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AZUSA OHASHI ET AL

3,687,703

PRODUCTION OF PHOTOGRAPHIC SENSITIVE MATERIALS

Original Filed Nov. 5, 1964

2 Sheets-Sheet 1

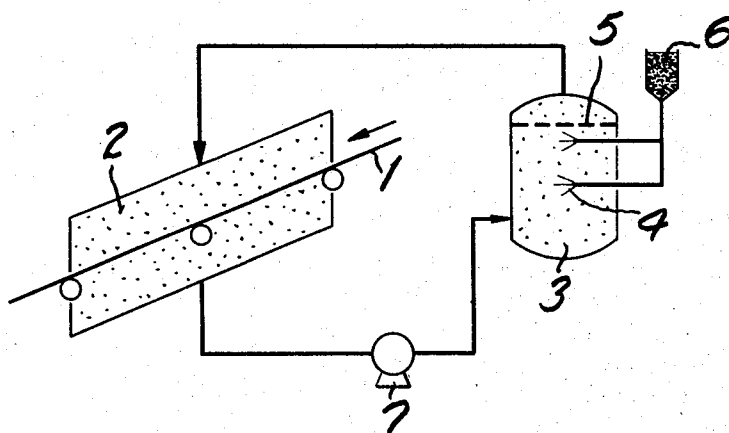


FIG. 1

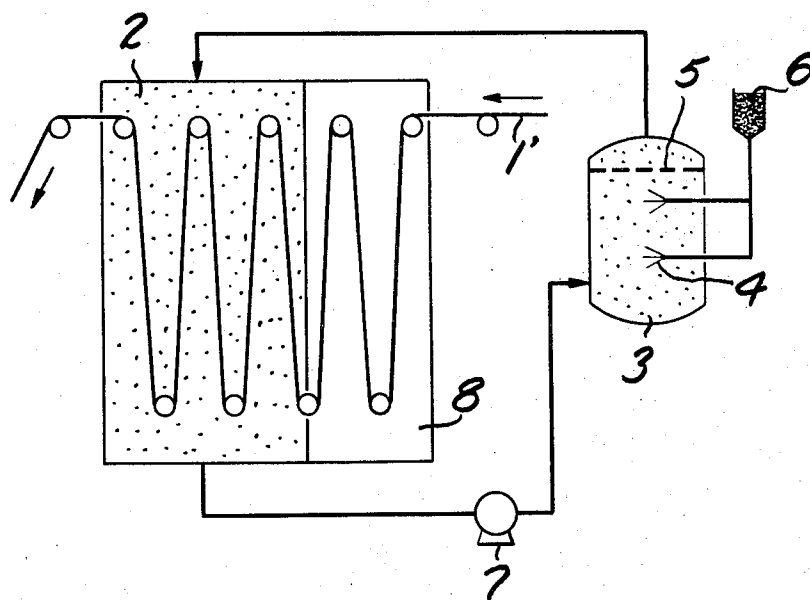


FIG. 2

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FIG. 3

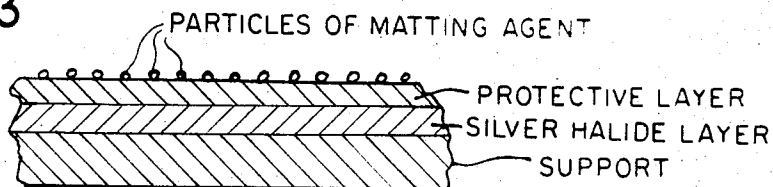
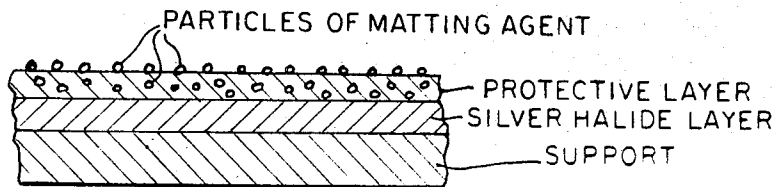


FIG. 4



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PRODUCTION OF PHOTOGRAPHIC SENSITIVE MATERIALS

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Continuation-in-part of application Ser. No. 744,610, June 26, 1968, which is a continuation of application Ser. No. 409,178, Nov. 5, 1964. This application Sept. 3, 1969, Ser. No. 866,782

Int. Cl. B44d 1/094; G03c 1/32

U.S. Cl. 117—16

15 Claims

ABSTRACT OF THE DISCLOSURE

A photographic material comprising a photographic emulsion layer on a support is coated with a dry powdered matting agent applied to the emulsion layer, or to the uppermost layer above the emulsion layer, to prevent injury from self-adhesion or from contact with various parts of a photographic apparatus.

