

Dec. 19, 1967

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3,359,112

SENSITIZATION OF PHOTOGRAPHIC MEDIA

Original Filed Dec. 11, 1962

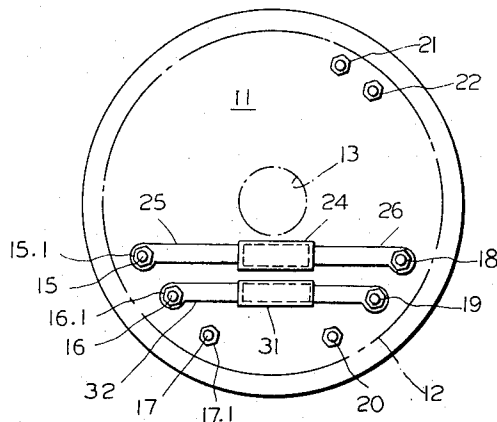


FIG. 1

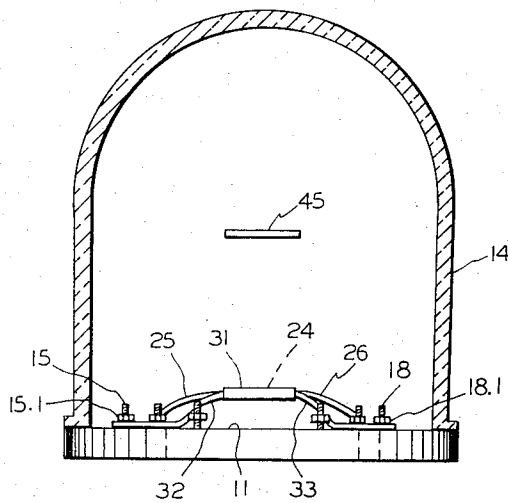


FIG. 2

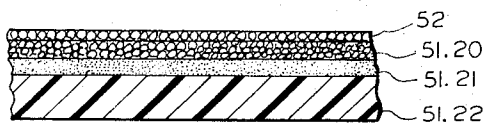


FIG. 3

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SENSITIZATION OF PHOTOGRAPHIC MEDIA

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Continuation of application Ser. No. 243,949, Dec. 11, 1962. This application Sept. 3, 1965, Ser. No. 489,789

11 Claims. (Cl. 96—102)

This invention relates in general to the field of photographic materials, and more particularly to novel surface sensitized silver halide photographic materials. Specifically, the present invention is directed to the sensitization of photographically responsive layers of silver halide, such as are prepared by evaporation of silver halide from a molten pool, and the condensation of those vapors on an appropriate substrate material. The resultant stratum of condensed silver halide is formed of a large number of microcrystals which are supported on the substrate primarily by being adhered directly to each other and directly to the substrate. Such material is therefore binder-free as distinguished from conventional gelatin type photographic materials; and even if a retaining surface layer is applied over the binder-free material, the silver halide is still substantially binder-free. This material, as a photographic medium, and a process for preparing same is described in French Patent, No. 1,267,623 granted June 12, 1961, to Technical Operations, Incorporated.

Other photographic media which are now known and in use are generally characterized by an emulsion or gelatin in which aggregates of photosensitive material are suspended. The use of an emulsion to hold photosensitive material on a supporting surface has many disadvantages. Among these is the fact that developing agents must penetrate the emulsion to reach the photosensitive material. Another disadvantage is the fact that there is a limit to the minimum grain size that can be achieved, due in turn to the fact that the aggregates of photosensitive material which are suspended in the emulsion cannot individually be reduced beneath a certain size without losing or suffering diminution of their photographic properties. Still another is the fact that a substantial portion of the area of the photographic medium consists of gelatin, rather than photosensitive material, and this fact coupled with the minimum limit on grain size places a limitation on the fineness of detail that can be recorded. Further, the aggregates themselves are in the nature of particles of photosensitive material entrapped in globules of gelatin, so that each aggregate has the chemical characteristics of the emulsion as well as its photographic characteristics. Among the characteristics of gelatin emulsions are sensitivity to radioactive energy, such as gamma rays, and a tendency to pick up moisture, both of which cause fogging of negatives and shorten the storage life of photographic media. Further, as is well known, a gelatin, once wet, cannot be quickly dried without taking special measures which are costly and tend generally to harm the photographic image, and, as is also well known, special measures are required to bond a gelatin, which is hydrophilic in nature, to a film base, which is hydrophobic in nature. Another distinct disadvantage of known emulsion-type films is the fact that they can be used only once.

