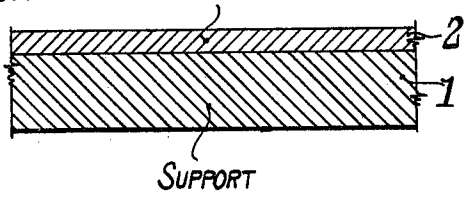
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PRINT-OUT EMULSION

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PRINT-OUT EMULSION FORMED OF SILVER HYDROXIDE-ORGANIC ALKALI COMPLEX AND A HALIDE IN GELATINE OR CELLULOSE ACETATE PHTHALATE



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PRINT-OUT EMULSION

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This invention relates to photographic material and more particularly to a photographic emulsion, of the type known as print-out emulsions, having increased sensitivity of light.

There are two types of commonly used photographic sensitive emulsions, known respectively as developing emulsions and print-out emulsions. The former class includes most of the materials used for making negatives in the camera, and lantern slides, and the printing papers known as developing out papers. They are characterized in that the action of the light during normal exposure does not produce a visible image. The image is rendered visible by treatment with a solution known as a developer. In the case of print-out emulsions a visible image is produced directly by the action of light. It is to emulsions of this character that the present invention applies; and specifically to those in which the light-sensitive element is a compound of silver.

Print-out emulsions are usually prepared by the precipitation in a colloidal medium of a halide of silver, usually the chloride, by interaction of a solution of a soluble halide with a solution of a soluble compound of silver. In the case of print-out emulsions of silver chloride, the silver chloride is usually precipitated in such a way that the final product contains an excess of soluble silver compound, for instance, silver nitrate, the silver salt of an organic acid, such as silver citrate or silver tartrate together with some of the free organic acid. The emulsions are not washed after precipitation. Print-out emulsions of silver bromide may be prepared similarly, but give a generally weaker image of a blue color. In many cases the silver nitrate used for precipitating the silver halide is compounded with ammonia so as to give a solution of silver ammonium nitrate.

It is known that the sensitivity to light of print-out emulsions may be increased by the addition of halogen absorbers, such as soluble nitrites, and alkaline materials such as borax, sodium hydroxide, ammonium hydroxide, and organic alkalies such as pyridine or amines.

Photographic emulsions made by precipitating silver bromide in the presence of a colloidal medium such as gelatine by the interaction of silver ammonium nitrate and potassium bromide are old in the art. These are formed by precipitating silver hydroxide with ammonia from a silver nitrate solution, dissolving the precipitate in a further quantity of ammonia and reacting the compound thus formed with potassium bromide in the presence of a gelatine medium.

It is an object of this invention to provide a photographic print-out emulsion having increased sensitivity to light. It is a further object to provide novel carrying media for the sensitive silver salt to replace gelatine. It is a still further object to provide a method for incorporating the sensitive material in the carrier.

The increase in sensitivity according to this invention is accomplished by the use of a complex solution of silver hydroxide in an organic alkali such as pyridine. The complex solution containing the organic alkali is then used for the precipitation of silver bromide by the use of an alkaline bromide such as potassium bromide. In methods previously used a silver halide was first formed in the presence of gelatine and the material for producing increased sensitivity, such as an organic alkali was added later.

We have found that if the silver hydroxide precipitated with ammonia from a silver nitrate solution is dissolved in an organic base instead of ammonia and the salt thus formed mixed with a carrier such as gelatine and reacted with a halide such as potassium bromide, a compound results which has greatly increased sensitivity and photographic speed. We have also found that the addition of a further quantity of silver nitrate, either before or after the precipitation of the sensitive salt with the halide, results in a further increase of sensitivity. The addition of sodium nitrite at any stage in the preparation of the sensitive salt, either before or after its precipitation with the halide, also produces an increase in sensitivity.

While the sensitive salt formed in this way is essentially a silver halide, it is to be understood that we do not limit our invention to halides alone. The reactions which occur during the formation of the sensitive salt are varied and complex, and the formulas of the compounds formed cannot be stated with certainty. The occurrence of novel reactions is indicated by the improved products which we obtain.

The following is an example of a method of preparing our emulsions:

Three solutions are formed—

Solution A is formed by dissolving 375 grams of silver nitrate in 1125 cc. of water. To this is added 75 cc. of ammonium hydroxide (28% concentration). A precipitate of silver hydroxide is formed which is redissolved by adding 500 cc. of pyridine. To this solution is added 2,000 cc. of water.

Solution B consists of 300 grams of potassium

bromide and 37.5 grams of potassium iodide in 2945 cc. of water.

Solution C consists of 570 grams of gelatine in 6500 cc. of water.

These solutions are treated as follows:

To A add about one-half of the gelatine mixture C, both at 60° C. The balance of the gelatine mixture C is added to the halide solution B. The mixture AC and BC thus formed are poured together alternately. The temperature at which this mixing takes place should preferably be 60° C., although equally satisfactory results may be obtained at a temperature as low as 40° C. To further increase the sensitivity 180 grams of silver nitrate dissolved in 750 cc. of salt is added and the temperature brought to 60° C. The mixture is held in this temperature for one-half hour with occasional stirring and a solution of 375 grams of sodium nitrite in 375 cc. of water is added and the temperature brought to 60° C. The emulsion thus formed may be coated on the paper at once or may be chilled to be remelted and coated later.

