

[54] **PHOTOGRAPHIC PROCESS**

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96/87 R, 114.7; 106/135; 260/117, 118

[56] **References Cited**

UNITED STATES PATENTS

3,687,703	8/1972	Ohashi et al.	117/34
3,370,951	2/1968	Hasenauch et al.	96/87 R
2,322,037	6/1943	Linguist.	96/114.7
2,992,213	7/1961	Gates et al.	96/87 R
2,391,181	12/1945	Minsk et al.	96/87 R
3,411,907	11/1968	Whitmore.	96/87 R

FOREIGN PATENTS OR APPLICATIONS

528,850	11/1940	Great Britain.	96/87 R
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837,529 6/1960 Great Britain 96/87 R

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[57]

ABSTRACT

A photographic element having improved matting properties is prepared by deionizing or deashing an aqueous gelatin solution containing at least about 5 percent by weight gelatin and then adding a matting agent which comprises discrete particles of a polymer containing free carboxyl groups to the resulting aqueous gelatin solution. The resulting gelatin solution containing the matting agent can be employed with other addenda employed in photographic materials. Deionizing can be carried out by passing the aqueous gelatin solution through an ion-exchange resin or deashing can be effected by washing the gelatin solution with an aqueous acid solution.

7 Claims, No Drawings

PHOTOGRAPHIC PROCESS

BACKGROUND OF THE INVENTION

This invention relates to preparation of photographic materials containing matting agents. It also relates to photographic materials containing the described matting agents in gelatin compositions.

DESCRIPTION OF THE STATE OF THE ART

It is known to employ matting agents such as copoly-methylmethacrylate — methacrylic acid beads in photographic materials. Photographic materials containing such matting agents are described, for example, in U.S. Pat. No. 2,322,037 of Lindquist issued Jun. 15, 1943. Such polymers have also been employed for other purposes in photographic materials such as described in U.S. Pat. No. 2,992,101 of Jelley et al. issued Jul. 11, 1961.

Various matting agents are also known in photographic materials which do not contain free carboxyl groups. Such matting agents include, for example, polymethylmethacrylate particles as described in U.S. Pat. No. 3,411,907 of Whitmore and Coryell issued Nov. 19, 1968. Various other matting agents are described in British Pat. No. 837,529 published Jun. 15, 1960.

In the preparation of photographic materials containing matting agents in gelatin wherein the matting agents are polymers containing free carboxyl groups, a problem has been encountered which involves the tendency of the matting agent to dissolve during preparation of the materials for coating on a suitable support. This problem is especially troublesome when matting agent particles comprising copolymethylmethacrylate — methacrylic acid are added to an aqueous solution containing more than about 4 percent gelatin and, in particular, a solution containing more than about 8 percent by weight gelatin. Processes up to this point have resulted in less than the desired matting properties in the photographic materials.

It is accordingly an object of this invention to provide an improved process for providing photographic materials having improved matting properties wherein a matting agent is employed comprising a polymer containing free carboxyl groups in gelatin.

SUMMARY OF THE INVENTION

It has been found according to the invention that photographic materials having improved matting agent properties, containing a matting agent which comprises a polymer containing free carboxyl groups, can be provided by deionizing or deashing an aqueous gelatin solution, containing more than about 5 percent gelatin, before adding the described matting agent to the gelatin solution. Deionizing can be carried out as described in British Pat. No. 528,850 published Nov. 8, 1940. Deashing of the gelatin solution can be carried out as described in Example 1 of U.S. Pat. No. 2,992,213 of Gates et al issued Jul. 11, 1961.

DETAILED DESCRIPTION OF THE INVENTION

One embodiment of the invention is in a process for preparing a photographic element comprising a support having thereon a gelatin composition comprising a matting agent which comprises discrete particles of a polymer containing free carboxyl groups such as an alkyl acrylate polymer containing free carboxyl groups, by adding the matting agent to an aqueous solution

containing at least about 5 percent by weight gelatin, preferably at least about 8 percent to about 20 percent by weight gelatin, and coating the resulting composition on the support, the improvement comprising deionizing or deashing the aqueous gelatin solution before adding the matting agent. While the mechanism by which improved matting properties is provided according to this process is not completely understood, it is believed that the dissolution of the polymeric particles, also known as beads, is caused by the presence of calcium ions. It is believed that the deionizing or deashing procedure provides removal of the calcium ions from the gelatin thereby helping to prevent dissolution of the polymeric particles.

