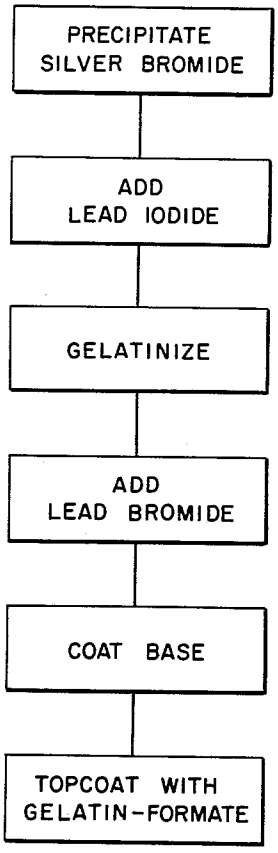
June 19, 1962 T. A. SCOTT 3,039,871

PHOTOGRAPHIC COMPOSITION

Filed March 2, 1961



INVENTOR.
TROY A. SCOTT
BY Frederick E. Lange
ATTORNEY

United States Patent Office 3,039,871 Patented June 19, 1962

3,039,871

PHOTOGRAPHIC COMPOSITION

Troy A. Scott, Minnetonka Village, Minn., assignor to Minneapolis-Honeywell Regulator Company, Minneapolis, Minn., a corporation of Delaware

Filed Mar. 2, 1961, Ser. No. 93,289
8 Claims. (Cl. 96—85)

The present application is a continuation-in-part of my copending application Serial Number 75,338, filed December 12, 1960, entitled Photographic Composition, and assigned to the same assignee as the present application.

The present invention relates broadly to photographic sensitive films and more particularly to photographic films of the "print-out" type. The term "print-out" for purposes of this discussion refers to that type of photosensitive substance upon which a latent or visible image is obtained after an initial exposure to light or electromagnetic radiation of relatively high intensity; a fairly permanent visible image being obtained from the initial exposure or simply by exposing the photosensitive substance to a lower intensity radiation. This additional exposure is known as "latensification" and is general in its application, including exposing the area upon which the initial image was formed as well as the surrounding background area to the lower intensity radiation. "Print-out" emulsions are distinguished from development emulsions which require a development treatment by wet chemical methods after initial exposure in order to produce a distinct, stable contrast between the background and the image of the exposure. The "print-out" coatings comprising a dispersion or emulsion of the composition of the present invention, are particularly sensitive to a high intensity beam of light or other electromagnetic energy of either visible or invisible wave length radiated across a portion of the area of the film. While the material of the present invention is particularly sensitive to such exposure, the background or non-exposed area is sufficiently insensitive to lower intensity radiation to render a highly contrasting image upon subsequent latensification. Of course, the intensity of the light of the initial exposure may be of various intensities dependent on the writing speed desired. High intensity will produce a trace at both high and low speed while lower intensities result in lower maximum speeds. The initial exposure intensity will be higher than that used to latensify.

The film of the present invention provides a high degree of sensitivity to a high intensity light source coupled with a lower degree of sensitivity to lower intensity light sources. This combination produces a maximum contrast between the image produced by the higher intensity trace light and the background when applied to recording operations such as oscillographic recording and the like. In addition, the present invention provides a photosensitive "print-out" film which may be developed by latensification or more conventional wet chemical techniques.

The present invention provides these advantages through the use of a combination of two halides of lead in conjunction with silver bromide. A top coat composed of a formate will further enhance the contrast and stability of the trace and background.

"Print-out" films have recently received renewed interest due to their desirable properties for high speed recordings such as oscillographic recording and the like. These papers possess a desired property of producing an image without resort to wet chemical techniques. However, the "print-out" papers of the prior art have not proved entirely satisfactory for use on recording devices for a number of reasons. In a pending application of John F. Byrne Serial Number 64,192, filed October 21,

1960, entitled Photographic Compositions, and assigned to the same assignee as the present invention there is disclosed a "print-out" emulsion which utilizes lead iodide or lead bromide as a sensitizing agent for the silver halide. The "print-out" emulsion of the Byrne application constitutes an improvement over the formulations of the prior art in that higher writing speeds are possible and a better contrast of the trace and background are produced by this emulsion. While the emulsion of the Byrne application is an improvement over prior art formulations, the present invention provides specific compositions which possess certain useful properties not taught by the Byrne application.

