United States Patent Office

3,271,158

Patented Sept. 6, 1966

3,271,158

PHOTOGRAPHIC SILVER HALIDE EMULSIONS HAVING HIGH WET DENSITY RETENTION

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No Drawing. Filed Aug. 9, 1963, Ser. No. 301,177
5 Claims. (Cl. 96—114)

This invention relates to photographic silver halide emulsions and, more particularly, to gelatino-silver halide emulsions having improved wet density or covering power retention.

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 interest 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 have 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 in 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, 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.

It is accordingly an object of this invention to provide novel gelatino-silver halide emulsions having reduced wet-dry density changes.

It is another object of this invention to provide novel gelatino-silver halide emulsions having high covering power.

It is still another object of this invention to provide novel large grain gelatino-silver halide emulsions that have improved wet density retention.

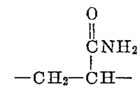
It is likewise an object of this invention to provide novel photographic gelatino-silver halide emulsions having particular utility in the graphic arts field.

It is also an object of this invention to provide new photographic gelatino-silver halide emulsions having an increased gamma for a given development time.

These and other objects of the invention are accomplished with photographic gelatino-silver halide emulsions wherein the silver halide comprises a substantial amount of large grain silver bromoiodide, and wherein the emulsion contains a minor proportionate amount of a low molecular weight, water-soluble polyacrylamide. We have found that a narrow segment of a specific polymeric class significantly improves the wet density retention and related properties of certain large grain silver halide emulsions as outlined above and as described in more detail below.

The polyacrylamide emulsion addenda of the invention are low molecular weight, water-soluble polyacrylamides of the type described in Minsk et al., U.S. Patent 2,486,191

issued October 25, 1949. Such polymers have the following recurring structural unit,



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

$$\eta_i = \frac{2.30 \log \eta_r}{C}$$

wherein η_i is the inherent viscosity, η_r 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 utilized in the present gelatino-silver halide emulsions at concentrations of about 5 percent to 50 percent, and preferably 10 to 40 percent, by weight based on the gelatin in the emulsion.

The preparation of photographic gelatino-silver halide emulsions such as are utilized with the described polyacrylamides 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 Photographich Process, 1954.

The water-soluble polyacrylamides utilized in our emulsions can be added to the emulsion at any stage of the preparation of the emulsion, such as before the final digestion or after-ripening, or immediately prior to coating.

The silver halide utilized in the present photographic gelatino-silver halide emulsions comprises a substantial amount of silver bromoiodide, and preferably consists essentially of silver bromoiodide, the silver bromoiodide being .5 to 10 mole percent iodide. The silver bromoiodide crystals of suitable emulsions have a mean grain size of at least about .4 micron and more generally in the range of .4 to 1.5 microns. Other silver halides than silver bromoiodide, and silver halides having other grain sizes, can be mixed in the present gelatino-silver bromoiodide emulsions. The present emulsions are the conventional negative-type, developing-out emulsions.

The photographic gelatino-silver halide emulsions of the invention can contain conventional photographic addenda such as optical sensitizers, chemical sensitizers, antifoggants, gelatin plasticizers, gelatin hardeners, coating aids, and the like photographic addenda.

The above-described emulsions of the invention can be coated on a diversity of photographic supports in accordance with usual practice. Typical supports for the photographic emulsions 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.

The invention is further illustrated by the following examples of preferred embodiments thereof.

EXAMPLE 1

A negative-type, developing-out, gelatino-silver bromoiodide emulsion (93% bromide, 7% iodide) wherein the silver bromoiodide had a mean grain size of 0.6 micron was prepared and coated on a polyethylene terephthalate film support at a coverage of 375 mg. of silver per square foot and at a coverage of 1250 mg. of gelatin per square foot. A second identical coating was made except that a water-soluble, low molecular weight polyacrylamide having an inherent viscosity of 0.30 as determined in water at 25° C. was incorporated into the emulsion just prior to coating at a coverage of 55 grams per mole of silver halide. Samples of the two prepared films were then exposed in an Eastman IB sensitometer, developed for 5 minutes in the developer described below at about 70° F., fixed in the fixing bath described below, and thereafter washed and dried.

Developer

	G.
N-methyl-p-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite (anhydrous)	30.0
Sodium metaborate·octahydrate	10.0
Potassium bromide	0.5

Water to make one liter.

Fixing bath

Sodium thiosulfate ____g__	240.0
Sodium sulfite (anhydrous) ____g__	15.0
Acetic acid, 28% ____cc__	48.0
Boric acid ____g__	7.5
Potassium alum ____g__	15.0

Water to make one liter.

Then densities of the sensitometric steps for both of the processed film samples were measured before and after drying, the density change on drying being measured at a wet density of 2.0. The results are summarized by the data set out in Table I below.

