

1

3,507,678

PROCESS FOR THE PRODUCTION OF A MATTED PHOTOGRAPHIC MATERIAL

Ikuo Shimizu, Hideo Kawano, and Shunzo Yagami, Ashigara-Kamigun, Kanagawa, Japan, assignors to Fuji Shashin Film Kabushiki Kaisha, Ashigara-Kamigun, Kanagawa, Japan, a corporation of Japan

No Drawing. Filed Sept. 27, 1966, Ser. No. 582,268

Claims priority, application Japan, Sept. 28, 1965,

40/59,267

Int. Cl. C03c 1/00, 1/74, 3/26; G03c 1/00

U.S. Cl. 117—34

4 Claims

ABSTRACT OF THE DISCLOSURE

Process for producing a photographic light sensitive material having a matted surface, particularly developing the matted surface by applying non-deliquescent crystalline water soluble salts to the protective coating surface in fine sized particles.

The present invention relates to a process for producing a photographic light-sensitive material having a matted surface.

In photographic light-sensitive material using silver halide, the surface is matted, sometimes by applying to or in its light-sensitive layer, protective layer or antihalation layer fine particles of starch, starch derivatives, synthetic resins such as polystyrene resin, or inorganic compounds, such as silicon dioxide, titanium dioxide, barium sulfate and strontium sulfate, each being called a matting agent.

The first object of matting the surface of a photographic light-sensitive material, in general, is to prevent adhesion of the light-sensitive layers among themselves or with the antihalation layer at high temperature and high humidity. The second object is to prevent the unevenness of exposure caused by the Newton ring-like unevenness due to tight adhesion of the layer and glass during printing when the photographic light-sensitive material is for a negative material. The third object is to make it easy to write on the surface of a light-sensitive material with a pencil or the like after copying when the light-sensitive material is a film for copying. The fourth object is to prevent the occurrence of obstacles by static electricity during production or handling. Furthermore, the fifth object is to lower the coefficient of friction, although it seems inconsistent.

However, such a matting agent cannot be adapted to all photographic materials unconditionally, except the case where it is employed for the purpose of devitrifying as in a film for a second original, since the matting agent is white and opaque fine particles or differs remarkably in the index of refraction from a gelatin in which a sensitive silver halide is suspended and hence it tends to damage the transparency of the finished film. The use of a great amount should be avoided particularly in the case where a very high transparency is required, for example, in films for plate making and X-ray films.

Further, a method has also been proposed in which other matting agents than the above-mentioned, which can mat sufficiently the surface of a light-sensitive element and gives no bad influences on the transparency of the support after photographic processings of developing,

2

fixing, water-washing and the like, for example, fine particles of a material capable of being dissolved off in an acid or alkaline solution, such as, zinc carbonate or strontium carbonate is added in a neutral or substantially neutral coating solution. However, such compound is often retained undissolved depending upon the kind of a treating solution, the degree of fatigue, treating temperature, treating time, etc., resulting in a bad influence upon the transparency of a film after processings.

Accordingly, the object of the present invention is to overcome such disadvantages by matting the surface of a silver halide photographic material with readily soluble fine particles not dependent upon the kind of treating solution, degree of fatigue, treating temperature, treating time, etc.

In accordance with the present invention, there is provided a process for the production of a photographic light-sensitive material having a matted surface, which is characterized by adding a water-soluble, non-deliquescent crystalline compound to a coating solution composed of water as a main solvent and gelatin as a binder in a proportion of 1-30% by weight to the gelatin, applying the resulting solution to the surface of a support or photographic material, coagulating the coating at a low temperature and drying whereby to deposit the fine crystals of said compound on the surface of the coating.

Illustrative of the water soluble, non-deliquescent crystalline compounds used in the present invention are potassium sulfate, sodium sulfate, zinc sulfate and cadmium sulfate.

The coating solution used in the present invention is a photographic light-sensitive emulsion, coating solution for protecting and coating solution for antihalation, but another coating solution may be specially prepared. The coating solution of the present invention uses gelatin as a binder, but a water-soluble high molecular compound such as polyvinyl-pyrrolidone, polyvinyl alcohol and hydroxyalkyl starch may be employed together with gelatin.

The support is a plastic film, such as cellulose triacetate and polyethylene terephthalate, having a subbing layer for advantaging the subsequent coating and those on which a light-sensitive emulsion layer or antihalation layer is coated.

The solidification of the coating solution in the invention is carried out by cooling it to a temperature of below the coagulation point thereof, for example, by contacting the back side of the coating layer with a cooled roller or exposing to a cooled air, preferably, at below 10° C.