The present invention is based upon the use of lead iodide and lead bromide as doping agents in conjunction with silver bromide. In addition, the use of a solution of sodium formate, applied as a top coat over the primary silver bromide emulsion, considerably improves the trace stability. Although the formate top coat causes a darkening of the background, it also increases trace density so that overall contrast is approximately maintained. The essential function of the formate top coat is to prevent rapid fading of the trace upon extended exposure to ambient light.

Gelatin or the like is desirable in the formulation of "print-out" emulsions when it is desired that the trace be developable either by latensification or by wet chemical techniques. It is sometimes desirable to maintain the trace as a permanent record. While latensification provides a reasonably long storage life, there is a tendency to lose contrast of background and trace on prolonged exposure to ambient lighting. Chemical treatment of the trace and background is thus desirable in those instances where a permanent record is wanted. In the present emulsion, chemical treatment may be utilized directly following the recording operation or it may be used after latensification by exposure to a lower intensity light.

I have found that the two halides of lead noted above may be advantageously employed together to produce an emulsion having the desirable properties for use in high or low speed recording. When gelatin is used as a binding agent, the use of lead iodide alone as a doping agent provides a high sensitivity to a high intensity light beam although the contrast between the trace so formed and the background is not as satisfactory as in my formulation. When other binders, such as starch, are used, this is also the case, although the effect is not so pronounced. A further disadvantage in the use of lead iodide as the sole doping agent in a gelatin system is the loss of sensitivity on storage (i.e. poor shelf life).

Use of lead bromide alone as a doping material in conjunction with gelatin base photographic emulsions results in a background which is stable to ambient light. However, the trace formed by high intensity light is less stable with lead bromide than in the instance where lead iodide is the doping material. Further, the use of lead bromide is not as effective as lead iodide as a sensitizing agent. Thus, when lead bromide is used as a sole doping agent a considerable loss of recording speed results. Lead iodide alone produces a dark trace line; however, the background on initial latensification is dark and tends to darken even further on prolonged exposure to ambient light.

I have found that by proper blending of the two doping materials, lead bromide and lead iodide, the advantages of each may be realized. That is, the high sensitivity produced by the use of lead iodide as well as the storage stability and background suppression available from use of lead bromide are realized.

Accordingly it is an object of the present invention to

provide improved "print-out" sensitive coating compositions which possess both a high degree of sensitivity to a high intensity light source along a portion thereof together with a high degree of background stability upon general latensification by a lower intensity source.

It is a further object of the present invention to provide "print-out" sensitive coating compositions which may be developed both through latensification exposure to a lower intensity and/or an emulsion which may be developed by wet chemical techniques.

Other and further objects will become apparent to those skilled in the art upon a study of the following specification, appended claims, and accompanying drawings wherein:

FIGURE 1 is a flow chart of the process used in the preparation of a photosensitive dispersion of the present invention.

The present invention utilizes halides of lead as doping materials for the purpose of both sensitizing silver-bromide or silver bromo-iodide to high intensity light and further, utilizes the lead halide also as a means of suppressing background. By lead halide is meant the bromide and iodide; the fluoride and chloride are specifically excluded.

The exact mechanism involved in the reaction is not completely understood. The general mechanism can be explained through the understanding of the relative degrees of sensitization available through the use of the iodide versus the bromide. The iodide provides the necessary doping material for providing the extreme sensitivity desirable in emulsions of this type. The bromide likewise provides a sensitizing agent; however, the degree of sensitization is considerably less. The degree of sensitivity of lead bromide doped emulsions to ordinary ambient light is considerably less than that with the iodide as the sole doping material. This property of the lead bromide at low intensity when combined with the high sensitivity produced by lead iodide at high intensity yields the improvement possible with the present invention. That is, the lead bromide complements the lead iodide as a doping material to produce an emulsion showing maximum contrast of trace and background.

