United States Patent Office 3,514,289 Patented May 26, 1970

3,514,289

PHOTOGRAPHIC MATERIALS CONTAINING METAL SALTS

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No Drawing. Application Nov. 24, 1965, Ser. No. 509,616, which is a continuation-in-part of application Ser. No. 395,913, Sept. 11, 1964. Divided and this application Jan. 21, 1969, Ser. No. 792,801

Int. Cl. G03c 1/04

U.S. Cl. 96—67 12 Claims

ABSTRACT OF THE DISCLOSURE

Photographic silver halide emulsions comprising a water-soluble, poly-N-vinyl pyrrolidone or polysaccharide and a water-soluble zinc or calcium salt. In one aspect, the above combination of ingredients in a silver halide emulsion provides improved resistance to the formation of dark ring water spots on rewetting of the emulsion.

This application is a divisional application of U.S. Ser. No. 509,616 filed Nov. 24, 1965, now abandoned, which, in turn, is a continuation-in-part of U.S. application Ser. No. 395,913 filed Sept. 11, 1964, now abandoned.

This invention relates to photographic materials, their preparation and use. In one of its aspects, this invention relates to gelatino-silver halide emulsions and elements which produce silver images exhibiting very little change in density on drying.

Various addenda can be added to photographic silver halide emulsions to increase the covering power of the silver in the emulsion. Emulsions of increased covering power are of special interst to the emulsion maker since their use results in what is equivalent to an increase in speed at a constant silver level or to a saving in silver at a constant density level. In many applications of photographic materials such as in graphic arts processes, it is essential for the photographic technician to maintain rigid control of contrast and density in his photographic negatives or positives. In order to save time, these characteristics are often measured immediately after processing while the film is still wet. However, as pointed out by Blake and Meerkamper in The Journal of Photographic Science, vol. 9, 1961, pages 14 to 25, the wet covering power of a gelatino-silver image can change substantially during drying. With such changes of covering power on drying, the photographic technician is not able to reliably predict the ultimate contrast or density of the dried silver image by observing the film while still wet. Moreover, a loss in density on drying represents a loss of covering power of developed silver, to wit: a less efficient production of practical density for a given amount of silver. As pointed out in the noted Blake and Meerkamper publication, large grain emulsions show this effect the most. It is thus highly desirable that density or covering power changes on drying be reduced or eliminated.

Various polymers can be used in photographic silver halide emulsions and elements to improve covering power. Such polymers include, for example, low molecular weight water-soluble polyacrylamide as described in Allentoff et al. U.S. Pat. 3,271,158 issued Sept. 6, 1966. Photographic materials containing such polymeric addenda are greatly improved with respect to wet-dry density changes, but still further improvement is desirable as a perceptible dark ring is sometimes visible around areas which are locally rewet and dried after normal processing and drying of the film. Since it is sometimes advantageous to wet a processed and dried film locally, e.g., in certain retouching operations, it is highly desirable to

provide an improvement in photographic elements and emulsions of the type described in the Allentoff et al. patent referred to above whereby the occurrence of dark rings on rewetting is eliminated. In addition, photographic emulsions and elements which fail to exhibit a visible dark ring upon local rewetting or drying are less subject to water-spotting or other density non-uniformities caused by uneven drying either after processing or after subsequent wetting operations.

Accordingly, it is one object of this invention to provide a means for improving the wet density or covering power retention of photographic materials.

Still another object of this invention is to provide silver halide emulsions having improved wet density or covering power retention.

Another object of this invention is to provide improvements in photographic gelatino-silver halide emulsions having good wet density or covering power retention.

Another object of this invention is to provide a means for improving the wet density or covering power retention of photographic emulsions and elements containing polymeric addenda which increases the covering power of silver.

A further object of this invention is to provide improved photographic gelatino-silver halide emulsions having particular utility in the graphic arts field.

Other objects of this invention will appear herein.