The drying of the coating in the invention is carried out by passing it through a stream of the air heated or at normal temperature and the air is preferably adjusted to a dry bulb temperature of 18-50° C. and a relative humidity of 25-70%.

The quantity of the compound used in our invention may vary with the degree of matting required, kind of a coating solution and drying conditions, but it is generally within 1-30% weight to the gelatin composing a layer. For example, a quantity of 3-15% is preferably applied to the gelatin by weight in order to prevent adhesion in the case of an antihalation layer and 10-25% is preferred in the case of applying to a protective layer in order to prevent electrification. The average size of fine particles deposited on the surface is within a range of 1-10 microns, a slow drying resulting in relatively large particle sizes

and a rapid drying vice versa. Moreover, it is found that the distribution of the particles deposited consists in a gradual increase tendency of from the interior of a layer to the surface thereof. This tendency advantages a rapid dissolution of the deposited particles in a treating solution.

The present invention is applicable to various silver halide photographic materials such as amateur films, cinema, roentgen, printing and color photography. For example, the invention can be favorably applied to silver chloride emulsions for copying, silver chlorobromide emulsions and sulfur sensitized, reduction sensitized, gold sensitized and optically sensitized silver iodobromide emulsions for high-sensitive negatives without bad influences upon their photographic characters and without interactions with stabilizers, hardeners, surfactants and other additives to be added to these emulsions.

In addition, even if the compound sprouted from a coating surface is accumulated in a developing solution or fixing solution, its treating action is not hindered.

It will be understood from the above descriptions that the first, fourth and fifth object can be accomplished in accordance with the photographic material of the present invention and the second, third and fifth object can be accomplished also if the invention is applied to a previously treated light-sensitive material to thereby matted its surface.

The invention will now be illustrated by the following examples:

EXAMPLE 1

A silver chlorobromide emulsion for a lithographic film and a protective layer consisting mainly of gelatin were previously applied to one side of a support of polyethylene terephthalate having subbing layers on the both sides, and to the opposite side were then applied coating solutions for antihalation so as to give a coating thickness of 6 ± 1 microns on dry basis, which had been prepared by adding 80 ml. of an aqueous solution of 10% by weight of an antihalation dye, 10 ml. of an aqueous solution of 10% by weight of chrome alum and 3 ml. of an aqueous solution of 4% by weight of saponin to 1 kg. of an aqueous solution containing 15% by weight of gelatin, and dividing the resulting solution into three equal parts, to each of which potassium sulfate was added in an amount of 0 g., 2.5 g. or 5 g. The coating so obtained was first solidified by a cleaned air cooled to 7° C. and then dried by passing through a tunnel type drying chamber where the dry bulb temperature was gradually increased from 18 to 40° C., the drying being accomplished for about 35 minutes. In the case of adding potassium sulfate, its fine crystals having a particle size of about 3-6 microns in diameter were deposited on the surface uniformly to mat it.

The thus resulting films having different antihalation layers were conditioned in an atmosphere of 90% R.H. and 35° C. for 48 hours, allowed to stand for further 24 hours in the same atmosphere with protective layers piled thereon under a static pressure of 50 g./cm.² and thereafter the areas adhered were compared. At the same time, the coatings of the antihalation layer only with respect to the foregoing coating solutions were immersed in water at 18° C. for 30 seconds, dried and the sprouting velocities of the matting agent particles were compared while defining the transparency of the film free of the matting agent, i.e., potassium sulfate to 100. The results were tabulated below.

Amount of potassium sulfate (g.)	Area adhered, percent	Transparency after water treatment
0	78	100
2.5	5	100
5	2	99-100

EXAMPLE 2

The ratios of the areas adhered and sprouting velocities of the matting agent were compared in the similar manner to Example 1 as to two films prepared by the use of zinc sulfate in an amount of 0 g. and 5 g. in place of potassium sulfate of Example 1. The results were shown in the following table.