This application is a continuation-in-part of our U.S. application Ser. No. 744,610, filed June 26, 1968, now abandoned, which in turn, is a streamlined continuation of our U.S. application Ser. No. 409,178, filed Nov. 5, 1964, now abandoned.

This invention relates to a process for producing photographic sensitive materials. More particularly, the present invention relates to a process for the production of a photographic sensitive material having improved surface conditions.

In general, since the emulsion layer surface and/or the opposite surface of a conventional silver halide photographic sensitive material, in particular, of a photographic film is smooth, when the film is rolled or stacked in a pile, or when the film is loaded in a photographic apparatus, the film has a tendency to be injured or to form static marks by the intimate contact with itself, other film or parts of the photographic apparatus. In order to overcome these difficulties, efforts have been made to roughen the surface of the photographic sensitive material by various means.

For this purpose, powders of a water-insoluble inorganic material, such as silica, zinc carbonate, glass, cadmium carbonate, strontium carbonate, etc., or powders of an organic material, such as a calcium or magnesium salt of a fatty acid, starch, terephthalic acid, polycarbonate resin and the like have been incorporated in the emulsion layer, protective layer, and/or backing layer of the photographic material.

However, adding such materials to the photographic coating elements is apt to cause the precipitation and abnormal growth thereof before coating and cause the deterioration of the transparency of the coated layer due to the undesired presence of the matting agents in the layer in the same concentration as on the surface thereof. Even if matting agents which are capable of being dissolved during the processing are employed, it is not possible to obtain complete dissolution of the particles when rapid processing is done, which results in the deterioration of the transparency of the coated layer. Furthermore, when the matting agent is applied as a suspension in a liquid, it must be used in a large amount and must have a large grain size in order to prevent the undesirable sticking adherence and static marks, which results in reducing the transparency of the photographic material.

We have found that injury to a photographic material caused by self-adhesion or by adhesion to another photo-

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graphic material can be prevented by causing a dry, powdered matting agent to adhere to the top surface of the photographic light-sensitive material.

In general, the present invention involves coating a photographic emulsion on a support, coating additional layers on said photographic emulsion layer such as a protective layer, a filter layer, and/or an anti-halation layer, drying the coated layer or layers so that the water content after drying is from 6–20% by weight and then applying a dry, powdered matting to the top surface of the uppermost layer without the use of a liquid solvent.

In a further embodiment of the invention, a backing layer is formed on the support opposite to the photographic emulsion layer, and the powdered matting agent is applied to both sides of the photographic material.

In a further embodiment of the invention, the layers coated on the support, including the backing layer when present, are dried, the dried layers are humidified in an atmosphere of 90–95% relative humidity for from 5 to 300 seconds and then the dry, powdered matting agent is applied to the top surface of the uppermost layer.

Illustrative of the matting agents used in the present invention are silica, zinc carbonate, glass powder, cadmium carbonate, strontium carbonate, calcium and magnesium salts of aliphatic acids, starch, terephthalic acid, polycarbonate resin and the like. Any material which has a low hygroscopicity and can be formed into fine particles having a diameter of 0.05–50 microns may be employed, and, in particular, a material that is soluble in acid or alkali gives a good transparency. The diameter of the particles may be in general within the range of 0.1–10 microns, preferably 0.5–5 microns.

The matting agent may be caused to adhere to the top side of the uppermost layer coated on the support of the light-sensitive material or to both sides thereof. The amount is preferably 0.01–1 g./m.² per one side.

The procedure for applying a powdered matting agent utilized in the present invention, may comprise any suitable procedure, such as passing the photo-sensitive material through a chamber in which the matting agent is suspended in air (see FIG. 1 and FIG. 2), spraying the matting agent onto the surface of the photographic material by means of a powder spray, passing the photographic material through a fluidized zone of the powdered matting agent, or causing the matting agent to adhere electrostatically by giving different charges to the photo-sensitive material and the matting agent.

In accordance with the present invention, the surface of the light-sensitive material can be roughened enough to result in such improvement that the damages and static marks on the surface of the light-sensitive material, caused by sticking of the contact surface thereof with each other or to the support means of a camera, can be reduced to a minimum. Furthermore, the roughening material is present only on the surface of the light-sensitive material and therefore the amount thereof used is smaller than would be required if the matting agent were present in the layer. This reduced amount of matting agent results in an improvement in transparency. Also, when a matting agent capable of dissolving during processing is used, it can dissolve more rapidly as compared with case of the matting agent being incorporated in the layer. Even when a matting agent having a relatively low dissolving rate in acids or alkalis is used, the matted surface obtained by the use thereof in accordance with the present invention is excellent in its transparency.

