

1

3,561,971

PRINT-OUT EMULSION FOR ACTINIC LIGHT DEVELOPMENT AND PROCESS OF MAKING SUCH EMULSIONS

Henry W. Pestalozzi, Binghamton, N.Y., assignor to GAF Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Mar. 10, 1967, Ser. No. 622,028

Int. Cl. G03c 1/02

U.S. Cl. 96-108

10 Claims

ABSTRACT OF THE DISCLOSURE

This invention deals with light-sensitive materials for the recording of images produced by light of high intensity such as the scanning beams of oscillographs and the development of these latent images by post exposure with low intensity light. The silver halide emulsions used are prepared by forming silver iodide on the surface of the silver bromide grains, the amount of silver iodide ranging from 0.2 to 10 mole percent based on the silver content. The emulsions also contain from 1 to 25 mole percent of lead bromide based on the silver content.

The present invention relates to print-out emulsions developed by a post-exposure to low intensity actinic light and to a process of making such emulsions.

Light-sensitive silver halide systems used in photography can be divided into three groups; namely, those which are developed by chemical development after exposure; those which contain silver salts in excessive amounts so as to form a print-out image directly on exposure and, thirdly, those which are developed by a second prolonged exposure to actinic light of lower intensity.

The present invention deals with the third and more recent type of photography. This technique is coming into prominent use, particularly for recording purposes with high intensity light sources with instruments (e.g., electronic flash or the scanning beam of a recording oscillograph), or electron beams.

The resulting latent images are rendered visible by subsequent overall exposure of the emulsion to low intensity light sources. In some instances, it may be desirable to add a simultaneous heat treatment of the exposed sheet to accelerate the development action of the second or post-exposure.

Various materials suitable for this print-out technique are marketed under various trade names: including Du Pont "Linowrit," Eastman Kodak "Linagraph" and GAF's "Anscotrace" paper. These emulsions usually consist of silver chloride, silver bromide, silver-iodide suspensions or combinations of these silver halides in a gelatin binder to which divalent metal salts, such as tin chloride, lead bromide, lead iodide, or cadmium chloride are added.

The prior art has suggested, particularly the conjoint use of two lead salts, specifically the bromide and the iodide. The presence of the lead iodide imparts a yellow stain to the support which gradually turns brown on prolonged exposure as iodine is liberated.

Further, while some of the materials hitherto proposed have been quite satisfactory for use under specific conditions or for limited life, many have lacked the versatility often required for different conditions of exposure, development and storage.

It is, therefore, among the objects of the present invention to provide a print-out material of greater versatility.

It is another object of the present invention to provide emulsions which allow either a negative or a reversal print-out image to be formed under the same exposure conditions and in the same emulsion, depending on the ripening conditions and the coating finals used.

2

According to the present invention, a photographic emulsion is prepared which is suitable for recording of relatively very high intensity illumination and subsequent development by exposure to actinic light of relatively much lower intensity. The emulsion is made up in the usual manner. Gelatin is dissolved in water and then the silver nitrate and the alkali metal bromide are added simultaneously to the gelatin solution, preferably by the double-jet technique. This procedure is carefully adjusted so that it results in the production in the emulsion of essentially pure silver bromide crystals.

The next step involves adding a small proportion, preferably of about 0.5 to 10.0 mole percent potassium iodide based on the silver content. Other alkali metal iodides, of course, may be used, although the potassium salt is normally preferred. As set forth in Mees, "The Theory of the Photographic Process," McMillan Co., 1946, page 316, the treatment of silver bromide crystals with potassium iodide converts the surface of the crystals at least partially to silver iodide.

For a reversal print-out, the proportions of silver iodide should be relatively larger. The proportions of lead bromide, the only lead salt present, should be relatively low. Thus, proportions of 1.0 to 10.0 mole percent of potassium iodide based on the silver may be added. An aqueous slurry of lead bromide, in a molar ratio of 3 to 7 mole percent is added to the emulsion. The preferred ranges specifically are about 5 to 7 mole percent of potassium iodide and about 4 to 6 mole percent of lead bromide, again based on the silver present.

For the reversal print-out type of operation the emulsion must be of the digested or ripened type, whereas for negative print-out, it is necessary to use an unripened emulsion. In the latter case, lower proportions of the alkali metal iodide are added, for example, 0.2 to 2.0 mole percent, based on the silver, but preferably about 0.5 to 1.5 mole percent. At the same time, the proportions of lead bromide are substantially increased, being from about 3 to 20 mole percent, about 4 to 10 mole percent being preferred. As indicated, these modifying ingredients must be incorporated in the unripened emulsion in order to obtain a good negative print-out with low background. It is emphasized that the lead bromide should be the only lead salt present for the purposes of the invention. Other lead salts adversely affect the quality of the final print, particularly in promoting background fog.

Summarizing, it can be stated that the primitive, unripened emulsion with a low secondary iodide content will produce a negative print-out image within a wide range of lead bromide content. On the other hand, essentially the same type of emulsion will produce a reversal print-out image only when ripened and having a relatively high secondary iodide content and a relatively low lead bromide content.

The invention will be more fully understood and its potential practical applications will be better appreciated by reference to specific examples.

