Patented Feb. 7, 1928. 1,658,510

UNITED STATES PATENT OFFICE.

MURRAY C. BEEBE, OF WATERBURY, CONNECTICUT; ALEXANDER MURRAY, OF CINCINNATI, OHIO; AND HAROLD V. HERLINGER, OF SOUTHGATE, KENTUCKY, ASSIGNORS TO THE WADSWORTH WATCH CASE CO., OF DAYTON, KENTUCKY, A CORPORATION OF KENTUCKY.

PHOTOGRPAHIC MEDIUM AND PROCESS.

No Drawing. Application filed March 15, 1926. Serial No. 94,939.

This invention relates to improved photographic media and processes.

The primary object is to provide an improved photographic medium which is capable of being used advantageously in the industrial arts for varied purposes. The invention provides an improved light-sensitive medium adapted for various uses, a process of preparing such medium and a photo-process employing the medium and also an improved negative resulting therefrom.

The invention is in the nature of a species of, or closely related to some of the inventions disclosed in U. S. patents, including the following:

Beebe and Murray, Patent No. 1,574,357, filed February 23, 1926.

Beebe, Murray and Herlinger, Patent No. 1,587,269, filed June 1, 1926.

Beebe, Murray and Herlinger, Patent No. 1,587,270, filed June 1, 1926.

Beebe and Murray, Patent No. 1,587,271, filed June 1, 1926.

Beebe, Murray and Herlinger, Patent No. 1,587,272, filed June 1, 1926.

Beebe, Murray and Herlinger, Patent No. 1,587,273, filed June 1, 1926.

Beebe and Murray, Patent No. 1,587,274, filed June 1, 1926.

In accordance with the present invention, a light-sensitive medium is prepared by incorporating in one of the cellulose esters a small percentage of a suitable sensitizer. Preferably, the sensitizer employed is an organic halogen compound capable of liberating halogen under the action of light. Iodoform may be employed advantageously for the purpose, and may be considered typical of the best type of sensitizer for the purpose of this invention.

Another feature of the invention pertains to the development of the image or print after the light-sensitive film has been selectively acted upon by light in accordance with an image, design or character transmitted or projected thereon. Here, it is found that a print produced in a sensitized solution of a cellulose ester can be developed by immersing it in a standard silver-reducing solution, for example. The same is found to be true with respect to light-sensitive media prepared from synthetic resins as described in certain of the applications referred to above. It seems to be true that the use of a halogen sensitizer in these substances enables the silver-reducing solution to function more effectively than where such a sensitizer is not employed. For example, the furfural-ethyl-methyl ketone resin described in patent 1,587,269, mentioned above, produces a print which will not receive a deposit of silver effectively unless the medium has been sensitized, as, for example, with iodoform. On the other hand, a solution of such a resin is sufficiently light-sensitive to quickly produce a good print without the use of a sensitizer, and such print may be developed in benzine.

In accordance with the present invention, a light-sensitive medium may be produced by sensitizing cellulose acetate, cellulose nitrate, or other cellulose esters by means of a small percentage of an organic halogen-liberating compound, such as iodoform.

If desired, iodine, or other halogen, may be introduced into the medium. This course may be followed, for example, where metal salts, such as lead tungate, or the like, are introduced into the compound. In such case, when a solution of a halogen, such as iodine, is introduced, the halogen combines with such salts to form metallic halides. These halides may be suspended in the solution in the form of colloids and may operate to liberate halogen under the action of light. In place of iodoform, any suitable halogen-substituted hydrocarbon may be employed as a sensitizer.

As an example of the manner in which a light-sensitive medium may be produced by employing a cellulose ester, the following is given:

Add to 150 cc. of collodion 1% iodoform. This may be introduced in any desired manner. The sensitized medium thus produced may be applied as a film to any desired surface, and when exposed to the selective action of light in accordance with an image, design or character, the portion of the film most strongly effected by the light will be

transformed, or will undergo some kind of reaction, so that an image is produced in the film. The image may be projected upon the film before it is thoroughly dry by means of an arc light acting through a transparency; or the light may be transmitted through a transparency which is in contact with the film after the film has been dried. It is found that an exposure of from fifteen seconds to one minute suffices to produce a print.

The print may be developed by immersing it in a silver-reducing solution which may comprise a mixture of two solutions, as follows:

Solution "*A*."—Add 11 cc. of a 10% solution of silver nitrate to 10.4 cc. of a 10% solution of ammonium hydroxide; dilute the mixture to 60 cc.

Solution "*B*."—Mix the following: 20 grams Rochelle salts, 20 grams sugar, 4 grams silver nitrate, 1,000 cc. water.

Mix equal quantities of Solution "A" and Solution "B", for example, 60 cc. of Solution "A" and 60 cc. of Solution "B". This mixture gives a suitable reducing solution. The print produced in the manner set forth above may be developed by immersing it or exposing the film in this reducing solution until silver deposits upon the portion which has been transformed by the action of light in sufficient quantity to produce a dense image. The film may then be washed and dried.