In accordance with this invention, it has been found that water-soluble salts of zinc or calcium can be employed to enhance density retention during initial drying and subsequent rewetting and drying of photographic silver halide materials containing a polymer which increases the covering power of silver in said materials. For example, water-soluble salts of zinc or calcium can be incorporated into photographic gelatino-silver halide emulsions containing a low molecular weight; water-soluble polyacrlyamide and such emulsions will not exhibit dark rings around areas where the emulsion is wet a second time. In contrast, dark rings are formed upon rewetting of these same emulsions which do not contain the water-soluble zinc or calcium salts.

A significant feature of this invention is that the water-soluble zinc and calcium salts appear to be unique in improving the uniformity of density changes upon rewetting of photographic silver halide materials containing polymers which will increase the covering power of the silver in the material. Thus, as shown in Example 3 which follows, other similar water-soluble metal salts do not give the desired results.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

Example 1

Two photographic silver bromoiodide emulsions having an average silver halide grain size of about 0.4 to 1.0 micron, and containing less than about 10 mole percent iodide, and dispersed in a binder of gelatin and polyacrylamide, are coated on polyethylene terephthalate film supports at a coverage of 400 mg. silver, 1476 mg. gelatin and 107 mg. polyacrylamide per square foot. In one emulsion, 17.4 grams zinc nitrate per mole of silver is incorporated just prior to coating. No zinc nitrate is added to the other emulsion which is coated as a control for comparison purposes. The films obtained are exposed and developed for 5 minutes in the following developer:

Methyl p-aminophenol—2.5 g.
Sodium sulfite—30.0 g.

Hydroquinone—2.5 g.
Sodium carbonate—10.0 g.
Potassium bromide—0.5 g.
Water to make—1.0 liter

The films are fixed, washed and dried in the usual manner. Portions of the film are rewet by swabbing with cotton moistened with water and dried. The control exhibits areas of reduced density and dark rings where the film has been rewet. However, the film containing the zinc nitrate salt shows substantially less density reduction and has no dark rings in areas where the film has been rewet. It is also noted that the emulsion containing the zinc nitrate salt exhibits less fog than the control after a two-week incubation at 120° F., and in addition, the speed of the emulsion containing the zinc nitrate remains substantially constant whereas the control exhibits an undesirable speed increase after the incubation period.

Similar results are obtained when the zinc nitrate in the above procedure is substituted by zinc sulfate, calcium acetate or calcium chloride.

Example 2

The procedure of Example 1 is followed except that calcium nitrate is substituted for zinc nitrate. The emulsion containing the calcium nitrate shows substantially less reduction in density, and a reduction in the tendency to form dark rings in areas where the film has been rewet when compared with the control. In addition, the emulsion containing calcium nitrate shows less fog after an incubation period of two weeks at 120° F. in comparison with the control.

Example 3

As already indicated, water-soluble metal salts closely related to water-soluble zinc and calcium salts utterly fail to provide an improvement in wet-dry density retention of photographic silver halide films. To illustrate, the procedure of Example 1 is followed except that cadmium nitrate and potassium nitrate are each substituted for zinc nitrate. Upon testing as described in Example 1, no change is noted in the emulsion containing cadmium or zinc nitrate as compared to the control with respect to the appearance of dark rings and density reduction in areas where the film has been rewet and dried.

Example 4

The water-soluble metal salts, e.g., zinc or calcium nitrate, are preferably used in combination with water-soluble polyacrylamides to improve the wet-dry density retention of photographic silver halide layers. However, other polymers which increases the covering power of silver can be used in place of, or in addition to, the water-soluble polyacrylamide. Suitable polymers include non-proteinaceous hydrophilic colloids such as polysaccharides, as exemplified by dextran, dextrin, as well as poly-N-vinylpyrrolidone and like polymers. To illustrate, two photographic silver bromoiodide emulsion samples having an average silver halide grain size of 0.4 to 1 micron, and containing less than about 10 mole percent iodide and dispersed in a binder of gelatin and dextran having an average molecular weight of about 75,000 as described in British Pat. 875,100 published Aug. 16, 1961, are coated on polyethylene terephthalate film supports at coverages of 450 mg. silver, 1665 mg. gelatin and 200 mg. dextran per square foot. In one emulsion, 16 grams of zinc nitrate per mole of silver are incorporated just prior to coating. No zinc nitrate is added to the other emulsion sample which is coated as a control for comparison purposes. The film samples are exposed, processed and tested at a density of 2.0, as in Example 1. The control exhibits areas of reduced density and dark rings where the film has been rewet. In contrast, the film containing the zinc nitrate shows no substantial reduction in density and no dark rings.