While the process of the invention is applicable to a range of matting agents, preferred matting agents are the alkali soluble polymeric esters of acrylic and methacrylic acid as exemplified by copolymethylmethacrylate — methacrylic acid (52 percent methacrylic acid). Such matting agents are described, for example, in U.S. Pat. No. 2,391,181 and U.S. Pat. No. 2,992,101. Particularly suitable matting agents are alkali soluble glkylacrylate-acrylic acid copolymers whereon the acrylic acid monomer may be substituted by an alkyl group, e.g. methacrylic acid.

The process of the invention is especially suitable when employing gelatin solutions containing a high concentration of gelatin such as at least about 5 percent by weight gelatin, typically at least about 8 percent to about 20 percent by weight gelatin.

The described matting agent particles or beads are added to the aqueous gelatin solution in a range of concentration which is typically about 0.5 percent to about 15 percent by weight of the described gelatin solution. The process, as described, is particularly advantageous when the described polymeric particles or beads are added to the gelatin solution in a concentration of at least 5 percent by weight of the gelatin solution. The problem of this dissolution of the described polymeric particles or beads is especially noticeable above this concentration.

A range of deionizing procedures can be employed, however, the gelatin solution is preferably treated with an ion-exchange resin such as an anionic resin available under the trade name AMBERLITE IRA-900 from the Rohm and Haas Company of Philadelphia, Pennsylvania, U.S.A. A cationic resin sold under the trade name AMBERLITE 200 is also suitable. This cationic resin is available under this trade name from Rohm and Haas Company of Philadelphia, Pa., U.S.A. These ion-exchange resins are known in the photographic art and available commercially.

The described deashing procedure can be carried out by treating the gelatin with an acid solution such as an aqueous acetic acid solution. Such acid treatments and deashing procedures have been employed for preparing gelatin for photographic subbing as described in U.S. Pat. No. 2,992,213 of Gates et al issued Jul. 11, 1961. For example, gelatin can be treated by leaching in an aqueous alkaline solution such as an aqueous ammonia or alkali metal hydroxide or alkali metal carbonate solution for a time such as 1 to 6 hours at a pH of 8 to 9.5 and at a temperature of about 15° to 20° C. After this alkaline treatment it can be subjected to washing with an aqueous acetic acid solution to remove undesired ions.

Various gelatins can be employed in the process of the invention. Gelatin for photographic purposes and the process of the invention is described, for example, in the "Theory of the Photographic Process" edited by Mess and James, 3rd Edition, 1966, pages 45-54.

The particles of matting agent in the gelatin composition can be incorporated in 1 or more layers of the photographic element. The gelatin composition containing the described matting agent can be in the photosensitive silver halide emulsion layer and/or a layer contiguous thereto. Various methods can be employed for dispersing the particles in the layer or layers. A gelatin layer or layer of other silver halide binding agent containing the described particles of matting agents can be coated as a protective layer over a silver halide emulsion layer and/or as a backing layer on a suitable support.

Photographic elements prepared according to the process of the invention containing the described matting agents in a protective layer which is outer most from the support exhibit good resistance to abrasion.

The coverage of the described matting agents on a support for a photographic element is subject to variation depending on the desired degree of matting properties, processing conditions and the like. Typical coverage of the polymeric matting agents is about 0.75 milligrams to about 5 milligrams of polymeric particles or beads per square decimeter of support.

Various supports can be employed for compositions prepared according to the invention. Typical supports are those employed in the photographic art. Typical supports are film, paper, glass or the like.