The present invention is illustrated by the accompanying drawings, in which:

FIGS. 1 and 2 are schematic flow sheets showing apparatus for carrying out the present invention;

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FIG. 3 is an enlarged cross-sectional view of a photographic material prepared by the method of the present invention, and

FIG. 4 is an enlarged cross-sectional view of a photographic material prepared by the prior art.

FIG. 1 refers to a system of applying a matting agent to an undried coated surface of a photo-sensitive material and FIG. 2 refers to a system of applying a matting agent to a dried coated surface of a photo-sensitive material.

Referring to FIG. 1, a photographic material 1, comprising a support on which has been coated one or more silver halide emulsion layers and, if desired, a protective layer, filter layer, and antihalation layer, the coated layers having been dried to a moisture content of from 6 to 20% by weight, enters chamber 2 and comes into contact with a suspension of a dry, powdered, matting agent in air. The dry, powdered, matting agent in chamber 2 adheres to the top surface of the uppermost layer of the photographic material 1. The excess powdered matting agent is removed from chamber 2 and transferred to chamber 3 by means of a circulating fan 7. A spray means 4 suspends dry, powdered, matting agent in an air stream, fresh matting agent being supplied to the system from hopper 6. A dis-

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protective layer was formed over the silver halide layer by coating the silver halide layer with solution A in an amount to provide a dried protective layer of 1.5 microns in thickness. In Runs 1-7, the matting agent was applied to the protective layer after the layers were dried to reduce the moisture content to 6 to 20% by weight. In Runs 1, 2, 4, 5 and 7, the dried protective layer was humidified in an atmosphere of 95% relative humidity for 5 seconds. In Runs 8-10, the matting was added to solution A, and then solution A containing the matting agent was applied to the silver halide layer and dried to form a 1.5 micron protective layer. The matting agents of Runs 8-10 were used in the following amounts:

- (8) Terephthalic acid—1 g./liter of Solution A
- (9) Silver powder—0.5 g./liter of Solution A
- (10) Zinc carbonate—2 g./liter of Solution A

In Run 11, the procedure of Runs 1-7 was followed, except that no matting agent was used.

Solution A is prepared from:

- 18 g. gelatin
- 55 cc. dodecylbenzene sodium sulfonate (1%)
- q.s. to make one liter.

Run	Matting agent	Diam. (micron)	Process		Sticking and static prevention	Transparency after processing
			Coating process	Condition		
1.....	Zinc carbonate.....	0.5-5	This invention.....	95% RH, 5 sec.....	Good.....	Very good.
2.....	Terephthalic acid.....	1-10	do.....	95% RH, 5 sec.....	do.....	Do.
3.....	do.....	1-10	do.....	Nothing.....	do.....	Do.
4.....	Glass powder.....	1-10	do.....	95% RH, 5 sec.....	do.....	Good.
5.....	Silica powder.....	1-10	do.....	95% RH, 5 sec.....	do.....	Do.
6.....	do.....	1-10	do.....	Nothing.....	do.....	Do.
7.....	Polycarbonate resin.....	1-10	do.....	95% RH, 5 sec.....	do.....	Do.
8.....	Terephthalic acid.....	1-10	Liquid dispersion.....	do.....	do.....	Not good.
9.....	Silica powder.....	1-10	do.....	do.....	do.....	Do.
10.....	Zinc carbonate.....	0.1-1	do.....	do.....	do.....	Good.
11.....	Control.....	do.....	do.....	do.....	Not good.....	Very good.

tributor 5 is provided to uniformly suspend the matting agent.

A similar system is shown in FIG. 2, except that the photographic material 1' is a support carrying a silver halide photographic layer and one or more of a protective layer, a filter layer and an anti-halation layer, the layers having been dried. In the embodiment shown in FIG. 2, the dried photographic material 1' first passes through a humidifying chamber 8 before it enters chamber 2.