Similar results are obtained when the concentration of zinc nitrate in the above procedure is increased to 24 grams per mole of silver and when calcium nitrate is substituted for zinc nitrate.

Example 5

The procedure of Example 4 is repeated except that the dextran is substituted by poly-N-vinyl-2-pyrrolidone, as described in U.S. Pat. 3,043,697 issued July 10, 1962, or water-soluble dextrin, as described in British Pat. 897,497 issued May 30, 1962. Each control sample shows dark rings where the film has been rewet. In contrast, the films containing the poly-N-vinyl-2-pyrrolidone or the dextran with the water-soluble zinc nitrate show no dark rings on rewetting.

The preparation of photographic silver halide emulsions such as are utilized herein typically involves three separate operations:

(1) Emulsification and digestion of silver halide,

(2) The freeing of the emulsion of excess water-soluble salts, suitably by washing with water, and

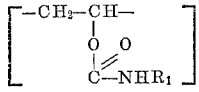
(3) The second digestion or after-ripening to obtain increased emulsion speed or sensitivity, reference being made to Mees, The Theory of the Photographic Process, 1954.

The water-soluble salts utilized in the emulsions in accordance with this invention can be added to the emulsion at any stage in the preparation of the emulsion such as before final digestion or after-ripening, or immediately prior to coating. The salts can be incorporated in emulsions to provide improvements in wet-dry density reduction in concentrations of about 2 to about 50 grams per mole of silver and preferably at concentrations of about 8 to about 25 grams per mole of silver. These salts are preferably incorporated in a photographic silver halide layer of a photographic silver halide element. However, they can be used in other layers, e.g., layers which are contiguous or adjacent to the emulsion layer. The salts can be in the same or different layer with the polymer which increases the covering power of the silver. Any water-soluble salt of zinc or calcium can be employed in the practice of this invention. Suitable salts include the zinc or calcium salts of inorganic acids such as hydrochloric, nitric, sulfuric, and the like, as well as salts of organic acids such as aliphatic carboxylic acids and the like. Examples of such salts are zinc chloride, zinc nitrate, zinc sulfate, calcium acetate, calcium chloride and the like.

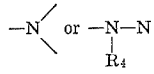
This invention is broadly applicable to improving photographic silver halide emulsions, particularly photographic gelatino-silver halide emulsions, which have good wet-dry density retention. Such emulsions include dispersions of silver halide, preferably large grain silver bromoiodide, in a binder comprising gelatin and a polymer which increases the covering power of silver in the emulsion, e.g., water-soluble polyacrylamide. Advantageously, the water-soluble salts employed in this invention are utilized in emulsions comprising a substantial amount of silver bromoiodide, preferably emulsions in which the halide consists essentially of silver bromoiodide containing about .5 to about .10 mole percent iodide. Particularly good results are obtained with silver bromoiodide crystals having a mean grain size of at least about .4 micron, such as those having a mean grain size in the range of about .4 to about 1.5 microns. Other silver halides than silver bromoiodide, and silver halides other grain sizes, can be mixed with the preferred gelatino silver bromoiodide emulsions. The preferred emulsions are the conventional negative-type, developing-out emulsions.