The same procedure may be followed with cellulose acetate, or other cellulose esters; also with prints produced in films formed from solutions of the synthetic resins.

A variation of the process of producing prints can be made by incorporating in collodion, for example, about 1% iodoform and magenta dye. When a film of light-sensitive medium prepared in this manner is printed for about two minutes and developed in alcohol, the image is retained in those portions of the film transformed by the action of light. Presumably, the magenta dye is sufficiently light-sensitive and the cellulose ester becomes so hardened that the magenta is retained where the transformation under the action of light has occurred, after development of the print in alcohol.

Instead of adding the sensitizer to the cellulose nitrate solution before applying as a film, the film of cellulose nitrate solution may first be applied as a film to a glass plate, for example; and, after drying the film, it may be soaked in a solution of one gram of iodoform with 200 cc. of alcohol. After being thus sensitized, the film may be subjected to the selective action of light, projected, or transmitted through a suitable transparency in accordance with an image, design or character.

Variations of the process are possible, such as adding chemical indicators, thus litmus, phenolphthalein and iodoform may be added, and then after exposing to light, developed in a weak ammonia solution which will react upon the chemical indicator to thus bring the image clearly to view.

Any suitable developing agent may be employed. It is to be remarked, however, that differential solvents suitable for dissolving the unreacted portions of the cellulose ester, while not attacking the reacted portions, are not so readily available as in the case of the synthetic resin varnishes, or the light-sensitive oil varnishes; hence, it is preferred to use a silver-reducing solution, or the like, for development purposes. Such reducing solution may be of any suitable composition.

A useful application of the process is in producing glass negatives, or positives, which may be used as transparencies through which light may be projected or transmitted for the purpose of making a reproduction in a light-sensitive coating.

If desired, after an image has been produced and developed on a metal plate, a glass plate, or the like, the plate, or surface, may then be subjected to an etching operation by employing a suitable etching agent.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations should be understood therefrom, but the appended claims should be construed as broadly as permissible, in view of the prior art.

What we regard as new, and desire to secure by Letters Patent, is:

1. A photographic medium comprising a cellulose ester base and a sensitizer incorporated therein comprising an organic halogen-liberating compound.

2. A photographic medium comprising a cellulose ester base and a sensitizer incorporated therein comprising a halogen-substituted hydrocarbon.

3. A photographic medium comprising a cellulose ester base and a sensitizer incorporated therein comprising a halogen-substituted hydrocarbon and a metallic halide.

4. A photographic medium comprising a cellulose ester base and a sensitizer incorporated therein comprising iodoform.

5. The process of producing a resistant image, design or character on a surface which comprises: applying to said surface a coating comprising a cellulose ester and a small percentage of an organic halogen-liberating sensitizer, and acting upon said coating selectively with light in accordance with an image, design or character to effect the desired transformation.

6. The process of producing a resistant image, design or character on a surface which comprises: applying to said surface a coating comprising a cellulose ester and a small percentage of an organic halogen-liberating sen-

sitizer, acting upon said coating selectively with light in accordance with an image, design or character to effect the desired transformation, and subjecting the print to a developing operation.

7. The process of producing and developing an image, design or character on a surface which comprises: applying to said surface a coating comprising a cellulose ester and an organic halogen-liberating sensitizing agent, acting upon said coating selectively with light in accordance with an image, design or character to effect the desired transformation, and developing the print in a reducing solution adapted to deposit metal upon the reacted portions of the coating.

8. The process of producing and developing an image, design or character on a surface which comprises: applying to said surface a coating comprising a cellulose ester and an organic halogen-liberating sensitizing agent, acting upon said coating selectively with light in accordance with an image, design or character to effect the desired transformation, and developing the print by exposing it to the action of a solution having a reducing action.

9. The process of producing a light-sensitive medium which comprises: incorporating with a cellulose ester a small portion of a sensitizer comprising an organic halogen-liberating compound.

10. The process of producing a light-sensitive medium which comprises: incorporating with a cellulose ester a small portion of a sensitizer comprising iodoform.

11. The process of producing an image which comprises: applying to a suitable surface a coating of a substance adapted to be transformed by the selective action of light, said substance having incorporated therewith a small percentage of a sensitizer comprising an organic halogen-liberating compound; acting upon said coating selectively with light in accordance with an image, design or character to effect the desired transformation; and subjecting the coating to the developing action of a reducing solution comprising silver nitrate.

12. A photographic medium comprising cellulose nitrate having incorporated therein about one percent of a sensitizer comprising a halogen-substituted hydrocarbon.

13. A photographic medium comprising cellulose nitrate having incorporated therein about one percent of a sensitizer comprising iodoform.

MURRAY C. BEEBE.
ALEXANDER MURRAY.
HAROLD V. HERLINGER.