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# RADIATION-SENSITIVE SILVER HALIDE EMULSIONS AND ELEMENTS, AND PROCESSES OF DEVELOPING THE SAME

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This invention relates to radiation-sensitive elements; and, more particularly, to light-developable, direct-writing, radiation-sensitive elements, and, still more particularly, this invention relates to light-developable, direct-writing, radiation-sensitive elements of high speed, high resolution, and good image and background stability. In still another aspect this invention relates to new and novel colloid silver halide emulsions for such radiation-sensitive elements and, in particular, colloid silver halide emulsions. This invention also relates to a process for exposing and developing the elements and stabilizing the images.

Radiation-sensitive papers adapted for light recording, e.g. oscillographic recording are known. Such materials are both of the developing-out type and the print-out type. The developing-out type, as the name implies, requires that the exposed material be chemically developed, fixed and washed in order to provide a stable visible image on said material. The print-out type of material requires no development step and may or may not be fixed. Such materials are generally much slower than those materials used in developing-out processes and have poor image permanency.

A third type of radiation-sensitive material especially suitable for light writing and oscillographic recording comprises a silver halide layer which, when exposed to a high intensity source of radiation forms a latent image which can then be developed by exposure to diffuse daylight or artificial light of lower intensity. Such materials are faster than print-out emulsions and require no chemical development; and, therefore, they afford considerable advantage in doing away with liquid solutions and the necessary processing apparatus. It is this third type of printing material with which the present invention is concerned.

The prior art suggests for this third type of printing material, silver bromide emulsions which have incorporated therein, sulfur-containing compounds such as halogen acceptors, e.g. thiourea, thiosemicarbazides, etc. The background and image densities of layers comprising such emulsions, however, are not sufficiently stable to permit rapid access to or prolonged examination of the recorded images. It has further been proposed to make radiation-sensitive emulsions for this purpose by introducing silver thiocyanate into a silver bromide emulsion. The sensitivity of this material is alleged to be considerably greater than pure silver bromide emulsions containing halogen acceptors and can be further increased by the use of halogen acceptors. However, such materials, after being light-developed by daylight or incandescent light, do not provide a stable image. Upon prolonged exposure to ordinary illumination, the background darkens which reduces the ratio between background and image densities. Also, where the development radiation contains a high proportion of ultra-violet light, subsequent exposure after light-development causes an increase in background density and rapid regression of the light-developed image. It is necessary to resort to bathing the light-developed image in a liquid developing bath containing a silver halide solvent to intensify and preserve the contrast or ratio of background to image density of the originally light-developed



image. Treatment in a fixing bath is also recommended for the same purposes.

Chemical sensitization of photographic developing-out emulsions and also print-out emulsions with stannous salts are known. Stannous compounds are used in developing-out systems in extremely small quantities (i.e., from $1\times10^{-7}$ to $44\times10^{-6}$ mol of stannous compound per mol of silver halide). In applicants' copending application U.S. Ser. No. 814,954, filed May 22, 1959, now abandoned, there are disclosed and claimed direct-writing, radiation-sensitive elements which contain stannous salts and lead salts in combination with a large excess of bromide ions.

An object of this invention is to provide new and commercially useful, light-developable, direct-writing, radiation-sensitive photographic emulsions, emulsion layers and elements, e.g., films and papers. Another object is to provide such elements which have high writing speeds. A further object is to provide such elements in which the background densities can be readily stabilized. A still further object is to provide a simple and efficacious process for stabilizing the background density of exposed light-developable, direct-writing, radiation-sensitive photographic elements.

The light-developable, direct-writing, radiation-sensitive emulsions of this invention comprise an aqueous emulsion or dispersion of light-sensitive silver halide grains having average grain size in the range 0.1–10 microns in a water-permeable, organic, macromolecular colloid having protective colloid properties, said dispersion containing from 0.5 to 120 mole percent and preferably 5 to 40 mole percent of a stannous salt, based on the light-sensitive silver halide. The photographic elements of the invention comprise a flexible support, e.g., paper or an organic polymer film, bearing on or in at least one surface a layer of stratum of the foregoing dispersion which has been dried.