Media of the type disclosed in the aforesaid French patent generally exhibit native sensitivities, in terms of ASA speed ratings, for example in the range of 1×10^{-2} to 1×10^{-4} , to white light with the response greatest in the blue region. For many photographic purposes, it is desirable to have media of higher speed, or media which exhibit a so-called panchromatic response.

It is, therefore, the principal object of this invention to impart increased sensitivity of binder-free, microcrystal-

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line, silver halide photographic media such as those hereinbefore described.

Another object of the present invention is to provide novel processes for surface sensitizing such photographic media, and the products of such processes.

Yet another object of the present invention is to provide a number of novel sensitizers for such media and techniques for applying same to achieve sensitization.

Other objects of the present invention are to provide sensitization of such media by the treatment of a surface with sensitizing material applied from the vapor phase thereof; to provide such sensitization by the vacuum deposition of sensitizing material on said surface; and to provide such sensitization by methods which can be practiced with apparatus similar to that which is used to prepare the binder-free microcrystalline, silver-halide photographic media.

Yet other objects of the present invention are to achieve novel optical sensitizations of such media; and to provide a number of novel sensitized photographic media.

A photographic salt, chosen from the group of silver chloride, silver bromide and silver iodide, and combinations of these, can be formed into a binder-free microcrystalline photographic medium, for example, by being evaporated in near vacuum and deposited by condensation in a microcrystalline form directly on a surface of a supporting medium, under controlled conditions of temperature, pressure and time. The supporting medium may be the surface of solid material, such as glass, photographic quality paper, or photographic quality polymeric film. Alternatively, the supporting medium may be coated on the silver halide receiving surface with a bonding agent, such as a gelatin, a lacquer, or a normally tacky adhesive, in order to cause the evaporated silver halide to adhere more securely thereto.

The thickness of the resultant layer or stratum of microcrystalline silver halide photographic material which can be used can likewise vary, but preferably should be a very thin film. Some degree of photographic utility can be obtained with evaporated silver halide strata as thick as about 3.5 microns; on the other hand, it has been found that generally there is a substantial and rapid fall-off of photographic properties with thicknesses in excess of an amount around 0.3 micron. It has been found that at silver halide stratum thicknesses of around 0.3 micron one usually obtains maximum photographic properties, i.e., maximum density, speed, and gamma, one or more of which the present invention can enhance by the sensitization defined hereinafter. Depending upon the exact conditions of temperature and pressure during the evaporation and condensation of the silver halide, and the particular substrate employed to collect the silver halide vapors, the exact thickness at which maximum photographic properties is obtained will vary about 0.1 or 0.2 micron, or thereabouts, to either side of the stated 0.3 micron thickness. However, the fall-off of photographic response is usually quite rapid to either side of that thickness which provides the maximum response. Accordingly, the preferred range of thickness for the evaporated silver halide stratum, for the purposes of this invention, is around a fraction of a micron, particularly around the 0.3 micron value, and most particularly from about 0.1 micron to about 0.5 micron.

Thus, there is provided a photographic medium consisting essentially of a continuous layer of microcrystalline photographic material, which is relatively grainless, or may be termed "superfine grain," as compared with prior photographic materials prepared in suspension in an emulsion. This photographic medium has the advantages, heretofore not available, that it can be developed more easily by liquid and even gaseous developers, since

there is no necessity for the developer to penetrate a gelatinous matrix to reach the photographic medium itself, that it lends itself to processes of image transfer and re-use after such transfer, and that it is practically insensitive to ionizing nuclear radiation.

Such photographic media may be made of a single one of the above-mentioned halides, or of two (or more) of them. In the latter case starting quantities of each desired halide are vacuum evaporated, in the same location or separate locations, their vapors mixed in the low pressure region if they started in separate locations, and their mixed vapors are condensed on a surface on the supporting medium. Thus, starting with appropriate quantities of silver chloride and silver bromide, a layer of silver chlorobromide is deposited. Or, starting with appropriate quantities of silver bromide and silver iodide, a layer of silver bromiodide is deposited. Like the single halide layer, these layers are of substantially homogenous microcrystalline form.