TABLE I

Addenda	γ	Percent Wet-Dry Density Change at Density of 2.0
(1) None	1.20	7.0
(2) Polyacrylamide	1.43	1.0

The relative speed and fog of the sample containing the polyacrylamide were not adversely affected. As can be observed from the data set out in Table I, the polyacrylamide imparted substantial wet density retention to the gelatino-silver halide emulsion.

Example 2

Three photographic film samples were prepared and coated as described in Example 1 wherein one coating was the gelatino-silver bromoiodide emulsion, the second coating was the gelatino-silver bromoiodide emulsion containing 55 grams per mole of silver halide of a water-soluble, low molecular weight polyacrylamide having an inherent viscosity of 0.30 as determined in water at 25° C., and the third coating was the gelatino-silver bromoiodide emulsion containing 55 grams per mole of silver halide of a water-soluble, high molecular weight polyacrylamide having an inherent viscosity of 1.68 as determined in water at 25° C. The three samples were thereafter exposed in an Eastman IB sensitometer and thereafter processed as described in Example 1. The wet-dry density behavior of the three coatings was thereafter observed as in Example 1 and summarized by the data set out in Table II below.

TABLE II

Addenda	γ	Percent Wet-Dry Density Change at Density of 2.0
(1) None	1.37	6.0
(2) Polyacrylamide (high molecular weight)	1.18	5.0
(3) Polyacrylamide (low molecular weight)	1.49	1.0

As can be observed from the data set out in Table II above, the low molecular weight polyacrylamide emulsion addenda of the invention resulted in a film having substantially less wet-dry density change than the film sample containing the high molecular weight polyacrylamide or the sample containing no polyacrylamide.

Example 3

Several coatings were prepared with negative-type, developing-out, gelatino-silver halide emulsions to illustrate the improved results that are obtained with the large grain silver bromoiodide emulsions of the invention as compared to finer grain silver bromoiodide and silver chlorobromide emulsions. The various coatings were prepared, exposed and processed by the general method described in Example 1. The components in the various coatings as well as the resulting percent wet-dry density changes are summarized by the data set out in Table III below. In Table III, the silver bromoiodide of emulsions 1 to 3 was 93% bromide and 7% iodide, the silver bromoiodide of emulsions 4 to 6 was 96% bromide and 4% iodide, the silver bromoiodide of emulsions 7 to 9 was 99% bromide and 1% iodide, and the silver chlorobromide of emulsions 10 to 12 was 80% chloride and 20% bromide.

TABLE III

Emulsion Type	Mean Grain Size	Gms. of Polyacrylamide per 100 g. of Gelatin	Mg. of Gelatin per sq. ft.	Mg. of Ag per sq. ft.	Percent Wet-Dry Density Change at Density of 2.0
(1) AgBrI	0.6	None	1,000	450	7.0
(2) AgBrI	0.6	16.0	1,000	450	None
(3) AgBrI	0.6	18.0	1,000	450	2.0
(4) AgBrI	1.0	None	1,680	762	7.0
(5) AgBrI	1.0	16.0	1,680	762	1.5
(6) AgBrI	1.0	18.0	1,680	762	1.0
(7) AgBrI	0.3	None	1,000	432	None
(8) AgBrI	0.3	16.0	1,000	432	4.0
(9) AgBrI	0.3	18.0	1,000	432	5.5
(10) AgClBr	0.3	None	381	206	11.0
(11) AgClBr	0.3	18.5	381	206	15.0
(12) AgClBr	0.3	23.0	381	206	15.5

As can be observed from the data set out in Table III above, substantially improved wet density retention characterizes the larger grain silver bromoiodide emulsions of the invention as is illustrated by emulsions 1 to 6 of Table III, and which wet density retention is not demonstrated by finer grain emulsions 7 to 12 of Table III.

Accordingly, the present invention provides new and useful photographic silver halide emulsions.

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 as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic gelatino-silver halide emulsion containing 5% to 50% by weight based on the said gelatin in said emulsion of a water-soluble polyacrylamide having an inherent viscosity of .1 to .6 as determined at 25° C. in water, said silver halide comprising a substantial

amount of silver bromoiodide having .5 to 10 mole percent iodide and a mean grain size of at least .4 micron.

2. A photographic gelatino-silver halide emulsion containing 10% to 40% by weight based on the said gelatin in said emulsion of a water-soluble polyacrylamide having an inherent viscosity of .15 to .5 as determined at 25° C. in water, said silver halide consisting essentially of silver bromoiodide having .5 to 10 mole percent iodide and a mean grain size of .4 to 1.5 microns.

3. A photographic gelatino-silver halide emulsion as described in claim 2 wherein the polyacrylamide has an inherent viscosity of about .3 as determined at 25° C. in water.

4. A photographic gelatino-silver halide emulsion as described in claim 2 wherein the silver bromoiodide has a mean grain size of about .6 microns.

5. A photographic support having coated thereon an emulsion as described in claim 1.

References Cited by the Examiner

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