Referring now to the lead halide additions, the relative proportions of the lead halides added to the silver halides has been found to be significantly beneficial only if held within certain limits. This is particularly true in the instance of the relative proportions of the quantity of lead iodide versus the quantity of lead bromide. Likewise, the over-all proportion in regards to the silver halide is also important in providing a paper of desirable sensitivity and background stability. The general range of compositions found to be beneficial in the invention comprises 100 parts by weight of silver bromide or silver bromo-iodide, .5 to 5 parts by weight of lead iodide and from 5 to about 30 parts by weight of lead bromide. The range of compositions of the active ingredients may be varied over considerably wider composition ranges than those indicated above. However, as a practical matter the upper and lower limits of compositions as defined above provide the most useful paper. Stated another way, the sensitivity and degree of stability of the background is not a precise matter. In compositions having in excess of 30% lead bromide or less than 5% lead bromide the effect is not appreciable. In the preferred form of the invention the composition will consist of 20 parts by weight of lead bromide, 100 parts by weight of silver bromide or silver bromo-iodide, and one part by weight of lead iodide. This formulation provides the greatest contrast of the background with the trace. The degree of contrast of the trace and background decreases as the composition limits are varied from the optimum concentration of the preferred form of the invention. The decrease of contrast is not a lineal decrease but one which accelerates with the deviation from the optimum composition. Therefore, while compositions outside the indicated ranges will provide a "print-out" emulsion capable of showing a trace, a useful commercial contrast will only be provided by compositions within the above indicated limits.

In accordance with the present invention it has been found that silver bromide provides the basic photosensitive ingredient for the preferred form of the invention. However, it has been found that co-precipitated silver iodide when present in amounts up to 1% by weight of the silver bromide is not detrimental. When present in a quantity in excess of 1% the silver iodide tends to have a negative effect on the performance properties of the emulsion. That is, when silver iodide is present in quantities over 1% by weight the contrast between the trace produced by a high intensity beam and the background by latensification is less marked than in the absence of silver iodide.

Various carriers or binders, and particularly organic colloid carriers, may be employed in order to facilitate application and adhesion of the sensitive composition to paper in dispersion or emulsion form. The preferred form of the invention utilizes a gelatin as the predominant binding agent although it has been found that small quantities of a material such as hydroxyethyl starch aid as a suspension agent during formulation. The use of the gelatin has been discussed above for its desirability as an agent for use both in paper which may be developed by latensification as well as for paper that may be developed by chemical means. The use of gelatin in the emulsion particularly requires the combination of the lead bromide in addition to the iodide as a doping material.

Among the various supports one may employ almost any material which does not react with the active ingredients. Various plastics or glass may be used. Conventional photographic base papers may be conveniently utilized. I have found a photographic base paper, baryta coated 80 gram glossy paper such as supplied by Allied Paper Company of Kalamazoo, Michigan, is particularly suitable for this purpose.

For exposure and latensification, the sensitivity of the emulsion is found to be below about 5,000 angstroms and maximum sensitivity below about 4,000 angstroms. Various commercially available light sources may be conveniently employed for producing the trace image. When maximum speed is desired I have found that the Osram lamp manufactured by Osram, Munich, West Germany, as hereinafter identified in Example 1 is particularly well suited as a light source. Although lower intensity sources may be satisfactorily utilized, these sources may require substantially higher total energies inasmuch as the material exhibits a low intensity reciprocity failure.

While the sensitive films are particularly sensitive to radiations of relatively high intensity they are also suitable for use at lower intensities, with a corresponding drop in writing speed. For latensification, a less intense source of light available generally across the extent of the paper is desired. Ordinary fluorescent lighting at close range is useful both in its intensity and its output wave length characteristics. For example, latensification may be carried out under the influence of illumination of the order of 50 foot candles of "cool-white" fluorescent light.

In order to more particularly set out the features of the present invention, specific examples of preparation are presented herein:

EXAMPLE 1

The following solutions and materials were prepared as basic constituents to be blended.

(1) 300 ml. concentrated ammonium hydroxide (28% NH_3)

(2) 273 grams silver nitrate dissolved in 450 ml. of water

(3) 228 grams of potassium bromide dissolved in 450 ml. of water

(4) 3 grams of lead iodide

(5) 90 grams of 4% Penford Gum #300

(6) 45 grams gelatin—Kind and Knox G72 (Kind and Knox Gelatin Company of Camden, New Jersey)
(7) 49 grams of gelatin—Kind and Knox G72
(8) 60 grams of lead bromide

The order of addition given hereinbelow provides the best overall properties. Variation in the order of addition will also yield a useful composition, although the properties will be generally less satisfactory.

The Penford Gum referred to above is a hydroxyethyl starch material. I have found that the hydroxyethyl starch obtained from Penick and Ford, Limited, of Sioux City, Iowa, under their designation Penford Gum #300 is quite satisfactory for purposes of the invention.