By the term "sensitizer," without being limited to any particular theory of sensitization, it is intended to mean a material which, when applied to the microcrystalline binder-free layer of the photosensitive salt, will enhance the inherent sensitivity thereof over a predetermined spectral range.

According to one aspect of the invention, a particulate, i.e. microcrystalline binder-free silver halide photographic medium is sensitized by the treatment of the surface of a binder-free stratum by one or more sensitizing materials applied from the vapor phase, the deposition of the sensitizing material being accomplished substantially in vacuo and controlled to limit the amount of sensitizing material deposited.

Specifically, a binder-free microcrystalline, silver-halide photographic medium of the type described is sensitized by the deposition onto its surface of a sensitizing dyestuff from the vapor phase of the latter and subsequent treatment by wetting of the dye layer thus formed.

Concentration of the sensitizing deposit is controlled in vapor deposition according to the invention by control of the pressure, temperature of evaporation and condensation of the sensitizing material, and the time allowed for condensation or deposition of the sensitizing material.

In an important embodiment the invention provides a photographic medium comprising a substrate, such as a sheet-like support of, for instance photographically inert material, having at least on one surface thereof, with or without intervening binding strata, a binder-free microcrystalline layer of silver halide, the latter in turn being treated with a sensitizing material.

Other and further objects and features of the invention will become apparent from the following description of certain embodiments thereof and of methods and apparatus for preparing them. This description refers, for purposes of illustration, to the accompanying drawings, wherein:

FIG. 1 is a top view of a portion of a known vacuum evaporation machine which is useful in practicing the method of the invention;

FIG. 2 is a schematic side view of a portion of such a machine; and

FIG. 3 is a schematic cross-section of a sensitized medium of the invention.

FIG. 1 shows the table 11 of an existing machine for the vacuum deposition of metals and similar materials and which is employed in the invention not only to form the binder-free microcrystalline medium, but, in some cases, to apply the sensitizing material to the medium. A basic machine of the kind referred to is illustrated and described in the book *Vacuum Deposition of Thin Films*, by L. Holland, published by John Wiley and Sons, Inc., New York city, 1948, pages 7 and 8. A vacuum coating machine Model LCI-14A of the Consolidated Electrodynamics Corporation was used in achieving some of the re-

sults mentioned below. This machine has a bell-jar (FIG. 2) about 13 inches in diameter and 24 inches in height on the table 11 under which a low-pressure, near vacuum region is provided. The location of the bell-jar when in place on the table 11 is indicated by the dashed circle 12. The space under the bell-jar is exhausted through an opening 13 in the table 11.

Electric power terminals 15, 16, 17 and 18, 19, 20 (FIG. 1) are provided on the table 11 for supplying current for melting the silver halide source material or the sensitizing material, as the case may be, to be evaporated in vacuum, and a pair of auxiliary terminals 21 and 22 (FIG. 1) supply operating voltage (e.g. 110 volts, A.C.) for auxiliary devices. These terminals are all within the locus 12 of the rim of the bell jar. A first electrically conductive container, boat or "filament," 24, which may be made of molybdenum, tantalum or tungsten, for example, is connected by two stiff electrical conductors 25 and 26 to a pair of the power terminals 15 and 18, respectively. The conductors 25 and 26 also support the open boat or filament 24 in a fixed position above the table 11. Bolts 15.1 and 18.1 (FIG. 2) fasten the free ends of these conductors to the two power terminals 15 and 18, which are usually threaded for that purpose. The starting material (not shown) to be vacuum evaporated is placed in the open boat or filament 24.

When it is desired to vacuum evaporate two quantities of starting material in separate locations, a second boat or filament 31 can be employed, supported on two conductors 32 and 33, as is shown in FIG. 1. These conductors may be connected to two separate power terminals 16 and 19, respectively, as shown in FIG. 1, or if desired they may be connected to the same power terminals 15 and 18 as the first filament 24. With two filaments connected to separate pairs of terminals as in FIG. 1, it is possible to control the current to each filament independently. Obviously, a third filament (not shown) can be added, connected to a third pair of power terminals 17 and 20, if desired.