Among the organic bases or alkalies, which may be used to dissolve the silver hydroxide precipitate, are the amines, such as methylamine, benzylamine, naphthylamine and triethanolamine; heterocyclic nitrogen bases such as pyridine, piperidine, quinoline (in methyl alcohol) and acridine (in methyl alcohol) and α-picoline; amides such as acetamide. As halides, it has been found that both potassium bromide and potassium chloride or mixtures of these two, with or without potassium iodide, are satisfactory.

We have further found that the gelatine may be replaced by mixed esters of cellulose, such as cellulose acetate phthalate. Cellulose acetate phthalate is soluble in aqueous alkali solution but insoluble in aqueous acid solution. For this reason it is desirable to dissolve the cellulose acetate phthalate in organic solvents. When using cellulose acetate phthalate in organic solvents the alkali halides which are reacted with the basic silver complex to form a sensitive salt are not soluble in many of the solvents which it is desirable to use. We have found that the halides, such as potassium bromide, may be replaced by bromacetic acid or other halogenated aliphatic acids or with other bromide or halide substituted compounds, such as bromo-esters. The following example illustrates a method of forming an emulsion according to this process:

Three solutions are formed:

Solution A is formed by dissolving 25 grams of silver nitrate in 50 cc. of water, adding 5 cc. of ammonium hydroxide (28% concentration), and redissolving the silver halide precipitate by adding 40 cc. of pyridine.

Solution B consists of 24 grams of bromacetic acid in 25 cc. of water.

Solution C consists of 500 cc. of cellulose acetate phthalate in a solvent such as acetone, ethyl alcohol, cellosolve or methyl cellosolve acetate.

The emulsion is formed as follows:

To solution A is added about one-half of the cellulose acetate phthalate solution C.

The bromacetic acid solution B is added to the remainder of C. Mixtures AC and BC are then mixed with stirring. This entire process may be carried out at room temperature or about 20 to 25° C. The mixture is then coated on the paper.

A material sensitized with our emulsion is shown in the single figure of the drawing in which 1 is a paper or other base which supports the emulsion and 2 is the sensitized emulsion formed according to our process.

The emulsions produced by our process are approximately 50 to 100 times the sensitivity of ordinary print-out paper. They have good contrast. It has been found that two minutes exposure at ten foot candles is adequate to give a definite color. This sensitivity is sufficient to enable prints to be made with incandescent tungsten light or by very much shorter exposure to sunlight than is at present possible.

It is to be understood that we are not limited to the specific compounds and methods of procedure outlined in the specification, but that these are given only for example. Our invention comprises all modifications and equivalents coming within the terms of the appended claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in an organic alkali, mixing the solution with an inert carrier therefor, and adding an alkali metal halide to the mixture.

2. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in a heterocyclic nitrogen base, mixing the solution with an inert carrier therefor, and adding an alkali metal halide to the mixture.

3. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in an amine, mixing the solution with an inert carrier therefor, and adding an alkali metal halide to the mixture.

4. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in an organic alkali, mixing the solution with a solution of cellulose acetate phthalate, and adding an alkali metal halide to the mixture.

5. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in a heterocyclic nitrogen base, mixing the solution with a solution of cellulose acetate phthalate, and adding an alkali metal halide to the mixture.

6. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in an amine, mixing the solution with a solution of cellulose acetate phthalate, and adding an alkali metal halide to the mixture.

7. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in an organic alkali, mixing the solution with a solution of cellulose acetate phthalate, and adding a solution of bromacetic acid to the mixture.

8. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in a heterocyclic nitrogen base, mixing the solution with a solution of cellulose acetate phthalate, and adding a solution of bromacetic acid to the mixture.

9. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in an amine, mixing the solution with a solution of cellulose acetate phthalate, and

adding a solution of bromacetic acid to the mixture.

10. In the production of light-sensitive emulsions, the step of mixing a halogenated aliphatic acid with a silver salt to form a light-sensitive silver halide.

11. In the production of light-sensitive emulsions, the step of mixing bromacetic acid with a silver salt to form a light-sensitive silver bromide.

12. A process of producing a light-sensitive emulsion which comprises precipitating silver hydroxide in an aqueous solution, dissolving the precipitate in an organic alkali, mixing the solution with an inert carrier therefor, adding an alkali metal halide to the mixture, and thereafter adding sodium nitrite to the mixture to increase the sensitivity.

13. A light-sensitive surface comprising the product resulting from the reaction of a complex solution of silver hydroxide in organic alkali, on an alkali halide in the presence of a carrier.

14. A light-sensitive surface comprising the product resulting from the reaction of a complex solution of silver hydroxide in a heterocyclic nitrogen base, on an alkali halide in the presence of a carrier.

15. A light-sensitive surface comprising the product resulting from the reaction of a complex solution of silver hydroxide in an amine, on an alkali halide in the presence of a carrier.

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