This invention also includes a process for improving the background density of a localized, radiation-exposed, light-developable, direct-writing, radiation-sensitive photographic element bearing on or in at least one surface of a flexible support a layer of the emulsion described in the previous paragraph which is characterized by heating the exposed element to a temperature of at least 200° F. but below the decomposition temperature of the element and preferably to 250° F. to 280° F., and then developing the image by an overall exposure of the element to radiation of wavelength in the range 350 to 700 millimicrons for 0.2 second up to about 15 seconds or more, while maintaining such a temperature for at least a part of the light-development step. The heat treatment stabilizes and keeps the background density down. However, the elements are not limited in their use to this preferred heat-stabilization treatment as the image and background density can be stabilized by exposure to visible radiation of moderate intensity, e.g., 50-foot-candles.

The photographic silver halide emulsions with which the stannous salts are incorporated preferably are the silver bromide or silver chlorobromide type but other types, i.e., chloride, iodobromide, etc. can be used. The silver halides may be precipitated in a manner well known to those skilled in the art, e.g. by slowly adding an aqueous solution of silver nitrate to an aqueous solution of a water-soluble halide salt containing a water-soluble dispersing agent, e.g. gelatin. Any water-soluble halide salt or salts may be used depending on the silver halide composition which is desired. In the case of large-grained silver bromide and silver chlorobromide emulsions it has been found desirable to use either calcium bromide or magnesium bromide in an amount to provide a considerable excess of bromide ion over that necessary to react with the silver nitrate. A variety of soluble halide salts can be used in the presence of active or inert gelatins. Potassium, sodium and ammonium salts of chloride and bromide can be used.

After precipitation and ripening to provide the proper grain size, a relatively large percentage, e.g. at least 0.5 mole percent and preferably from 5 to 40 mol percent of a stannous salt based on the silver halide is added. This is of the order of magnitude of $1\times10^2$ more than the amount found to be necessary for chemically sensitizing developing-out emulsions. The emulsion may or may not be digested as desired and then a further amount of gelatin or other colloid is added. The resulting emulsion can then be coated without further treatment. The emulsion may be washed, if desired; but, in this case, additional soluble bromide salts must be added to maintain the considerable excess of bromide ions. The stannous salt may be any water-soluble salt, i.e., stannous chloride, stannous sulfate, etc. The salts may be dissolved in water, ethanol, cellosolve, glycerine or similar solvents. The stannous may also be added in dry form.

When washed emulsions of the pure silver bromide type are used, other soluble bromide salts in addition to the calcium and magnesium salts mentioned above may be used with equivalent results provided that bromide ions are present in considerable excess, e.g. at least 50% excess of that necessary to convert all of the silver to silver bromide when the molten emulsion is coated. For example, potassium, sodium and/or ammonium bromide may be used as an additive after washing. In the case of washed emulsions, the tin salt usually is added as a final addition before coating or just before making the final gelatin addition. The images may be made completely stable by the usual fixing process, but this is unnecessary if the light-developed images are exposed to light only infrequently and kept in the dark when not in use. Heating the image during light development or amplification also stabilizes the image.

Although the role of the stannous ion is not clearly understood, it is believed to function as a halogen acceptor during the amplification of the image. In this role, the amount of silver reduced is directly dependent on the amount of stannous ion present. Thus the stannous ion can be viewed as a developer in situ which functions when the system is exposed to low intensity light.

The preferred method of exposing and processing material coated with the emulsions of the invention comprises exposing the material to radiation from a xenon tube or high-pressure mercury arc lamp containing a high proportion of blue and ultraviolet radiation for a period ranging from about 0.1 to 10,000 microseconds. After exposure, the material may be light developed by exposure to daylight or low intensity incandescent or fluorescent light or by the use of photoflood lamps commonly used in photography.

When using fluorescent lights of the type used in ordinary office lighting and heating by any suitable means, e.g., a heated platen, the image is easily visible in approximately 0.1 to 15 seconds with development to maximum image density in several minutes. With this type of development, a much more stable background and more permanent image is obtained. Light-development by means of photoflood lamps can result in a readable image in about one second or less, with only a slight increase in background density. Although the ratio of image quality to background quality may be somewhat lower under this latter condition of light-development, a high ratio can be maintained by photographic fixing.