In operation, a body or substrate 45 (FIG. 2), to be coated with the condensate from the vapor of a material (not shown) vacuum evaporated from the filament or boat 24, is supported by any suitable means (not shown) within the bell jar 14 above the filament 24 at a suitable distance therefrom. Where it is desired to form the binder-free microcrystalline silver halide medium, the starting material is at least one silver halide, chosen from the group of silver chloride, silver bromide and silver iodide. If only one of these compounds is to be coated on a surface on the body 45 a single filament 24 will suffice. If two of these compounds are to be coated simultaneously on the body 45, for example, silver chloride and silver bromide, or silver bromide and silver iodide, a quantity of each compound may be placed on the single filament 24, or two filaments 24 and 31, as in FIG. 1, may be employed and a quantity of each compound may be placed separately on each filament. Where it is desired to sensitize the medium by evaporation, a quantity of sensitizer is placed on filament 24 and the medium is then used as body 45. In both cases the region under the bell jar 14 is evacuated to a low pressure, preferably in the range of about 10^{-4} to about 10^{-6} millimeters of mercury, although pressures within wider limits, from 0.1 millimeter of mercury to less than 10^{-6} millimeters of mercury can be used. It is preferred to evacuate the region under the bell jar to the working pressure prior to applying heating current to the filament 24 (and filament 31, if used), so that the elevated conditions of temperature are not prolonged.

The body 45, which is the target for the vapors of the starting material, is spaced from the filament 24 (and filament 31, if used) a distance such that condensation of the vapors occurs at a condensation temperature above room temperature, preferably in the range of 30° C. to 50° C. At a pressure in the range of 10^{-4} to 10^{-6} milli-

meters of mercury, the temperature in the region above the filament 24 is substantially in this range at a distance about $3\frac{1}{2}$ inches from the filament, as measured by a copper-constantan thermocouple. Under these conditions, the process is carried on for a period of time, about one minute or less to one-half hour, depending upon the temperature and pressure conditions selected, until the starting material has been deposited on the target body 45 to a desired thickness.

It is preferred that the temperature of the silver halide pool and the pressure of the system be substantially stable during the silver halide coating operation; for example, the temperature may be at about 560°C . and the pressure at about 10^{-5} mm. Hg when evaporating silver bromide. To attain stable values before coating of the substrate body 45 begins, a mask (not shown) may be interposed between the boat and the substrate, and after the desired temperature and pressure are obtained and stabilized, the mask would be removed and coating of the substrate would be commenced. After a desired thickness of coating is obtained said mask may again be interposed to stop the substrate coating operation while the silver halide pool is cooled and the vacuum broken.

When forming the unsensitized medium, the substrate body 45 as shown in FIG. 2, may be a sheet of glass or alternatively, it may be a sheet of paper, plastic film, or other conventional and suitable photographic quality substrate material. The silver halide starting material evaporated from the filament 24 in FIG. 2 condenses on a surface of the substrate sheet as a microcrystalline coating or layer. As the silver halide vapors condense on this surface, small crystal particles form and coalesce to form a tightly-packed layer wherein the crystals are supported on the substrate by being adhered directly to each other and to the substrate without the need of a binder. The density of a layer formed in this manner, has been measured as follows:

Using a body 45 masked by a shield having an aperture which was a square 5.7 cm. on each side, a layer of silver bromide was deposited on a surface on the body through the aperture to a mean thickness of 2.2 microns as measured by a spectrophotometer using the method of optical path differences between reflections of controlled light from the front and back surfaces of the layer. In this example, the thickness of the polycrystalline layer of silver bromide varied from 1.94 microns at the edge of 2.24 microns at the center. The body 45 was weighted before and after coating to obtain the weight of the layer. The volume of the layer was calculated from the dimensions of the aperture and the mean thickness, and found to be:

$$2.2 \times 10^{-4} \times 5.7 \times 5.7 = 7.15 \times 10^{-3} \text{ cc.}$$

The weight of the silver bromide layer was found to be 0.44 gram. From these values, the density of the silver bromide layer was calculated to be 6.16 grams/cc. The density of solid silver bromide crystals is 6.47 grams/cc. as given in the Handbook of Chemistry and Physics, 14th Edition, page 265. The ratio of the densities of this polycrystalline layer to solid crystal is therefore

$$\frac{6.16}{6.47} = 95.3 \text{ percent}$$

This indicates that the layer 46 is very tightly packed and has a density closely comparable to that of the solid crystal of the starting material.