FIGS. 3 and 4 are enlarged cross-sectional views of a photographic material reduced by the present invention into prior art respectively. Since the dry, powdered matting agent is applied to the photographic material after it has been formed, it can be seen that the particles of the matting agent adhere simply to the surface of the uppermost

EXAMPLE 2

In Runs 12 and 13, a gelatino silver halide emulsion layer was coated on a support, the emulsion layer was dried to 6-20% by weight water to provide a dried emulsion layer of 5 microns in thickness and then was coated with each of the matting agents shown in the following table by using the apparatus as shown in FIG. 2. In Runs 14 and 15, the matting agent was added to a gelatino silver halide emulsion in a concentration of 0.4 g./kg.Em for Run 14 and 0.2 g./kg.Em for Run 15 and then the emulsion was coated on a support and dried. In Run 16, no matting agent was employed, and the gelatino silver halide layer was simply formed on the support.

Run	Matting agent	Diam. (microns)	Process	Sticking and static prevention	Transparency after processing
12.....	Terephthalic acid....	1-10	This invention.....	Good.....	Very good.
13.....	Silica powder.....	1-10	do.....	do.....	Good.
14.....	Terephthalic acid....	1-10	Liquid dispersion.....	do.....	Not good.
15.....	Silica powder.....	1-10	do.....	do.....	Do.
16.....	Control.....	do.....	do.....	Slightly good.....	Very good.

layer. In contrast, the particles of the matting agent in the prior art photographic material are distributed throughout the uppermost layer because the prior art applied the matting agent by incorporating the matting agent in the solution used to form the uppermost layer.

The examples of this invention are as follows.

EXAMPLE 1

A gelatino silver halide emulsion layer and then a protective layer were applied on a support to give a light-sensitive material, the layers were dried to 6-20% by weight of water, and on the surface of the material was applied each of the matting agents shown in the following table by using the apparatus shown in FIG. 2.

In particular, for Runs 1-7, a gelatino silver halide photographic emulsion was applied to a support, and the

EXAMPLE 3

In Runs 17 and 18, a gelatino silver halide layer was applied to one side of a support and a backing layer was applied to the other side of the support. After drying the layers to 6 to 20% by weight of water to provide a dried backing layer of 5 microns in thickness, the matting agents were applied to both layers by using the apparatus shown in FIG. 2.

In Runs 19-21, the silver halide and backing layers were formed on opposite sides of the support, with the matting agents of Runs 19 and 21 being added to the gelatino solution in a concentration of 0.4 g./kg.solu. for Run 19 and 0.2 g./kg.soln. for Run 20. No matting agent was used in Run 21.

Run	Matting agent	Diam. (microns)	Process	Sticking and static prevention	Transpar- ency after processing
17.....	Terephthalic acid....	1-10	This invention.....	Good.....	Very good.
18.....	Silica powder.....	1-10	do.....	do.....	Good.
19.....	Terephthalic acid....	1-10	Liquid dispersion.....	do.....	Not good.
20.....	Silica powder.....	1-10	do.....	do.....	Do.
21.....	Control.....			Not good.....	Very good.

In each of Runs 1-21, a 6 x 6 cm. support was used. The results of the runs were evaluated as follows.

Each of the 6 x 6 cm. samples obtained in Runs 1-21 was humidified in an atmosphere of 90% RH for 24 hours, and was placed upon a sheet of polyester film so that the matted surface of each sample would contact the sheet of polyester film. Then a weight of 1.15 kg. was applied to the overlapped sample and polyester film sheet. The overlapped sample and polyester film sheet were then peeled apart to determine the percentages of the surfaces that were stuck together. In Examples 1-4 above, the term "very good" refers to 0-10% of the surfaces being stuck together; "good" refers to 10-50% of the surfaces being stuck together; and "not good" refers to 90-100% of the surfaces being stuck together.

Each of the 6 x 6 cm. samples was tested for transparency after processing, by calculating the haze values with a Haze meter employing the following equation:

$$\text{Haze (percent)} = \frac{T_d}{T_t} \times 100$$

T_t : total transparency of sample

T_d : diffusion rate of sample

The transparency rating is referred to the Haze values as follows:

Haze (percent):	Transparency
Less than 5.0	Very good.
5.0 to 7.0	Good.
7.1 to 9.9	Slightly good.
10 or more	Not good.

Examles 1-3 show that the prior art technique of incorporating the matting agent in the photographic material during the formation of the various layers thereof reduces the "transparency after processing" of the photographic material.

It is of interest to note that the sample of Run 8 which was prepared by incorporating the matting agent into the protective layer during the preparation thereof, was completely transparent when washed with water and dried after having been treated in a developing bath (alkali), but when said sample was passed through a fixing bath (acidic) after having been treated in the developing bath, it became opaque. On the contrary, the samples of Runs 2 and 3, which were prepared according to the invention, were completely transparent after the fixing treatment.