Various materials can be used in combination with the matting agents and gelatin in photographic materials as binding agents and for other purposes. Such binding agents include synthetic materials and natural resins as described, for example, in U.S. Pat. No. 3,411,907 of Whitmore and Coryell issued Nov. 19, 1968. This invention may be used with elements designed for color materials, for example, elements containing color-forming couples such as those described in Graham U.S. Pat. 3,227,554; Vittum et al. U.S. Pat. 2,360,290 or elements to be developed in solutions containing color-forming couples such as described in Mannes et al. U.S. Pat. No. 2,252,718.

Photographic materials prepared according to the process of the invention can contain additional addenda which do not adversely affect the matting properties of the described matting agents. These include, for example, various photosensitive silver halide emulsions, chemical sensitizers for such emulsions, development modifiers, antifoggants, stabilizers, developing agents, hardeners, plasticizers, coating agents, brighteners, spectral sensitizing dyes, absorbing and filter dyes, and the like as described, for example, in Dunn U.S. Pat. No. 3,297,446 issued Jan. 10, 1967 and U.S. Pat. No. 3,411,907 of Whitmore and Coryell issued Nov. 19, 1968.

The following examples are included for a further understanding of the invention.

Example 1

A. Into an aqueous 8 percent by weight bone gelatin solution are dispersed copolymethylmethacrylate-methacrylic acid beads which have an average diameter of 3 microns. To the solution are added appropriate spreading and hardening agents. The solution is then

coated on a film support at the rate of 9.79 mg of gelatin/dm² and 1.6 mg of polymethacrylate beads/dm².

B. An element is prepared in a manner similar to (A) above except the bone gelatin solution is deionized using an ion-exchange resin as described in British Pat. No. 528,850 in columns 1 and 2.

C. An element is prepared in a manner similar to (A) above except the bone gelatin solution is deashed by washing in an acid solution as described in Example 1 in U.S. Pat. No. 2,992,213.

The results of Example 1 A, B and C indicate that the product of 1B and 1C contains a significantly higher concentration of matting agent particles or beads than the product produced by process 1A. On an arbitrary scale of 1 to 5 wherein 1 represents few matting agent particles showing on the surface of the element and 5 represents a good matted surface of the element, the product of process A receives a rating of 1 and the products of B and C receive a rating of 5.

Example 2

Three separate coatings are prepared as described in Example 1A, B and C, except pig gelatin is employed in place of bone gelatin.

The results of Example 2A, B and C are similar to those of Example 1A, B and C. On the arbitrary scale described in Example 1, the product of Example 2A receives a rating of 2 and the products of 2B and 2C receive a rating of 5.

Example 3

The procedure in Example 1B and 1C is repeated with the exception that the described gelatin solution containing the polymeric particles is coated on a photosensitive silver bromoiodide gelatin emulsion layer on a film support. A photographic element having good matting properties is produced.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. In a process for preparing a photographic element comprising a support having thereon a gelatin composition comprising a matting agent which comprises discrete particles of a polymer containing enough free carboxyl groups to cause said polymer to dissolve in an aqueous gelatin solution containing at least 5% by weight gelatin when said particles are blended with said aqueous gelatin solution;

which process comprises (1) adding said matting agent to said aqueous gelatin solution, (2) applying the resulting composition to said support and (3) drying the resulting coated support; the improvement which comprises deionizing or deashing said aqueous gelatin solution before adding said particles of said polymer.

2. The process of claim 1 wherein said matting agent is an alkyl acrylate polymer containing free carboxyl groups.

3. The process of claim 1 wherein said matting agent is copoly (methyl methacrylate — methacrylic acid).

4. The process of claim 1 wherein said matting agent is added to said gelatin solution in a concentration of about 0.5 percent to about 15 percent by weight of said gelatin solution.

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5. The process of claim 1 wherein said gelatin solution contains about 5 percent to about 20 percent by weight gelatin.

6. The process of claim 1 wherein said deionizing is carried out by passing said aqueous gelatin solution

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through an ion-exchange resin.

7. The process of claim 1 wherein said deashing is carried out by washing said gelatin solution with an aqueous acetic acid solution.

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