

UNITED STATES PATENT OFFICE

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PREPARATION OF PHOTOSENSITIVE PHOTOGRAPHIC EMULSIONS

No Drawing. Application filed August 11, 1928, Serial No. 299,115, and in Germany August 19, 1927.

The present invention relates to a process for increasing the photosensitiveness of photographic emulsions containing, as photosensitive substances, mercuric oxalate or its complex amine compounds which are to be regarded as equivalents for the purpose of the present invention.

We have found that the sensitiveness to light of such emulsions is increased if sensitizing agents, especially inorganic metallic salts or organic dyestuffs, be generated in or added to the emulsions. Typical sensitizing agents, which may be advantageously used either alone or conjointly, are the salts of the heavy metals, especially of silver, thallium, gold, platinum and the like, also dyestuffs such as eosine, erythrosine and many other dyestuffs commonly used in photography.

The photographic emulsions prepared according to this invention may be used in the manufacture of printing out papers, and also of papers to be developed after copying until the image is partially visible as well as of papers similar to the usual gas light or bromide papers.

In order to use the said emulsions in the manufacture of printing out papers, the rate of direct darkening can be increased by incorporating from 1 to 3 per cent by weight of mercuric iodid and, if required, of small amounts of silver nitrate, with the emulsion. The silver nitrate may be added, for example, to the finished photosensitive substance, or also after the film has been poured out, by immersion in a bath of dilute silver nitrate solution, as for example of 1 per cent strength. This method furnishes a printing out paper which is two to three times as sensitive as a highly sensitive, glossy celloidin paper.

By altering the conditions of working, the sensitiveness may also be influenced in such a manner as to furnish an emulsion which furnishes a slightly visible image already in the printing out stage, the said image being then developed. This method of reproduction has the great advantage that the appearance of the image can be observed in the printing frame.

To enable these emulsions to be used in de-

veloping processes as usual for gas-light or bromide papers, the production and developing of the latent image may be facilitated by the presence of mercuric iodid and small amounts of silver iodid in the emulsion. The proportion of mercuric iodid is preferably between 0.5 and 2 per cent by weight of the other mercuric salt employed with only very small amounts as for example about 0.05 to 0.2 per cent of silver iodid. The latent image of these emulsions may be developed with a metol hydroquinone developer diluted to about 1/3rd to 1/5th of the strength at which it is generally used for photographic plates. The action of the developer is arrested by immersion in a bath of dilute acetic acid containing potassium metabisulfite. The prints are fixed in a 15 to 20 per cent solution of ammonium thiosulphate or sodium thiosulphate, which also contains potassium metabisulfite, the fixing taking from 20 to 30 minutes. After washing, the pictures can be toned in the same way as silver prints, brownish tones, for example, being obtained with uranyl nitrate and potassium ferricyanid. Brown tones may also be obtained, for example, by adding tannin, or organic substances with a similar action, to the emulsion or developer.

The following examples will further illustrate the nature of the said invention which however is not limited thereto. The parts where not otherwise stated are by weight. In so far as in the following examples reference is made to parts by weight and parts by volume, it is to be understood that these expressions refer for example to metric tons and cubicmeters, or kilograms and liters respectively.

Example 1

27 parts of mercuric chlorid in hot saturated solution are precipitated with 17 parts of potassium carbonate and 2 parts of potassium iodid dissolved in 100 parts of water, and the product is washed by decanting four times or by centrifuging. It is then treated with 15 parts of oxalic acid dissolved in 150 parts of distilled water and warmed for a short time on the water bath, whereby

the brown product formed at first is converted into the pure white oxalate. This is again washed, and then treated with 20 parts by volume of concentrated ammonia solution, warmed on the water bath for 10 to 20 minutes, rewashed, and finally after, if required, being sensitized with erythrosine (see Schultz, "Farbstofftabellen" 5th Edn. 1914, No. 591/3) suspended in 200 to 300 parts of a 10 per cent solution of gelatin. This method furnishes an excellent emulsion for printing out paper.

Example 2

27 parts of mercuric chlorid in hot saturated solution are precipitated with 17 parts of potassium carbonate dissolved in 100 parts of water. The precipitate is treated, up to the amine stage, as in Example 1, washed three times by decantation and treated with 10 parts by volume of $n/20$ potassium iodid solution, 9 parts by volume of $n/20$ silver nitrate solution and a few drops of ammonia, then warmed for several minutes on the water bath and decanted twice, being finally suspended in from about 200 to 250 parts by volume of a 10 per cent solution of gelatin. The product is a very good developing emulsion.

