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UNITED STATES PATENT OFFICE.

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PHOTOGRAPHIC MEDIUM.

No Drawing. Application filed November 18, 1922. Serial No. 601,884.

To all whom it may concern:

Be it known that we, (*a*) MURRAY C. BEEBE and (*b*) ALEXANDER MURRAY, (MURRAY C. BEEBE is a citizen of the United States, ALEXANDER MURRAY is a subject of Great Britain), residing at Cincinnati, in the county of Hamilton and State of Ohio, have invented certain new and useful Improvements in a Photographic Medium, of which the following is a specification.

Our invention relates to improvements in the process of forming sensitized photographic mediums, and it more especially relates to the features pointed out in the annexed claims.

The purpose of our invention is to provide a non-aqueous photographic medium that is stable and not liable to deterioration during storage; that contains an emulsoid base such as oleaginous materials permanently sensitized in a non-aqueous medium; that through the cooperation of the colloidal characteristics of the sensitizer and a single developer produces brilliant results; that overcomes the difficulty of clearing the high lights encountered in the use of oleaginous coatings with non-colloidal sensitizers; and that provides a photographic medium, in which a change from the sol to the gel state is effected by light through the cooperation of a colloidal suspension of a metal halide, combined therewith as a sensitizer.

With these and other ends in view, we herewith set forth such expedients as will be exemplifications or instances of adaptation of the broad underlying features of our invention without limiting ourselves to the specific details described herein.

The following description of procedure in practically applying our invention is exemplary and not a limiting disclosure, as variations in degree and within the range of practical equivalents may be made without departing from the spirit of our invention. Among numerous other oleaginous mediums we may use glycerides of unsaturated fatty acids such as tung oil, perilla oil etc., combined with metallic resinates and a colloidal sensitizer approximately as follows or in practical variations therefrom. The proportions given are by weight

Oleaginous medium.

	Per cent.
Tung oil	7.50
Perilla oil	1.91

Colloidal sensitizer.

	Per cent.
Lead resinate	0.67
Iodoform	5.00
Lead triethyl iodide	7.00

Solvents.

	Per cent.
Ketones	27.00
Benzene	45.50
Solvent naphtha	5.42

The combined sensitizer and coating medium may be made as follows: A solution of 4.2 grams of lead triethyl iodide contained in approximately 30 cc. benzene is combined with 10 grams of the oleaginous medium, to which is added 3 grams of iodoform dissolved in 20 cc. of ethyl methyl ketone. The lead resinate may be mixed with the benzol (benzene) and lead triethyl iodide, and the solvent naphtha may be added as a thinner for the varnish which comprises the other substances.

The coating medium with its incorporated sensitizer, soon after mixing, changes to a canary-yellow color when observed by reflected light, and an orange red when inspected by transmitted light, having, in either case, an opalescent appearance. This color is likely due to the formation of an iodide of lead which is in a suspensoid state known as an organosol because an organic dispersing medium is used. Small amounts of water or any aqueous reagents cause a rapid deterioration through the formation of a non-colloidal suspension which produces an unstable medium that will rapidly decrease its sensitivity.

In preparing the resist or coating in about the manner described we secure a reasonably permanent photo-sensitive menstruum which can be kept in brown bottles, in the dark for

days and weeks in contrast to sensitizers which are non-colloidal. To secure the required sensitivity it is not necessary to form the lead iodide; but by allowing the salt, if formed, to remain in a colloidal state it plays an important cooperating function of sensitization by avoiding rapid deterioration which would inevitably take place if the lead salt was allowed to precipitate. By reason of these safeguards our non-aqueous photographic medium has many practical advantages over our prior procedures in this art.

Another important feature lies in the property of the sensitizer to not deleteriously affect the oil colloids during storage of the medium. Since no catalytic drier like cobalt linoleate etc., is used, a metallic or other suitable plate can be coated and kept for many hours without drying or becoming set. When a plate with such a coating is exposed to a luminous image, the parts which are subjected to the greatest illumination gel very rapidly, and become comparatively insoluble and non-detergiable producing a result of maximum contrast, even when a low luminous intensity is used; for instance in making great enlargements from small sized half-tone negatives by optical projection for poster work.

The plates are coated by flowing the medium over them or applying it otherwise and are then set on edge to drain and also permit the solvents to evaporate. Our present medium is more highly sensitive than when only free iodine is used as a sensitizer. In proof of this we may state that we have optically enlarged a 4″ x 5½″ half tone negative to 32″ x 42″ on a grained zinc plate in ten minutes under the illumination usually produced by arc printing lamps found in process engraving establishments. In contrast to this result when mediums are sensitized with free iodine the exposure was 16 minutes under the same conditions and the print was very much inferior in sharpness and contrast. After exposure the print was developed by means of kerosene gently swabbed over the surface and then washed with water securing a clear print which retained all the sharpness of the half-tone dots, without the presence of "scum" between them. When working same size the exposure time is approximately 10 seconds under a similar source of luminosity.

Our process is specially adaptable for the production of poster enlargements by direct or off-set lithography. Heretofore the difficulties have been, lack of permanency of the prepared medium, disturbing side reactions causing a combination of the free halogen with the oil, and an oxidation reaction which made it impossible to coat plates by flowing or to preserve coated plates for some time. There has existed a limitation in the use of developers which resulted in a lack of sharp detail. Under the same degree of luminosity we now avoid this and secure a brilliancy, speed and accuracy that has not been attainable hitherto.

By eliminating the side action we secure uniform conditions as to exposure which under other procedures has been variable and uncertain.

What we claim is:

1. A photographic medium comprising a hydrophobic colloid and a sensitizer comprising lead triethyl iodide.

2. A photographic medium comprising a hydrophobic colloid and a sensitizer comprising lead triethyl iodide and a halogen-liberating organic compound.

3. A photographic medium comprising a hydrophobic colloid and sensitizing means dispersed therein comprising lead triethyl iodide and iodoform.

4. A photographic medium comprising a hydrophobic colloid and sensitizing means dispersed therein comprising lead triethyl iodide, iodoform, and a resinate.

5. A photographic medium comprising a light-sensitive oil and a sensitizer comprising lead triethyl iodide and iodoform.

In testimony whereof we affix our signatures.

MURRAY C. BEEBE.
ALEXANDER MURRAY.