As already indicated, the binder for the photographic silver halide emulsion comprises a polymer which increases the covering power of the silver in the emulsion. Such polymers are generally used in combination with other binding materials such as gelatin. The polymers generally replace at least a part of the gelatin and/or other photographic binding material usually employed in photographic silver halide emulsions and elements. Their use increases the covering power of the silver in

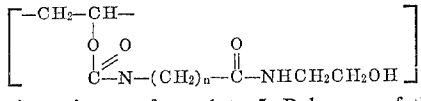
the emulsion or emulsion layer of the element. Such polymers generally increase covering power at least about 5 percent, often 10, 20, 20 percent, or more. Many different polymers can be used for this purpose including, for example, the hydrophilic colloids such as water-soluble polyacrylamide or other water-soluble vinyl polymers. While particularly efficacious results are obtained with water-soluble polyacrylamide of the type shown in Allentoff et al. U.S. Pat. 3,271,158 issued Sept. 6, 1966, other polymers, particularly non-proteinaceous hydrophilic colloids can be used in combination with the polyacrylamide or in lieu thereof. Specific examples include water-soluble polymers such as polysaccharides, e.g., dextran, as disclosed in U.S. Pat. 3,063,838 issued Nov. 13, 1962; hydrolyzed glycogen, as disclosed in U.S. Pat. 3,069,267 issued Dec. 18, 1962; laminarin, as disclosed in U.S. Pat. 3,085,010 issued Apr. 9, 1963; mannan, as disclosed in U.S. Pat. 3,085,009 issued Apr. 9, 1963; araban, arabogalactan and galactan, as disclosed in U.S. Pat. 3,087,818 issued Apr. 30, 1963; dextrin, as disclosed in British Pat. 897,497 published May 30, 1962; polyfructose, as disclosed in Belgian Pat. 607,210 granted Aug. 31, 1961; vinyl polymers, e.g., poly-N-vinyl pyrrolidones, as disclosed in U.S. Pat. 3,043,697 issued July 10, 1962; polyvinyl alcohol derivatives, e.g., acid derivatives such as succinoylated polyvinyl alcohol, as disclosed in Minsk and Abel U.S. Pat. 3,165,412 issued Jan. 12, 1965; cellulose derivatives, e.g., hydroxyethyl cellulose, as disclosed in Illingsworth and Minsk U.S. Pat. 3,003,878 issued Oct. 10, 1961; and like compounds. Additional hydrophilic colloids that can be used to increase the covering power of silver are polymers containing repeating units having the following formula:



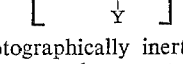
where R_1 is a carbon chain of 1 to 5 carbon atoms substituted with 1–3 substituents having the formula $—COXR_2R_3$, X being



R_4 being hydrogen or lower alkyl, and R_2 and R_3 each being hydrogen or alkyl groups containing up to 5 carbon atoms, alkoxy substituted alkyl groups containing up to 5 carbon atoms or hydroxy substituted alkyl groups containing up to 5 carbon atoms. Preferred polymers of this contain repeating units having the following formula:



where n is an integer from 1 to 5. Polymers of this type can also include monomeric units such as vinyl alcohol or other vinyl monomeric units including those represented by the formula:

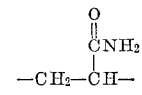


where Y is a photographically inert group such as hydroxy, an ester group such as acetoxy, an amide group such as N-alkyl where the alkyl group contains up to 5 carbon atoms, carbamate groups such as

$$—OCONHR_5—COOR_6$$

where R_5 and R_6 are each carbon chains, preferably alkylene, containing up to 5 carbon atoms. These additional polymers and copolymers can be prepared by any convenient method suitable for this purpose. For example, they can be prepared by treating the reaction product of poly(vinyl alcohol) and an ester of isocyanato mono-or polybasic fatty acid with an amine. The reaction of the isocyanato compound with the poly(vinyl alcohol) may be partial or complete, as may be the reaction of the amine with the initial reaction product. A polymer of this type which can be employed in the practice of this invention is one which contains, in combined form, monomeric units of vinyl alcohol, vinyl carboxy-methyl carbamate and vinyl —N—B-hydroxyethylcarbamyl methylcarbamate. The concentration of polymer which increases the covering power of silver is subject to wide variation and depends upon the nature of the specific polymer employed, its molecular weight and other variables. However, suitable concentrations are generally in the range of about 5 to about 80, preferably about 5 to about 50 percent, by weight, based on the weight of gelatin or other binding material employed, not including the weight of polymer added to improve covering power of the silver. In practicing the invention, the polymeric covering power addenda are employed in a photographic silver halide emulsion, in at least one photographic silver halide emulsion layer of a photographic element and/or in a layer contiguous or adjacent to said emulsion layer.