The compositions of the materials used in Examples 1 to 3, to form the emulsion layer and the backing layers were as follows:

Material of the emulsion layer:

Gelatin	gr--	69.2
Silver bromide	gr--	58.2
Water	liter--	1

Material of the backing layer:

Gelatin	gr--	70
Water	liter	1

The terms "support," "protective layer," "backing layer," "filter layer" and "antihalation layer" are all well known in the art. Thus, a "support" is an inert, dimensionally stable layer upon which the various elements of the photographic material are carried. A "protective layer" is a transparent gelatin layer designed to protect the silver halide emulsion. The "filter layer" and "antihalation

layer" contain filter dyes and antihalation dyes, respectively. The "backing layer" is the gelatin layer designed to aim at curling balance and antistatic.

We claim:

1. A method for the production of a photographic light-sensitive material having a matte surface, which comprises coating a photographic silver halide emulsion layer on at least one side of a support, drying said coated layer to such an extent that the water content of said layer is from about 6 to about 20% by weight, and applying a dry powdered matting agent to only the top surface of said dried layer, in the absence of liquids, said dry powdered matting agent consisting essentially of particles of low hygroscopicity and having a particle size in the range of 0.05 to 50 microns.

2. A method for the production of a photographic light-sensitive material having a matte surface, which comprises coating a photographic silver halide emulsion layer on at least one side of a support, coating on at least one of the outer surfaces of said silver halide layer and support at least one of a protective layer, a filter layer and an antihalation layer, drying said coated layers to such an extent that the water content of said layers is from about 6 to 20% by weight, and applying a dry powdered matting agent to at least one of the outer surfaces of the outermost layers said dry powdered matting agent consisting essentially of particles of low hygroscopicity and having a particle size in the range of 0.05 to 50 microns.

3. The method according to claim 1, wherein a photographic silver halide emulsion layer and a protective layer are coated on said support.

4. The method according to claim 1, wherein said photographic silver halide emulsion layer is coated on both sides of the support.

5. The method according to claim 1, wherein said matting agent is selected from the group consisting of silica, glass, starch, terephthalic acid, zinc carbonate, cadmium carbonate, strontium carbonate, calcium salts of fatty acids, magnesium salts of fatty acids and polycarbonate resin.

6. The method according to claim 1, wherein said dry powdered matting agent is applied by spraying the dry powder in the absence of a liquid.

7. The method according to claim 1, wherein said dry powdered matting agent is applied by exposing said uppermost surface to a fluidized zone of said dry powder in the absence of a liquid.

8. A method for the production of a photographic light-sensitive material having a matte surface, which comprises coating a photographic silver halide emulsion layer on at least one side of a support, drying said coated layer, humidifying said dried layer in an atmosphere of 90-95% RH for 5 to 300 seconds, and applying a dry powdered matting agent to only the top surface of said humidified layer, in the absence of liquids, said dry powdered matting agent consisting essentially of particles of low hygroscopicity and having a particle size in the range of 0.05 to 50 microns.

9. A method for the production of a photographic light-sensitive material having a matte surface, which comprises coating a photographic silver halide emulsion layer on at least one side of a support, coating at least one of the outer surfaces of said silver halide layer and support with at least one of a filter layer, a protective layer and an anti-halation layer, drying said coated layers, humidifying said dried layers in an atmosphere of 90-95% RH for

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5 to 300 seconds, and applying a dry powdered matting agent to at least one of the outer surfaces of the outermost layers of said humidified layers, said dry powdered matting agent consisting essentially of particles of low hygroscopicity and having a particle size of in the range of 0.05 to 50 microns.

10. The method according to claim 8, wherein a photographic silver halide emulsion layer and a protective layer are coated on said support.

11. The method according to claim 8, wherein said photographic silver halide emulsion layer is coated on both sides of the support.

12. The method according to claim 8, wherein said matting agent is selected from the group consisting of silica, glass, starch, terephthalic acid, zinc carbonate, cadmium carbonate, strontium carbonate, calcium salts of fatty acids, magnesium salts of fatty acids and polycarbonate resin.

13. The method according to claim 8, wherein said dry powdered matting agent is applied by spraying the dry powder in the absence of a liquid.

14. The method according to claim 8, wherein said dry powdered matting agent is applied by exposing said uppermost surface to a fluidized zone of said dry powder in the absence of a liquid.

15. The method according to claim 1 wherein the amount of the matting agent is 0.01-1 g./m.² per side of the light-sensitive material.

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