

UNITED STATES PATENT OFFICE.

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PHOTOGRAPHIC MEDIUM AND PRODUCTION THEREOF.

No Drawing.

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This invention relates particularly to photographic media involving the use of hydrophobic colloids and sensitizers, and to processes of preparing the same.

The primary object of the invention is to provide a highly sensitive medium comprising hydrophobic colloids and a suitable sensitizer, or sensitizers, which is of stable character, in the sense that the photographic medium may be stored, or kept, without deterioration, for long periods of time, as distinguished from a few hours, or a few days.

The invention finds a particularly useful application to sensitive varnishes, involving the use of considerable percentages of oil, which is either naturally light-sensitive, or which has associated therewith a suitable sensitizing agent, preferably a sensitizing agent which will liberate halogen under the action of light when a coating of the varnish is exposed in a photographic process of any character. More broadly, the invention is applicable to a light sensitive varnish embodying a solution of hydrophobic colloids, derived from any suitable source, which are capable of transformation under the selective action of light, in accordance with a luminous image, design or character, to which a coating of the varnish is subjected.

Among such hydrophobic colloids may be mentioned synthetic resins, asphaltum, and, generally, resinous bodies derived from various unsaturated compounds. Natural resins and other resins, such as kauri resin, shellac, cumar resin, etc. may be incorporated to such extent as may be desired in light-sensitive varnishes of the character herein described. Also, cellulose acetate, cellulose nitrate, and other compounds may be sensitized in accordance with the present process. Various compounds within the scope of the invention, and not herein specifically mentioned, may be used, including incipiently gelled oils.

It may be stated, preparatorily, that while some of the oils, such as Chinawood oil, and some of the synthetic resins, such as certain of the resins derived from furfural, are quite light-sensitive, it is desirable, generally speaking, in connection with compounds, or bases, which are capable of being transformed under the selective action of light to a condition enabling the film, or coating, to be developed, or fixed, by any suitable method

to employ in association with such compounds, or bases, suitable sensitizing agents; and it has been found highly advantageous to employ more than one halogen-liberating compound in many of the photographic media of this character.

Generally speaking, it is not desirable to have a halogen, such as iodine, bromine or chlorine, present in free condition in a varnish of this kind. It is, on other hand, desirable to have the halogen present in a combined state in the form of a colloidal sensitizer dispersed throughout the varnish and capable of liberating halogen, under the action of light, the halogen doubtless serving as a catalyzer in the action which occurs when the hydrophobic colloid is transformed under the action of light into such condition as to enable the film to be developed.

It has been found, also, that in these varnishes, by employing a plurality of different kinds of sensitizers, the sensitizers apparently produce an additive effect. It is desirable, for example, to have present in the varnish metallic halides, such as lead iodide, and an organohalogen compound, such as iodoform. In those varnishes, especially, wherein considerable proportions of oil are employed, the use of both metallic halides and organohalogen compounds as sensitizers is desirable; but, in order that the varnish may be of stable character, enabling it to be kept for an indefinite period, the presence of free halogen in the varnish is to be avoided.

The following is given as an example of an improved varnish medium and method of preparing the same:

Heat in a kettle a mixture of ingredients, as follows: 200 grams Chinawood oil, 20 grams cumar resin, 6 grams lead resinate.

Such a mixture may be heated at a rate which will bring it to a temperature of about 250° C. within a period of about forty-five minutes. Then add to the cooked compound, a solvent medium, such as a mixture of 50 cc. of benzine and 100 cc. of benzol (benzene.) This yields 300 cc. of varnish.

Take 100 cc. of said varnish; stir therein a solution of 8 grams of iodoform in 80 cc. of benzol; then stir in 10 cc. of a gutta percha solution, such as may be formed by dissolving 20 grams of gutta percha in a

solvent comprising 50 cc. of carbon tetrachloride and 50 cc. of benzol.

Finally, add slowly, with stirring, 6 cc. of a solution of iodine formed by dissolving 10 grams of iodine in 100 cc. of benzol.

The order of procedure is of considerable importance. It seems that the gutta percha tends to prevent the precipitation of portions of the lead resinate, or the resulting compound of lead, when the iodine is added.

The amount of iodine added is such as to combine with substantially all of the lead present in the form of a resinate. In other words, the lead resinate is completely converted to lead iodide, and no free iodine remains in the varnish. The amount of lead resinate employed, in the example given, is substantially sufficient to give a saturated varnish, so far as the lead compound is concerned. Less iodine than is necessary to completely convert the lead resinate into lead iodide may be used, but this will result in a varnish which will print more slowly. The use of more iodine than is sufficient to combine with the lead resinate will make the varnish unstable, or of such character that it will spoil in a few hours, or a few days, whereas the stable solution remains clear and prints uniformly after a lapse of weeks and months.

The gutta percha employed also serves to give additional body to the varnish, and this is true, also, of the cumar resin employed. Lead resinate has been given merely as an example of suitable compounds of metals which may be employed. Resinates, tungates, or similar soaps, or salts of various metals, may be employed. A mixture of such materials, taken in comparatively small proportions, the aggregate approaching a saturation point, may be employed. Thus, for example, resinates, or tungates of lead, manganese, aluminum, zinc, and cobalt may be used. In fact, the metals employed may be present in any suitable form which will enable them to be carried in colloidal suspension in the varnish, provided they are of such character as to enable them to combine with the free halogen employed in preparing the varnish.