Amount of zinc sulfate (g.)	Area adhered, percent	Transparency after water treatment
0	74	100
5	5	98-99

EXAMPLE 3

An antihalation layer consisting mainly of gelatin and an antihalation dye was previously applied to the one side of a support of cellulose triacetate having subbing layers on the both sides, and to the other side were applied firstly a silver iodobromide emulsion for panchromatic high sensitivity negatives, followed by drying, and then a coating solution for protecting so as to give a coating thickness of 1.5 ± 0.5 micron on dry basis, which had been prepared by adding 15 ml. of an aqueous solution of 2% by weight of mucochloric acid, 5 ml. of an aqueous solution of 10% by weight of chrome alum and 2 ml. of an aqueous solution of 4% by weight of saponin to 1 kg. of an aqueous solution containing 3% by weight of gelatin and dividing the resulting solution into two equal parts, in each of which sodium sulfate was dissolved in an amount of 0 g. or 3 g. The coatings so obtained were solidified by a clean air cooled to 7° C. and then dried by passing through a tunnel type drying chamber where the dry bulb temperature of the air was gradually raised from 18 to 35° C., the drying being accomplished for about 30 minutes. In the case of adding sodium sulfate, its fine crystals having a particle size of about 2-5 micron in diameter were uniformly deposited to thereby mat the layer surface.

The ratios of the areas adhered were compared in the similar manner to Example 1 with respect to the thus resulting films having the foregoing two different protective layers. Further, the coefficients of static friction of the protective layers to an antihalation layer were measured and compared after conditioning the coatings in an atmosphere of 65% R.H. and 23° C. for 48 hours. The quantity of electrification was measured as follows. Two test pieces of 2.5 cm. x 20 cm. were cut from the two films respectively, adhered to the both sides of an adhesive tape in such a manner that the each protective layer was exposed, conditioned in an atmosphere of 40% R.H. and 23° C. for 48 hours, passed through two hard rubber rollers revolving in tight contact each other and the quantities of electrification thereon were found by means of a Faraday cage. The results were tabulated below.

Amount of Sodium Sulfate (g.)	Area Adhered, percent	Coefficient of Static Friction	Quantity of electrification (V.)
0	69	0.585	130-140
3	8	0.425	65-75

EXAMPLE 4

As antihalation layer consisting mainly of gelatin and an antihalation dye was applied previously to the one side of a support of polyethylene terephthalate having subbing layers on the both sides, and to the other side was applied a coating solution so as to give a coating thickness of 7 ± 1 micron on dry basis, which had been prepared by adding 20 ml. of a methanol solution of 1% by weight of a fog inhibitor, 20 ml. of an aqueous solution of 2% by weight of mucochloric acid, 10 ml. of an aqueous solution of 10% by weight of chrome alum, 3 ml. of an aqueous solution of 4% by weight of saponin and 30 ml. of an aqueous solution of 20% by weight of hydroxypropyl starch to 1

kg. of a silver chlorobromide emulsion for copying containing about 7% by weight of gelatin and dividing the resulting coating solution into two equal parts, in each of which potassium sulfate was dissolved in an amount of 0 g. or 3.5 g. The drying conditions were substantially similar to Example 1. In the case of adding potassium sulfate, fine crystals having a particle size of about 2-6 micron in diameter were deposited on the layer surface to thereby mat it. The quantities of electrification were measured in the similar manner to Example 3 with respect to the two films so obtained to give the following results tabulated.

Amount of

Potassium Sulfate, g.:	Quantity of electrification (v.)
0 -----	100-110
3.5 -----	60- 70

It is well known that a water soluble salt is added in the step of producing a photographic emulsion or salts are by-produced in the production of a photographic emulsion. For example, it has been proposed to carry out water washing of a photographic emulsion effectively by the use of a large amount of sodium sulfate to precipitate the gelatin in the emulsion with the silver halide. When a silver bromide emulsion is prepared by the reaction of silver nitrate with potassium bromide, potassium nitrate remains in the emulsion. In the prior art, however, such salt was removed as a harmful matter. On the contrary, the present invention is based upon the discovery that the presence of a non-deliquescent crystalline compound of water soluble salts rather advantages the matting action only if deposited on the surface of a layer as fine crystals.

We claim:

1. A process for producing a photographic light sensitive material having a matted surface comprising:

- (A) applying an antihalation layer consisting mainly of gelatin and an antihalation dye to one side of a support of polyethylene terephthalate having subbing layers on both sides;
- (B) applying a coating solution to the other side of said support so as to give a dry coating thickness of 6-8 microns prepared as follows:
 - (i) add 20 ml. of a methanol solution of 1% by weight of a fog inhibitor;
 - (ii) add 20 ml. of an aqueous solution of 2% by weight of mucochloric acid;
 - (iii) add 10 ml. of an aqueous solution of 10% by weight of chrome alum;
 - (iv) add 3 ml. of an aqueous solution of 4% by weight of saponin;
 - (v) add 30 ml. of an aqueous solution of 25% by weight of hydroxypropyl starch, to
 - (vi) 1 kg. of a silver chlorobromide emulsion for copying containing about 7% by weight of gelatin;
- (C) dividing the resulting coating solution into first and second equal parts;
- (D) adding 3.5 grams of potassium sulfate 2-6 microns in diameter after applying said second coat;
- (E) solidifying by air cooling; and
- (F) drying.