Example 3

27 parts of mercuric chlorid in hot saturated solution are precipitated with 17 parts of potassium carbonate and 0.5 part of potassium iodid dissolved in 100 parts of water and the precipitate is converted into oxalate in the manner described in Example 1. After washing, 15 parts by volume of $n/20$ potassium iodid solution, and 14 parts by volume of $n/20$ silver nitrate solution are added in quick succession, followed by 20 parts by volume of concentrated ammonia solution. The whole is warmed for 20 minutes on the water bath, at a temperature which must not exceed 60° C. After washing and suspending in 200 to 300 parts of a 10 per cent solution of gelatin, the emulsion, which is suitable for use in the developing process is ready for pouring.

Example 4

20 parts of mercuric nitrate are dissolved at from 60° to 80° C. in 2000 parts of water whereupon, after filtering off the basic mercury salt from the solution, 10 parts by volume of a $n/20$ silver nitrate solution are added to the latter. After heating the mixture to 85° C. a solution of 12 parts of oxalic acid and 0.4 part of potassium iodid in 120 parts of water is poured into it in the course of 10 seconds while actively shaking. The precipitate obtained hereby is then washed for from 3 to 4 times and, after adding 13.6 parts of a solution of ammonia (spec. gravity 0.91), warmed for 20 minutes at 60° C. After

washing again for from 3 to 4 times the precipitate is emulsified in 80 parts by volume of a 15 per cent solution of gelatin. By an addition of about 1/100 part of erythrosine the sensitiveness of the emulsion can be further increased.

What we claim is:—

1. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating a sensitizing agent with the emulsion at any stage of preparing the latter.

2. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating a sensitizing agent with the substances required for the preparation of the emulsion.

3. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating a sensitizing metal compound with the substances required for the preparation of the emulsion.

4. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating a sensitizing compound of a heavy metal with the substances required for the preparation of the emulsion.

5. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating the ingredients known to form a sensitizing metal compound with the substances required for the preparation of the emulsion.

6. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating a sensitizing metal compound and a sensitizing dyestuff with the substances required for the preparation of the emulsion.

7. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating a hydrohalic salt and a water-soluble salt of a metal which is known to form a sensitizing compound with the halogen radical of the aforesaid hydrohalic salt with the substances required for the preparation of the emulsion.

8. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric

oxalate and its complex amine compounds, which comprises incorporating a hydrohalic salt and a water-soluble salt of a metal which is known to form a sensitizing compound with the halogen radical of the aforesaid hydrohalic salt and a sensitizing dyestuff with the substances required for the preparation of the emulsion.

9. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating potassium iodid and silver nitrate with the substances required for the preparation of the emulsion.

10. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating potassium iodid, silver nitrate and a dyestuff of known sensitizing effect with the substances required for the preparation of the emulsion.

11. The process of producing photosensitive emulsions comprising a mercury salt selected from the group consisting of mercuric oxalate and its complex amine compounds, which comprises incorporating potassium iodid, silver nitrate and mercuric iodid with the substances required for the preparation of the emulsion.

12. As new articles of manufacture photographic emulsions comprising a salt of mercury selected from the group of mercuric oxalate or a complex amine compound thereof and a sensitizing agent.

13. As new articles of manufacture photographic emulsions comprising a salt of mercury selected from the group of mercuric oxalate or a complex amine compound thereof and a sensitizing compound of a heavy metal.

14. As new articles of manufacture photographic emulsions comprising a salt of mercury selected from the group of mercuric oxalate or a complex amine compound thereof and a sensitizing metal compound and a sensitizing dyestuff.

15. As new articles of manufacture photographic emulsions comprising a complex amine compound of mercuric oxalate and a sensitizing compound of a heavy metal.

16. As new articles of manufacture photographic emulsions comprising a complex amine compound of mercuric oxalate, a sensitizing compound of a heavy metal and a sensitizing dyestuff.

17. As new articles of manufacture photographic emulsions comprising a complex amine compound of mercuric oxalate and a silver halide.

18. As new articles of manufacture photographic emulsions comprising a complex amine compound of mercuric oxalate, mercuric iodid and silver iodid.

19. As new articles of manufacture photographic emulsions comprising a complex amine compound of mercuric oxalate, silver iodid and a dyestuff of known sensitizing effect.

In testimony whereof we have hereunto set our hands.

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