other conditions are the same) and the case of adding glycerine instead of the compound of this invention (other conditions are the same). As clear from the table, the formation of the annular ring-like pattern drying uneveness, or so-called stick mark by uneven drying, was extremely suppressed and the sticked areas were less in the case of adding the compound of this invention.

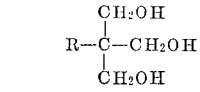
Compound	Addition Amount (g./100 g. gelatin))	Density difference	Sticked area, percent
Compound 2	7.5	0.02	20
Do	15.0	0.00	30
Compound 4	7.5	0.03	10
Do	15.0	0.00	20
Glycerine	7.5	0.04	60
Do	15.0	0.01	80
None		0.10	10

We claim:

1. A photographic gelatino silver halide light-sensitive element having enhanced resistance to mechanical stress comprising:

a support bearing a silver halide light-sensitive layer and at least one gelatin-containing layer consisting

essentially of gelatin and a compound represented by the general formula:



wherein R represents an alkyl group having 1 to 5 carbon atoms.

2. The photographic gelatino silver halide light-sensitive element as in claim 1, wherein said compound is selected from trimethylolethane, trimethylolpropane, trimethylolisobutane, and trimethylolhexane.

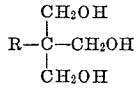
3. The photographic gelatino silver halide light-sensitive element as in claim 1, wherein the amount of said compound is from 1 to 30% by weight based on the weight of gelatin.

4. The photographic gelatino silver halide light-sensitive element as in claim 1, wherein said layer is a protective layer.

5. The photographic gelatino silver halide light-sensitive element as in claim 1, wherein said layer is an intermediate layer.

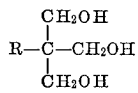
6. A photographic gelatino silver halide light-sensitive element comprising:

a support bearing thereon a light-sensitive gelatin-containing silver halide emulsion layer having incorporated therein a compound represented by the general formula:



wherein R represents an alkyl group having 1 to 5 carbon atoms.

7. The photographic gelatino silver halide element of claim 6 wherein said silver halide light-sensitive emulsion layer consists essentially of gelatin, a silver halide and said compound represented by the general formula:



wherein R represents an alkyl group having 1 to 5 carbon atoms.

8. A photographic gelatino silver halide light-sensitive element as in claim 6 wherein said compound is selected from trimethylolethane, trimethylolpropane, trimethylolisobutane, and trimethylolhexane.

9. The photographic gelatino silver halide light-sensitive element of claim 6 wherein the amount of said compound is from 1 to 30% by weight based on the weight of gelatin.

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UNITED STATES PATENTS

2,960,404 11/1960 Milton et al. ---------- 96—94

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1,111,016 2/1962 Germany.

NORMAN G. TORCHIN, Primary Examiner

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