2. A process for producing a photographic light sensitive material having a matted surface comprising:

- (A) applying silver chlorobromide and a gelatinous protective layer to one side of a polyethylene terephthalate support;
- (B) sequentially applying to the other side of said support a series of first, second and third coating solutions approximately six microns in dry thickness and prepared as follows:
 - (i) add 80 ml. of an aqueous solution of 10% by weight of antihalation dye;
 - (ii) add 10 ml. of an aqueous solution of 10% by weight chrome alum; and
 - (iii) add 3 ml. of an aqueous solution of 4% by weight of saponin, to

- (iv) 1 kg. of an aqueous solution containing 15% by weight of gelatin;
- (v) dividing the resultant solution into first, second and third parts;
- (vi) applying said parts as a first coating, second coating and a third coating;
- (vii) adding 2.5 grams potassium sulfate fine crystals having a particle size of about 3-6 microns in diameter after applying the second coating;
- (viii) adding 5 grams of potassium sulfate fine crystals having a particle size of about 3-6 microns in diameter after applying said third coating;
- (C) solidifying the coatings so obtained by air cooling to approximately 7° C.;
- (D) drying by passing said material through an environment of 18-40° C. approximately 45 minutes;
- (E) conditioning said material in an atmosphere at 90% relative humidity and 35° C. for 48 hours; and
- (F) applying approximately 50 g./cm.² pressure to said coatings.

3. A process for producing a photographic light sensitive material having a matted surface comprising:

- (A) applying silver chlorobromide and a gelatinous protective layer to one side of a polyethylene terephthalate support;
- (B) sequentially applying to the other side of said support a series of first and second coating solutions approximately six microns in dry thickness and prepared as follows:
 - (i) add 80 ml. of an aqueous solution of 10% by weight of antihalation dye;
 - (ii) add 10 ml. of an aqueous solution of 10% by weight chrome alum; and
 - (iii) add 3 ml. of an aqueous solution of 4% by weight of saponin, to
 - (iv) 1 kg. of an aqueous solution containing 15% by weight of gelatin;
 - (v) dividing the resultant solution into first and second parts;
 - (vi) applying said parts as a first coating and a second coating; and
 - (vii) adding 5 grams zinc sulfate fine crystals having a particle size of about 3-6 microns in diameter after applying said second coating.

4. A process for producing a photographic light sensitive material having a matted surface comprising:

- (A) applying an antihalation layer consisting mainly of gelatin and an antihalation dye to one side of support of cellulose triacetate having subbing layers on both sides;
- (B) applying silver iodobromide emulsion for panchromatic high sensitive negatives to the other side;
- (C) drying said support;
- (D) sequentially applying to the other side of said support a series of first and second coatings so as to give an approximately 1 to 2 micron dry coating thickness, each coating being prepared as follows:
 - (i) add 15 ml. of an aqueous solution of 2% by weight of mucochloric acid;
 - (ii) add 5 ml. of an aqueous solution of 10% by weight of chrome alum;
 - (iii) add 2 ml. of an aqueous solution of 4% by weight of saponin, to
 - (iv) 1 kg. of an aqueous solution containing 3% by weight of gelatin;
 - (v) dividing the resulting solution into two equal parts and applying one of said parts as first coating;
 - (vi) adding sodium sulfate crystals 2-5 microns in diameter 3 grams uniformly to another of said parts and applying as said second coating;
- (E) solidifying by air cooling at approximately 0° C.;
- (F) drying at a temperature range 18-35° C.;
- (G) conditioning said coating in an atmosphere of

approximately 65% relative humidity and 23° C. for 48 hours.

References Cited

UNITED STATES PATENTS

314,346	3/1885	Roche	96—94 X
804,039	11/1905	Pifer	117—34
1,631,421	6/1927	Lolofer	117—34
1,901,441	3/1933	Frankel	96—94
2,221,873	11/1940	Knoefel	117—34 X

3,224,878	12/1965	Klimkowski et al.	117—34 X
3,297,477	1/1967	Barkis et al.	117—161

WILLIAM D. MARTIN, Primary Examiner

W. R. TRENOR, Assistant Examiner

U.S. Cl. X.R.

96—67, 94; 117—42