The actual compounding of the constituents is as follows:

Heat (3) above to 50° C. Add (1) to (2) and without cooling add the combined solutions to (3) through capillary tubing. Capillary tubing should be of such size as to provide the addition over a period of from five to ten minutes. During the addition, the mixture should be stirred vigorously. Allow the precipitate to settle and then decant, wash twice with 1,500 ml. of distilled water, each wash followed by decantation.

While stirring the washed mixture, sprinkle in (4). When (4) has been thoroughly mixed in, add (5). Stir for two to three minutes. Following this addition cycle the mixture through an Eppenbach colloid mill for five minutes at a gap setting of ten. I have found that the colloid mill manufactured by Eppenbach under their model designation QV–6–3 is satisfactory for the purpose of the invention. The gap setting of ten is approximately .010 inch.

The mill is then discharged and rinsed to remove any retained solids. While stirring, sprinkle in (6). Digest with stirring for 30 minutes at 50° C. Cool with continued stirring until the solution gels. Store the resultant gel over night at four to five degrees C.

Following the storage period, shred the gel and wash with cold distilled water until a Nessler test of the wash water shows less than four p.p.m. of ammonia. Use two to three liters of water per wash and keep the temperature during the washing below 2° C.

Melt the gel by gradually increasing the temperature and add water to bring the total weight to 1125 grams. Continue heating until the solution temperature reaches 50° C. and then sprinkle in (7). Digest 15 minutes with continued stirring at 50° C. Sprinkle in (8) and continue stirring at 50° C. for 15 additional minutes. The mix is then cycled through a colloid mill for five minutes at a gap setting of ten. The colloid mill is then discharged and the resulting mix cooled with stirring until gelling appears. Store this mix at four to five degrees C.

All of the above operations should be performed under yellow light. I have found that the General Electric 25 watt yellow bug lamp located at least five feet from the work is satisfactory.

Coating of Emulsion

The emulsion may be coated on a suitable paper using a wire-wound rod as a control of thickness means. I have found that a suitable paper is 80 gram baryta paper. The wire-wound rod may advantageously be that supplied by the R.D. Specialties Company under their designation No. 20. Rod number may be varied to produce heavier or lighter coatings. Saponin may be added to the emulsion to produce smoother coatings. Chrome alum may be added as a hardener. The emulsion may be diluted with distilled water to lower the viscosity. The coating is then allowed to air dry.

Topcoat Formulation and Coating

The following materials are used in the formulation of the topcoat:

(1) Sodium formate	grams	105
(2) Gelatin—Kind and Knox G72	do	50
(3) Distilled water	liters	1

The gelatin is dissolved in the distilled water and the sodium formate dissolved into the resulting solution at 40° C. This solution is then applied with a RDS Laboratory rod No. 10 over the light sensitive coating above. Although the above composition is believed to be the most desirable, I have found that equivalent results can be obtained when the quantity of sodium formate is within the range of from 5 to 15% by weight. Others formates than sodium may also be used, for example, potassium or ammonium.

A sensitive material prepared in accordance with the above example was light yellow in color and upon desired exposure to light, a uniform dark brown image or trace was obtained. Sensitive papers prepared in accordance with the above example were determined, by extrapolation, to be capable of writing speeds exceeding 100,000 lineal inches per second when illuminated from a source having the intensity of about 10^8 erg/sec./cm.^{2}. Such a source is obtainable from a high pressure mercury vapor lamp such as the Osram lamp manufactured by Osram, Munich, West Germany, and identified as their model HBO–107/1, high pressure mercury lamp. A high proportion of this radiation is in the ultraviolet. A suitable lens system may be used to focus the light to the desired intensity and beam width.

EXAMPLE 2

The procedural steps in Example 1 were followed with the differences being the quantity of additives used. In this example, item 4 of the materials used in the preparation of the emulsion, lead iodide, was 1.5 grams rather than the three grams of the preferred form of Example 1. This emulsion produced a lighter background than Example 1, but also a lighter and less stable trace. The speed of this paper is also slightly less than that of Example 1.

EXAMPLE 3

Preparation in this case was the same as in Example 1 with the exception of item 4, the addition of lead iodide. In this example, 15 grams of lead iodide was used rather than the 3 grams of Example 1. This emulsion and paper produced a somewhat darker and more stable trace on exposure to high intensity light, but the background was also considerably darker than in Example 1.

