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3,143,419

## HIGH-SPEED PRINTOUT EMULSIONS CONTAINING SILVER IODIDE AND SILVER OXALATE

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This invention relates to high-speed, printout photographic silver salt emulsions and a method for preparing them.

Two general types of photographic silver halide emulsions are known. The most common type is a developing-out emulsion. A type of emulsion of less commercial interest is the printout type. The printout effect was at one time used rather extensively in preparing photographic positives from a negative by contact printing. However, the exposures required are quite long, in some cases as much as 15 to 20 minutes in bright daylight. Consequently, the developing-out emulsions have been investigated and improved upon in speed and stability much more extensively than the printout type of emulsion.

The silver halide sensitive salt employed in printout photographic emulsions is normally silver chloride. These silver chloride emulsions are prepared somewhat differently from developing-out emulsions in that an excess of soluble silver salt (silver nitrate) is used, rather than an excess of halide, as in the case of developing-out emulsions.

I have now found new photographic silver halide emulsions of the printout type which are characterized by quite high speeds, as contrasted with the relatively slow silver halide printout emulsions. The new printout emulsions of my invention comprise silver oxalate and silver iodide. A portion of the silver iodide can be replaced with another silver halide, such as silver bromide or silver chloride, if desired. They are sensitive principally to blue light and ultraviolet radiation.

It is, therefore, an object of my invention to provide new printout photographic silver salt emulsions comprising silver oxalate and silver iodide. Another object is to provide a method of preparing such photographic silver salt emulsions. Still another object is to provide photographic silver halide emulsions of the printout type which have speeds to tungsten or other artificial light, or daylight, many times higher than conventional printout photographic emulsions. Other objects will become apparent from a consideration of the following description and examples.

The novel photographic silver halide emulsions of my invention can be prepared using techniques which have been previously described in the art of emulsion making. Advantageously, I have found that the novel printout emulsions of my invention can be prepared by first precipitating silver oxalate and subsequently converting a portion of the silver oxalate to a silver iodide salt. The mixed precipitate of silver oxalate and silver iodide can then be washed by decantation, followed by the addition of a suitable binder-colloid, such as a water-permeable, water-insoluble hydrophilic colloid, such as gelatin, albumen, starch, polyvinyl alcohol, hydrolyzed cellulose ester, etc.

The prepared emulsion can then be coated on a con-

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ventional photographic support and dried. Suitable supports include, for example, paper, cellulose ester film, polyester film, polystyrene, polyethylene, glass, aluminum foil, etc.

It has been found that the concentration of silver iodide in the finished emulsion can advantageously be between about 0.03 mole and 0.9 mole per mole of total silver. Maximum sensitivity seems to occur at a silver iodide concentration of about 0.4 mole per mole of total silver. The total concentration of light-sensitive silver salts in the finished emulsion will obviously vary, depending upon the use intended for the finished emulsion. The manner of varying the silver concentration in photographic emulsions is well known to those skilled in the art, and it is to be understood that my invention is susceptible to variations and modifications in emulsions using these well known techniques.

The following examples will serve to illustrate more fully the method of preparing and using photographic emulsions of the printout type which are useful according to my invention.

### Example 1

The following solutions were prepared:

(A)

Gelatin..... 20 grams.  
Distilled water..... 150 ml.

(B)

Potassium oxalate-monohydrate. 54.2 grams.  
Distilled water..... 200 ml.

(C)

Silver nitrate..... 13.5 grams.  
Distilled water..... 150 ml.

(D)

Potassium iodide..... 5.6 grams.  
Distilled water..... 150 ml.

(E)

Distilled water to make..... 300 grams (total weight of emulsion).

The silver nitrate solution (Solution C) was added to Solution B and the resulting precipitate was then washed by decantation. Solution D was then added and the resulting mixed precipitate of silver oxalate and silver iodide was washed by decantation. The precipitate was then mixed with Solution A at 50° C., and Solution E was added to bring the total weight of the emulsion up to 300 grams. The resulting printout emulsion, which contained about 0.023 mol. of silver oxalate and about 0.034 mol. of silver iodide (0.4 mole of silver iodide per mole of total silver) was then coated on an ordinary paper support and dried. The photographic emulsion was then exposed to a step wedge using tungsten illumination (No. 2 Photoflood at 117 volts) and was found to have a printout speed approximately eight times faster than a pure silver oxalate emulsion made by method of Example 1 except omitting the addition of Solution D. The emulsion had a spectral response from about 300 to 440  $m\mu$  with a peak sensitivity at about 415  $m\mu$  and a very sharp cut-off at 440  $m\mu$ .

## Example 2

The following solutions were prepared:

## (A)

Potassium oxalate monohydrate. 40 grams.  
Distilled water----- 200 ml.  
Thiourea solution, 0.001 M----- 5 ml.

## (B)

Silver nitrate----- 13.5 grams.  
Distilled water----- 100 ml.  
Ammonium hydroxide to dissolve  
the precipitate first formed.

## (C)

Potassium bromide----- 3.0 grams.  
Potassium iodide----- 1.0 gram.  
Distilled water----- 200 ml.

## (D)

Gelatin----- 15 grams.  
Distilled water----- 100 ml.

## (E)

Distilled water to make----- 300 grams (total  
weight of emulsion).

In preparing Solution B, a small amount of ammonium hydroxide was added to form a precipitate of silver hydroxide which was then dissolved by adding just sufficient ammonium hydroxide to solubilize the precipitate.