EXAMPLE 1

An emulsion was prepared consisting of a pure silver bromide produced by double-jet mixing 0.5 mole of potassium bromide and 0.5 mole of silver nitrate in a solution of 20.0 grams of inert gelatin and 0.6 gram of potassium bromide (1 mole percent) in 480 ml. of water at 65° C. For the reversal print-out, ripening was accomplished by heating the emulsion at 65° C. for one hour. The emulsion was then precipitated with ammonium sulfate, washed and reconstituted with 60 grams of gelatin and sufficient water to make one liter. Thereafter, an aqueous solution of about 6 mole percent of potassium iodide, based on silver, was added and thoroughly mixed. After

3

this was completed, 5 mole percent, based on silver, of lead bromide, was added as an aqueous slurry. Thereafter, the emulsion was coated on baryta paper.

EXAMPLE 2

The procedure in the first example was repeated in part by preparing a pure silver bromide emulsion in inert gelatin by the double-jet precipitation technique, the digestion being omitted. After precipitation with a polystyrene-sulfonate solution, washing and reconstitution, 0.5 mole percent of potassium iodide, based on the silver content was added with stirring. After about 15 minutes of continued stirring, 20 mole percent of lead bromide, based on silver, was added as an aqueous slurry. This material was then coated onto a baryta paper or film base support. The coated and dried material is suitable for negative print-out use.

In both cases, namely in Examples 1 and 2, the emulsions were exposed to a high intensity pattern produced by an oscillograph. The oscillograph trace was then developed by exposure to fluorescent light of moderately low intensity. In each case a clear, strong image of the oscilloscope pattern was obtained, but the reversal or negative character of the image depended on the choice of the material. The finished record had good stability. The image (reversal in Example 1 and negative in Example 2) remained visible without excessive darkening of the background for a substantial length of time under ordinary office storage conditions.

It will be obvious that variations may be made in the practice of this invention. For instance, various types of gelatin may be employed, although the inert gelatin is preferred. It is obvious that some variations may be made in the emulsion making conditions described in the examples. Accordingly, the invention should be held limited only as necessitated by the appended claims.

I claim:

1. A photographic silver halide emulsion composition, suitable for recording high intensity illumination of short duration with subsequent development by a following exposure to actinic light of substantially lower intensity and longer duration, said emulsion consisting essentially of a binder containing silver bromide crystals, a small proportion, varying from 0.2 to 10 mole percent based on the silver, of silver iodide on the surface of the silver bromide crystals, said emulsion also containing 1 to 25 mole percent, based on the silver of lead bromide as essentially the only lead salt present.

2. A photographic silver halide emulsion according to claim 1, wherein the silver iodide content ranges from 0.2 to 2.0 mole percent and the lead bromide content ranges from 3 to 20 percent based on the amount of silver present in the silver halide emulsion, and wherein the emulsion is undigested.

3. A photographic silver halide emulsion according to claim 1, wherein the silver iodide content ranges from 1 to 10 mole percent and the lead bromide content ranges from 3 to 7 mole percent, and wherein the photographic emulsion is digested.

4. A photographic material carrying on a suitable support, the emulsion defined by claim 1.

5. A photographic material capable of giving upon exposure to high intensity and short duration light and

4

subsequent exposure to low intensity actinic light a negative print-out image, said material consisting essentially of a suitable support carrying the silver halide emulsion defined by claim 2.

6. A photographic material capable of yielding upon exposure to high intensity, short duration illumination, and subsequent development by a second exposure to actinic light a reversal print-out image, said material comprising a suitable base carrying the silver halide emulsion layer defined by claim 3.

7. A photographic silver halide emulsion according to claim 1, wherein said binder is gelatin.

8. A process of preparing a print-out emulsion for recording image patterns produced by high intensity short duration illumination, with subsequent development by post-exposure to relatively low intensity actinic light, which comprises precipitating the silver bromide crystals in a gelatin solution by double-jet precipitation with equivalent amounts of an alkali metal bromide and silver nitrate, by adding as finals first, about 0.2 to 10 mole percent, based on the silver, of an alkali metal iodide, thoroughly mixing, and then adding 1 to 25 mole percent, based on the silver of lead bromide as the only lead salt.

9. A process of preparing a print-out emulsion according to claim 8 for recording reversal image patterns by exposure to short duration high intensity illumination with subsequent development by post-exposure to relatively low intensity actinic light of longer duration, said process comprising the steps of forming in an aqueous solution of inert gelatin, silver bromide crystals by the double-jet precipitation of essentially equimolar amounts of potassium bromide and silver nitrate, the emulsion thus formed coagulating and washing the silver bromide emulsion, reconstituting the emulsion and adding thereto about 5.0 to 7.0 mole percent of potassium iodide, based on the silver, thoroughly mixing, and thereafter adding with agitation to the emulsion about 4 to 6 mole percent of lead bromide as an aqueous slurry.

10. A process of preparing a print-out emulsion according to claim 8 for recording negative image patterns by exposure to short duration and high intensity illumination and subsequent development by a second exposure to relatively low intensity actinic light of long durations, which process comprises the steps of forming in a solution of inert gelatin, silver bromide and silver nitrate, by double-jet addition of aqueous solutions of an alkali metal bromide, thereafter without ripening, adding 0.5 to 1.5 moles, based on the silver content, of potassium iodide, thoroughly mixing, and thereafter adding 4 to 10 mole percent, based on the silver content of lead bromide to form an emulsion suitable for a negative print-out.

References Cited

UNITED STATES PATENTS

3,123,474	3/1964	Byrne	96—94
3,436,221	4/1969	Sprung	96—94

J. TRAVIS BROWN, Primary Examiner

U.S. CI. X.R.

96—94, 119