Speed in oscillography is measured in inches per second and is called writing speed. The source in a typical instrument designed for direct-writing papers is the "Osram" super high pressure mercury arc lamp Type HBO 107/1. Writing speeds are determined from the frequency of the signal and the peak to peak amplitude of oscillation as recorded on the paper.

The writing-speed determination of a material was augmented by a $\sqrt{2}$ step wedge exposure to an electronic flash sensitometer similar to that described by Wyckoff and Edgerton, Journal of the Society of Motion Picture and Television Engineers, 66, 474 (1957). This instrument uses a xenon discharge tube as the source of radiation and has available two exposure times of 10 and 1,000 microseconds. Relative sensitivities of materials measured with this instrument may be expressed as the number of steps recorded in the image.

The recorded latent image was developed with radiation from fluorescent lighting or a reflector photoflood lamp, G.E. Rfl. No. 2A. Intensity was varied by distance of the lamp from the developing material.

The invention will be further illustrated by, but is not limited to, the following examples.

*Example I*

A gelatino-silver bromide emulsion was made by adding over a period of 88 minutes an aqueous solution of silver nitrate to an aqueous gelatin solution of magnesium bromide to provide a large grained emulsion, the magnesium bromide being present in sufficient quantity to provide bromide ions in an excess of 50% of that necessary to convert all of the silver to silver bromide. The precipitation was carried out under an Eastman Kodak No. 613 amber safelight. The temperature during precipitation was held at 150° F. The mixture was then cooled and a glycerine solution of stannous chloride in an amount to give 20 mol percent tin ion based on the silver halide was added. After digestion at 140° F. for 10 minutes the emulsion was cooled to coating temperature and diluted to the desired viscosity. The resulting emulsion, after the addition of the usual hardeners and coating aids, was coated on a paper support to give a dry coating weight of silver bromide of 30 mg. per square decimeter. The coated emulsion was dried in a conventional manner.

The coated material recorded an image at a writing speed of 20,000 inches/second using a 2,000-cycle/second signal and an amplitude of 3.2 inches.

Light development times and densities were determined from the step-wedge exposures using 40-watt white fluorescent light as the intensifying radiation. The image color is blue-gray on a light yellow background. The results are tabulated below.

| | |
|---|---|
| Exposure time | 10 microseconds. |
| Intensifying source | 40 watt white fluorescent light. |
| Illumination | 40 ft.-candles. |
| Steps visible | 10 |
| Background density | 0.20. |

The image appeared in 14 seconds.

*Example II*

A silver chlorobromide emulsion containing 13.5 mole percent chloride was made by slowly adding an aqueous solution of silver nitrate to an aqueous gelatin solution of potassium chloride and calcium bromide to provide a large grained emulsion. The calcium bromide was present in sufficient quantity to provide bromide ion in an excess of 25% of that necessary to convert all of the silver to silver bromide. The precipitation was carried out under Eastman Kodak No. 613 amber safelight. The temperature during precipitation was held at 120° F. The emulsion was ripened for 20 minutes at 120° F. Sufficient stannous chloride in a 3 N ammonium chloride aqueous solution was added to give 15 mole percent of stannous ion based on the silver halide. The pH was adjusted to 3.8 and the emulsion was coated on a paper support to give a coating weight of silver bromide of 40 mg. per square decimeter. Under the 10 microsecond exposure of Example I, 9 steps were visible after 60 seconds of light amplification with 40-watt white fluorescent light of 40 foot-candles intensity. The amplified image had good density and good stability. Heating the element to 120° C. during light amplification to the above light produced an image in 20 seconds and improved the image to background density ratio. A reflector photoflood lamp, G.E. Rfl. 2A, when used to amplify a heated sample containing a latent image could produce a visible image in 1 second.

*Example III*

Example II was repeated except that ammonium bromide was used in place of calcium bromide. The emulsion was made by slowly adding ammoniacal silver nitrate to the aqueous gelatin solution of the halide salts and the emulsion ripened for 20 minutes at 120° F. The sensitometric properties of the resulting coated material were similar to those of Example I.