In place of tung oil (Chinawood oil), one may employ a mixture of suitable oils, or may employ various oils, such as those enumerated in the patent of Murray C. Beebe and Alexander Murray, No. 1,574,357, granted February 23, 1926.

It is desirable to observe cleanliness in forming these light-sensitive varnishes and to avoid the introduction of any water.

In these light-sensitive varnishes, the organo-halogen compound, such as iodoform, and the metallic halide, such as lead iodide, are dispersed, as colloidal sensitizers, throughout the varnish. In a properly compounded varnish, these sensitizers will

remain dispersed throughout the varnish for a long period of time, so that a stable photographic medium is provided.

As an example of the use of such a medium, it may be stated that the light-sensitive varnish may be applied in any suitable manner, as by flowing, whirling, or brushing, upon a suitable surface, to form a thin coating, or film. Under the selective action of light transmitted, or projected, in accordance with a luminous image, design or character, the hydrophobic colloids are acted upon selectively in accordance with the light intensities, and polymerized, thickened, or hardened. This leaves the image, or film, in suitable condition to be developed, or fixed, in accordance with known methods, or any desired method.

As has been indicated, the developing may be effected in any suitable way. For example, the print may be dipped in a solution of oil red and carbon tetrachloride for about one-fourth of a second, and may then be washed in benzine until the image is developed to the desired degree. Any other suitable method of developing may be employed. For example, the soluble portions of the coating may be washed off in any suitable manner. Also, the hardened, or "set", image may be colored, or stained, in any suitable manner. The subject of development is not dwelt on at greater length herein for the reason that the present invention is not primarily concerned therewith.

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.

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

1. The process of producing a stable light-sensitive varnish which comprises: introducing a free halogen into a varnish comprising hydrophobic colloids, metal salts capable of combining with free halogen, and a solvent, the salts being present to a point approaching saturation, and the free halogen introduced being proportioned to combine with a substantial portion of the salts and avoid the presence of free halogen after the metallic halides have formed.

2. The process of producing a stable light-sensitive varnish which comprises: introducing a solution of a free halogen into a varnish comprising hydrophobic colloids, metal salts capable of combining with free halogen, and a solvent, the salts being present to a point approaching saturation, and the free halogen introduced being proportioned to combine with a substantial portion of the salts and avoid the presence of free halogen after the metallic halides have formed.

3. The process of producing a stable light-sensitive varnish which comprises: introducing a solution of iodine into a varnish comprising hydrophobic colloids, metal salts capable of combining with free halogen, and a solvent, the salts being present to a point approaching saturation, and the iodine introduced being proportioned to combine with a substantial portion of the salts and avoid the presence of free halogen after the iodides have formed.
4. The process of producing a photographic medium which comprises: combining an organo-halogen compound and a free halogen with a varnish comprising hydrophobic colloids, metal salts capable of combining with free halogen, and a solvent, the salts being present to a point approaching saturation, and the free halogen introduced being proportioned to combine with a substantial portion of said salts to form metallic halides and avoid the presence of free halogen in the final varnish.
5. The process of preparing a light-sensitive varnish which comprises: combining an organo-halogen compound with a varnish comprising a light-sensitive oil and metal salts capable of combining with free halogen; combining with the resultant mixture a solution of gutta percha; and then introducing a solution of a free halogen, the halogen being proportioned to combine with substantially all of the metal salts to form metallic halides and avoid the presence of free halogen in the final varnish.
6. The process of producing a light-sensitive varnish which comprises: introducing a solution of iodoform into a varnish comprising hydrophobic colloids, metal salts adapted to combine with a free halogen, and a solvent in which said hydrophobic colloids and said salts are dispersed; mixing therewith a solution of a body-giving compound, such as gutta percha; and finally introducing a solution of iodine proportioned to combine with a substantial portion of the salts and form metallic halides and avoid the presence of free iodine in the final varnish.
7. A stable light-sensitive varnish comprising: an organo-halogen compound and metallic halides, dispersed in a varnish comprising hydrophobic colloids and a solvent medium, said metallic halides being present to a point approaching saturation and no free halogen being present.
8. A stable light-sensitive varnish comprising: a light-sensitive oil, metallic halides, an organo-halogen compound, and a solvent medium in which said substances are dispersed, said metallic halides being present to a point near the point of saturation and the varnish comprising no free halogen.
9. A stable light-sensitive varnish comprising: a major portion of Chinawood oil, and a minor portion of resins, metallic halides, an organo-halogen compound, and a solvent medium in which said substances are dispersed, said metallic halides being present in a degree approaching saturation and the varnish comprising no free halogen.
10. A stable light-sensitive varnish which comprises: a major portion of an oil capable of being transformed under the action of light; a minor portion of a resin; a minor portion of gutta percha; metallic halides; and a solvent medium in which all of said materials are dispersed, said metallic halides being present in a degree approaching saturation and no free halogen being present.
11. A stable light-sensitive varnish comprising: Chinawood oil, a base adapted to give body to the varnish, metallic halides, and a solvent medium in which said substances are dispersed, said metallic halides being present in a degree approaching saturation and no free halogen being present.
12. A stable light-sensitive varnish comprising: a major portion of Chinawood oil; minor portions of cumar resin and gutta percha; metallic halides; and a solvent in which said materials are dispersed, said metallic halides being present in a degree approaching saturation and no free halogen being present.
13. A stable light-sensitive varnish comprising: a major portion of Chinawood oil; a minor portion of cumar resin and gutta percha; metallic iodides; iodoform; and a solvent in which said substances are dispersed, said iodides being present to a point approaching saturation and no free halogen being present.

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