Solution A was added to Solution B and the resulting precipitate was washed by decantation. Solution C was then added and the mixed precipitate of silver oxalate and silver bromide was dispersed in Solution D at 50° C. and Solution E was added to bring the total weight of the emulsion up to 300 grams. The resulting emulsion contained 0.025 mole of silver bromide, 0.006 mole of silver iodide and about 0.024 mole of silver oxalate.

The resulting emulsion was then coated on a paper support, dried, and exposed for two minutes to a step tablet using a No. 2 Photoflood lamp placed at a distance of one foot. As in the case of the emulsion in Example 1, this emulsion had a spectral response of from about 300 to 440 m $\mu$  with a peak sensitivity at 415 m $\mu$  and a very sharp cut-off at 440m $\mu$ . The emulsion of Example 2 had a printout speed approximately eight times faster than a pure silver oxalate emulsion, made according to Example 1 except omitting the addition of Solution D.

## Example 3

Example 1 was repeated except that the potassium iodide concentration was lowered to 0.35 g. in Solution D. The resulting silver oxalate-silver iodide emulsion contained about 0.03 mole of silver iodide per mole of total silver.

## Example 4

Example 1 was repeated except that the potassium iodide concentration in Solution D was increased to 12.0 g. The resulting silver oxalate-silver iodide emulsion had a concentration of 0.9 mole of silver iodide per mole of total silver. Examples 3 and 4 show less sensitivity than Example 1, but are the detectable lower and higher limits of silver iodide concentration which show greater sensitivity than silver oxalate alone.

While the above examples describe exposures using ordinary Photoflood illumination, it is apparent that other types of illumination can be used to expose these photographic printout emulsions. For instance, these emulsions can be exposed on many of the types of recording apparatus, e.g., 3M Thermo-Fax Secretary, or the Minneapolis-Honeywell-Heiland Oscillograph Visicorder as

described in Heiland U.S. Patent 2,580,427, issued January 1, 1952.

These silver oxalate-iodide printout materials exhibit some interesting behavior. In the case of after-treatment exposure of a printout image produced from a low intensity exposure to blue or ultraviolet light, e.g. from a G-E Photoflood lamp No. 2 placed at a distance of one foot for two minutes, the image density and contrast can be markedly increased by a post-exposure to infrared radiation, e.g., from a 250-watt infrared lamp placed at a distance of two feet for 15 to 20 seconds, increasing the effective speed by a factor of 20 times. This post-exposure intensification of the regular image exposure affords a convenient method to decrease very considerably the time of printout image exposure required to produce satisfactory image density and contrast. Such post exposure also makes visible certain areas which received some image exposure but too little to result directly in observable image density. Thus, a useful image exposure does not necessarily have to be sufficient to give a visible image directly.

In the case where the image exposure is made with a high intensity, short duration exposure to blue or ultraviolet light, e.g., a 900-watt lamp at 3000° K. placed at a distance of 120 mm. for 0.02 sec., no visible printout image was observed and no usable intensification was obtained by infrared post-exposure treatment of the type described above. However, post exposure to a fluorescent light source, e.g., Westinghouse 15-watt daylight or G-E 40-watt cool white fluorescent tubes, produced a reversal image on which the background darkened rapidly to a density much higher than the low density printout image, while the latter showed very little increase in density during the post exposure.

While potassium iodide was used as the source of iodide ion in the above examples, it is apparent that other water-soluble iodides, such as the sodium salt, ammonium salt, etc., can be likewise employed. Also, other water-soluble silver salts can be employed in place of the silver nitrate used in the above examples.

It has been found that the sensitivity of ordinary gelatino-silver-iodide emulsions can be increased by sensitizing these emulsions according to the method shown in Staud et al. U.S. Patent 1,925,508, issued September 5, 1933. For example, such emulsions can be chemically sensitized by treatment with various amines, such as 2-methylaminoethanol, 2-aminoethanol, tetrahydroxyethylenediamine, 2-dimethylaminoethanol, adducts of 2-dimethylaminoethanol and sulfur dioxide, etc. Such emulsions can also contain one or more photographic developing agents, such as hydroquinone, 3-pyrazolidones, etc., in which case the emulsions can be developed by simply treating with an alkaline bath after exposure.

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.

What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A method of preparing photographic images directly comprising photoexposing briefly and intensely a photographic element comprising a support and coated on said support a photographic emulsion of the printout type comprising a hydrophilic colloid having dispersed uniformly therethrough silver oxalate and silver iodide, said silver oxalate and said silver iodide being the only light-sensitive silver salts present in said photographic emulsion and the concentration of the silver iodide being between 0.03 and 0.9 mole per mole of total silver, and photodeveloping said photoexposed photographic element by exposing said photographic emulsion uniformly to

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fluorescent radiation until the previously unexposed background areas print out to a density substantially higher than that of the areas briefly and intensely photoexposed.

2. A photographic emulsion of the printout type comprising a hydrophilic colloid having dispersed uniformly therethrough light-sensitive silver salts consisting of silver oxalate and silver iodide, the concentration of the silver iodide being between 0.03 and 0.9 mole per mole of total silver.

3. A photographic element comprising a flexible support and coated thereon a photographic emulsion of the printout type comprising a hydrophilic colloid having dispersed uniformly therethrough light-sensitive silver salts consisting of silver oxalate and silver iodide, the concentration of the silver iodide being between 0.03 and 0.9 mole per mole of total silver.

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