*Example IV*

A silver chlorobromide precipitation in gelatin was carried out as described in Example III. After precipitation and ripening to obtain the desired grain size the emulsion was divided into 3 portions. To one (1) portion there was added 5.3 mole percent of stannous chlorde based on the silver halide in an aqueous solution. To a second (2) portion there was added 5.3 mole percent stannous chloride in ethanol. To a third (3) portion there was added 5.3 mole percent of stannous sulfate in water. Coatings were made of the emulsions and they were tested in a manner similar to that described in Example I. Coatings of all samples had sensitometric properties similar to those of Example I.

Other tin salts may be used in place of stannous chloride used in the above examples.

*Example V*

A silver bromide precipitation in gelatin was carried out as described in Example I. Four lots were prepared, two of which contained 5 mole percent excess bromide ion and two of which contained 50% excess bromide ion over that necessary to convert all of the silver to silver bromide. To one lot containing 5 mole percent excess bromide ion and one containing 50% excess bromide ion there was added 0.33 mole percent iodide ion in the form of potassium iodide. The emulsions were digested for 22½ minutes at 150° F. To each of the digested emulsions there was added a sufficient quantity of a 10% solution of stannous chloride in glycerine to provide a 10 mole percent, concentration of stannous ion based on silver. The pH was adjusted to 4.0 and the emulsion coated to a coating weight of 40 mg. per square decimeter.

Upon exposing the emulsions as described in Example I it was found that the emulsions containing excess bromide ion and iodide ions formed images from the $\sqrt{2}$ step wedge up to 13 steps for 5 mole percent excess bromide ion and 14 steps for 50 mole percent excess bromide ion. The emulsions containing 5 mole percent excess bromide and 50 mole percent excess bromide with the addition of iodide showed images at the 8th and 9th steps respectively. The images appeared on light development in about 14 seconds and showed good density with good image to background density ratio. The light development was at 40 foot-candles.

*Example VI*

A silver chlorobromide emulsion containing 104 mole percent chloride was made by slowly adding over a period of 20 minutes an aqueous solution of silver nitrate to an aqueous gelatin solution of magnesium chloride at 140° F. The resulting emulsion was held for 10 minutes at 140° F. and then there was added an aqueous solution of magnesium bromide in sufficient amount to provide bromide ion in an excess of 60% of that necessary to convert all of the silver to silver bromide. The precipitation was carried out under Eastman Kodak No. 613 amber safelight. After the addition of magnesium bromide the emulsion was digested for 60 minutes at 140° F.



The emulsion was then cooled until it gelled. The solid emulsion was noodled and washed in the conventional manner well known in the art. The washed emulsion was melted by warming to 140° F. and bulking gelatin sufficient to bring the total gelatin concentration to 300% based on silver bromide was added together with sufficient potassium bromide to provide an excess bromide concentration of 60 mole percent. A 50% glycerine solution of stannous chloride solution was added in an amount sufficient to give 20 mole percent of stannous ion based on the silver halide. Chrome alum was added as a hardener, the pH adjusted to 4.5 with sodium bicarbonate and the emulsion was coated on a paper support to give a coating weight of 30 milligrams of silver bromide per square decimeter.

Under a 10 microsecond exposure as described in Example I to 16 steps of a $\sqrt{2}$ step wedge were visible after 60 seconds of amplification under a 40-watt white fluorescent lamp at 40 foot-candles.

*Example VII*

A gelatino silver chlorobromide emulsion containing 104 mole percent chloride was made by adding over a period of 20 minutes at 140° F. an aqueous solution of silver nitrate to an aqueous gelatin solution of magnesium chloride and magnesium bromide. The halide salts were in a ratio of 51 parts of chloride to 1 part of bromide. The resulting emulsion was held at 140° F. for 10 minutes and then there was added an additional amount of magnesium bromide to give 60% excess bromide ion over that necessary to convert all of the silver to silver bromide. The emulsion was ripened at 140° F. for 10 minutes and dry gelatin was added to give a gelatin concentration of 300% based on silver bromide. The emulsion was cooled to the gel state, noodled and washed. After washing, the noodles were redispersed by warming to 140° F. Sufficient aqueous potassium bromide was added to provide a 60% excess of bromide ion over that necessary to react with all of the silver. A 50% glycerine solution of stannous chloride was added to provide 20 mole percent of stannous ion based on the silver halide. The pH was adjusted to 4.5 with sodium bicarbonate and the emulsion after the addition of hardener was coated on a paper support at a speed to give 30 milligrams per square decimeter of silver bromide.