EXAMPLE 4

The preparation is the same as in Example 1 with the exception that item 8 lead bromide, consisted of an addition of 15 grams rather than the 60 grams of Example 1. A paper produced in this manner had a darker and more stable trace but the background became much darker on latensification than was the case in Example 1.

EXAMPLE 5

Preparation was again the same as in Example 1 with the exception that item 8 consisted of an addition of 90 grams of lead bromide. The paper prepared with this formulation resulted in a trace which was lighter and less stable than that of Example 1, although the background was also somewhat lighter than that of Example 1.

Reference has been made above to the chemical development of the paper as an alternative to latensification as a means of "printing-out" or as a means of making more permanent a latensified trace. As has been noted when a permanent record is desired it is desirable to utilize chemical treatment rather than latensification alone. For chemical treating I have found that Kodak Linagraph Permanizing Solution at normal strength is suitable. The paper is developed for 2½ to 3 minutes at 100° F. The paper is then rinsed for 5 to 10 seconds in an acid rinse bath (Kodak SB–1) and then fixed for 5 minutes in Kodak Solution F–5. Following this treatment the paper is washed thoroughly for at least 30 minutes in cold running tap water.

I claim as my invention:

1. A photographic print-out composition comprising a precipitated silver bromide, said silver bromide being doped by having homogeneously dispersed therein a mixture of lead iodide and lead bromide, the AgBr, PbI_2, and $PbBr_2$ being present in a ratio of 100:1:20 in parts by weight.

2. A photosensitive print-out composition comprising a precipitated silver bromide, lead iodide, and lead bromide, the composition being further characterized in that the silver bromide comprises 100 parts by weight, the lead iodide from .5 up to about 5 parts by weight, and the lead bromide from 5 to 30 parts by weight.

3. A photographic print-out composition comprising organic carrier having dispersed therein a photosensitive substance, said substance consisting essentially of 100 parts by weight of a precipitated silver bromide, from about 5 up to about 30 parts by weight of lead bromide, and from about .5 to about 5.0 parts by weight of lead iodide.

4. A photographic print-out sheet material comprising a support member, a coating of an emulsion of gelatin and a photosensitive substance, said photosensitive substance consisting essentially of 100 parts by weight of a precipitated silver bromide, said silver bromide doped by addition of from about .5 up to about 5 parts by weight lead iodide and from about 5 up to about 30 parts by weight of lead bromide, said emulsion coated with a second emulsion consisting of from about 5 up to about 15% by weight of alkali metal formate in a gelatin.

5. A photographic print-out sheet material comprising a support member, a coating of an emulsion of gelatin and a photosensitive substance consisting essentially of 100 parts by weight of a precipitated silver bromide, said silver bromide being doped by addition of from about .5 up to about 5 parts by weight of lead iodide and from about 5 up to about 30 parts by weight of lead bromide.

6. A photographic print-out paper comprising an inert base paper, a coating of an emulsion of gelatin and a photosensitive substance, said photosensitive substance consisting essentially of 100 parts by weight of a precipitated silver bromide, said silver bromide being doped by an addition of 1 part by weight of lead iodide and 20 parts by weight lead bromide, said emulsion coated with a second emulsion consisting of 10 parts by weight of sodium formate in a gelatin.

7. A process for the production of photographic print-out paper including a support element coated with inert colloid carrier having dispersed therein a photosensitive substance consisting mainly of silver bromide with lead iodide and lead bromide dispersed therein, and topcoated with an alkali formate in a colloid carrier, said process comprising formulating a photosensitive substance by precipitating an amount equal to 100 parts by weight silver bromide, dispersing therein lead iodide in an amount equal to from about .5 up to about 5 parts by weight, gelatinizing the mixture and adding thereto from about 5 up to about 30 parts by weight of lead bromide, coating said support element with said photosensitive substance, formulating a topcoat substance by dissolving from about 5 up to about 15% by weight of an alkali metal formate in a gelatin solution, coating said photosensitive substance with said topcoat substance.

8. A process for the production of photographic print-out paper including a support element coated with an inert colloid carrier having dispersed therein a photosensitive substance consisting mainly of silver bromide with lead bromide and lead iodide dispersed therein, said process comprising formulating a photosensiitve substance by precipitating an amount equal to 100 parts by weight of silver bromide, dispersing therein from .5 up to 5 parts by weight lead iodide, gelatinizing the mixture by adding thereto from about 5 up to about 30 parts by weight of lead bromide, and coating said photosensitive substance.

No references cited.