As already indicated, the water-soluble polyacrylamides are the preferred polymeric addenda employed to improve covering power, although many water-dispersible resins are suitable for this purpose. Suitable polyacrylamides are low molecular weight, water-soluble polyacrylamides of the type described in Minsk et al. U.S. Pat. 2,486,191 issued Oct. 25, 1949. Such polymers have the following recurring structural unit:



and have an inherent viscosity in the range of about .1 to about .6, and preferably about .15 to about .5, as determined at 25° C. in water. As used herein, the term "inherent viscosity" is determined by the formula:

$$\eta i—\frac{2.30 \log \eta r}{C}$$

where ηi is the inherent viscosity, ηr is the relative viscosity of water solution of the polymer divided by the viscosity of the water in the same units and at the same temperature, and C is the concentration in grams (0.25) of polymer per 100 cc. of solution. The polyacrylamide is preferably utilized in photographic gelatin silver halide emulsions at concentrations of about 5 percent to about 50 percent, and most preferably about 10 to about 40 percent, by weight, based on the weight of gelatin in the emulsion. If desired, two or more contiguous emulsion layers can be coated on a support, which emulsions can contain the covering power addenda, e.g., polyacrylamide, and the water-soluble salts in one or more of the emulsion layers.

The emulsions of the invention can contain photographic addenda such as optical sensitizers, chemical sensitizers, antifoggants, gelatin plasticizers, gelatin hardeners, coating aids and the like photographic addenda. The emulsions can be coated on a diversity of photographic supports in accordance with usual practice. Typical supports for the photographic emulsion of the invention include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, polyethylene film, polypropylene film paper, polyethylene coated paper, glass and the like.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention.

We claim:

1. A photographic silver halide emulsion comprising a water-soluble, poly-N-vinyl pyrrolidone or polysaccharide and a water-soluble salt of zinc or calcium.

2. A photographic emulsion according to claim 1 in which the water-soluble salt is a calcium salt.

3. A photographic emulsion according to claim 1 in which the water-soluble salt is a zinc salt.

4. A photographic emulsion according to claim 1 comprising a water-soluble polysaccharide.

5. A photographic emulsion according to claim 4 wherein said polysaccharide is dextrin.

6. A photographic emulsion according to claim 1 comprising poly-N-vinyl pyrrolidone.

7. A photographic emulsion according to claim 1 in which said water-soluble salt is zinc nitrate.

8. A photographic element comprising a support and at least one layer comprising the photographic emulsion of claim 1.

9. The emulsion of claim 1 in which the photographic silver halide comprises silver bromoiodide having about .5 to about 10 mole percent iodide and a mean grain size of at least .4 micron, said silver bromoiodide comprising a substantial amount of the silver halide of the emulsion.

10. A photographic gelatino silver halide emulsion comprising about 5 to about 50 percent, by weight, based on the weight of gelatin, of a water-soluble, polysaccharide or poly-N-vinyl pyrrolidone, said silver halide comprising silver bromoiodide having about .5 to about 10 mole percent iodide and a mean grain size of at least .4 micron, said emulsion having incorporated therein about 2 to about 50 grams per mole of silver of a water-soluble salt of zinc or calcium.

11. A photographic silver halide emulsion comprising from 5 to about 50 percent, by weight, based on the weight of gelatin, of a water-soluble, poly-N-vinyl pyrrolidone or polysaccharide, and about 2 to about 50 grams per mole of silver of a water-soluble salt of zinc or calcium.

12. A photographic element comprising: a support, a photographic silver halide emulsion layer containing a water-soluble, poly-N-vinyl pyrrolidone or polysaccharide, and a layer adjacent to said emulsion layer containing a water-soluble salt of zinc or calcium.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96—114, 114.3, 110