Under a 10 microsecond exposure as described in Example I, 17 steps of a $\sqrt{2}$ step wedge became visible after 60 second light amplification with a 40-watt white fluorescent lamp at 40 foot-candles.

Stannous chloride may be used in aqueous solution but the tendency for these solutions to become cloudy due to the formation of precipitates of basic oxides on standing, especially in dilute concentrations, makes such solutions less desirable as compared to glycerine or sorbitol in which stannous chloride is very soluble, nevertheless, the cloudy aqueous solutions do give good results. The use of glycerine as a solvent also provides an easy means of adding an anticurl agent to the emulsion which is especially desirable in coatings on paper. Other soluble stannous salts may be used such as, for example, stannous sulfate. The action by stannous salts is not affected by the presence of excess bromide ions and in this respect the range of concentration of bromide ion is not critical. This is of considerable advantage compared with the prior art emulsions sensitized with sulfur sensitizers which are adversely affected by large amounts of excess bromide ions.

Where it is desired, other halides or combination of halides may be used to form the silver halide grains. For example, pure silver chloride may be used. Where soluble chloride salts are used it is desirable, because of solubility product differences, to form the silver halide grains of desired composition and size and then add sufficient soluble bromide salts to provide the desired concentration of excess bromide ions.

Other colloid carriers may be used in place of gelatin. For example, polyvinyl alcohol, polyvinyl acetals, water-soluble polyamides, polyvinyl pyrrolidone, celluose derivatives, polyacrylamides, etc., may be used alone or with gelatin.

Suitable supports for the novel silver halide emulsions and elements of this invention include the flexible supports used in the prior art for light-writing and oscillographic recording elements. In general the supports will be a photographic grade of paper that has a fair degree of opacity of which unsized, flexible paper is preferred. However, there can be used any opaque flexible material suitable for coating with a photographic colloid silver halide emulsion containing a large proportion of soluble salts.

The radiation-sensitive elements of this invention, in addition to being extremely convenient to use because of the elimination of wet-processing, also offer the outstanding advantage of high photographic speed. Dry processing allows the operator to see and use a print image rapidly after recording. Seismology, electrocardiograms, photocopying, X-ray recording and studio proof papers are fields in addition to oscillography where the novel light-sensitive elements of this invention may find utility.

I claim:

1. A light-developable, direct-writing, radiation-sensitive silver halide emulsion having average grain size in the range 0.1–10 microns in a water-permeable, organic, macromolecular colloid having protective colloid properties, said emulsion containing from 0.5 to 120 mole percent of a stannous salt based on the silver halide.

2. A photographic element comprising a flexible support bearing on at least one surface thereof a layer of a light-developable, direct-writing, radiation-sensitive silver halide emulsion having average grain size in the range 0.1–10 microns in a water-permeable, organic, macromolecular colloid having protective colloid properties, said emulsion containing from 0.5 to 120 mole percent of a stannous salt based on the silver halide.



3. A photographic element as defined in claim 2 wherein said support is paper.

4. A photographic element as defined in claim 2 wherein said support is paper and said stannous salt is present in an amount of 5 to 40 mole percent based on the silver halide.

5. A photographic element as set forth in claim 4 wherein said stannous salt is stannous chloride.

6. A photographic element as defined in claim 4 wherein said emulsion layer is a gelatino-silver bromide emulsion layer and said stannous salt is stannous chloride.

7. A process for improving the background density of a localized radiation-exposed, light-developable, direct-writing, radiation-sensitive photographic element having a support bearing a layer of a photographic silver halide emulsion containing from 0.5 to 120 mole percent of a stannous salt based on the silver halide, characterized by heating the exposed element to a temperature of at least 200° F. but below the decomposition temperature of the element, and then developing the image by overall exposure of said layer to radiation of wavelength in the range 350 to 700 millimicrons, for 0.2 to about 15 seconds, while maintaining said temperature for at least part of the light-development step.

8. A process as set forth in claim 7 wherein said support is paper and then heating it to a temperature from 250° F. to 280° F.

9. A process as set forth in claim 7 wherein said emulsion is a gelatino-silver bromide emulsion.

10. A process as set forth in claim 7 wherein said stannous salt is stannous chloride.

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