The polycrystalline layer of silver halide can be deposited also on a bonding type of substrate, as suggested above. The supporting body, for example, can be a film made of a cellulose derivative or other polymers. This film has on one surface a subbing stratum of soft material, such as a layer of shellac or a water-permeable colloid, for example gelatin. The evaporated layer of silver halide is deposited on the subbing stratum. Due to the softness of the subbing stratum the first crystal

particles of the silver halide which are deposited on it penetrate somewhat, and the coalescence of subsequent particles of the silver halide on the initial particles serves to bind the silver halide crystal layer to the supporting body somewhat more securely than had the subbing stratum not been employed. Obviously, a glass body can be used in place of the synthetic resin body if desired.

If it is desired to fix an image on a sample of the original photographic medium, the use of a layer 46 sufficiently thin to result in development of the image through the entire thickness of the layer will prevent removal of the image when the remaining silver halide is dissolved in the fixing bath. Otherwise, upon dissolution of the underlying silver halide, the silver image floats off. Alternatively, a liquid previous retaining sheet can be first applied to retain the developed image, and then dissolution of silver halide in the fixer will not cause loss of the developed silver particles. Rather than employ such expedients as this, it is preferred to use silver halide strata which are sufficiently thin to result in development of light struck areas down to the supporting substrate whether or not surface protective layers or sheets are employed. Since the crystal structure resulting from the present process of evaporating silver halide provides a continuity of contact between grains both laterally across the face of the photographic material as well as downwardly through the silver bromide layer to the substrate support material, the development process spreads laterally from a light struck to adjacent grains as well as downwardly through the thickness of the layer. Therefore, if the thickness of the silver halide layer is too great, development down to the substrate can result in an intolerable loss of acutance and image sharpness. It has been found that a silver halide layer of about 0.3 micron in thickness can be developed down to the substrate without appreciable loss of image sharpness and without fogging.

In view of the fact that maximum speed, density, and gamma, are all obtained with about a 0.3 micron thick layer of silver halide, and since the ability to develop down to the substrate without noticeable loss of image sharpness or fogging is likewise obtained at this thickness of around 0.3 micron, it is apparent that this thickness provides the approximate optimum for the sensitized photographic material of the present invention. These factors however are not intended to exclude entirely slightly thicker layers of silver halide, of say up to about 3.5 microns, from the scope of this invention, since such layers can be used where the maximum properties are not essential or desired and other considerations outweigh the loss of photographic properties suffered, such as are suggested in the aforesaid French patent.

The foregoing methods of the invention can be used with many forms of binder-free silver halide photographic medium. One embodiment is shown in FIG. 3 wherein is shown a binder-free microcrystalline silver-halide layer 51.20 held on a base 51.22 by, for example, subbing layer 51.21. On the top or outer surface of this layer (as seen in the figure) there is a layer 52 of sensitizing material. This layer 52 is illustrated exaggerated in size and is thinner than the drawing indicates. It would be impractical to attempt to illustrate the sensitizing layer to true scale.

The sensitizing materials which are vapor deposited onto microcrystalline binder-free silver halide medium to sensitize the latter according to the present invention are normally solid (i.e. at standard temperature and pressure) dyes selected from those which are evaporatable without substantial decomposition below approximately 300°C . Typical of the cyanine dyes which can be sublimed at reduced pressure are those disclosed in Experiments of the Electronic Mechanism of the Photoconductivity of Sensitizing Dyes, H. Meier, Phot. Sc. & Eng., vol. 6, #4, p. 235. An example of optical sensitization of a microcrystalline binder-free silver halide medium in this novel manner is as follows:

A quantity of 1,1' diethyl-2,2' carbocyanine chloride (pinacyanol) is sublimed at reduced ambient pressure of about 1×10^{-4} mm. of Hg at a temperature of approximately 200° C. onto a microcrystalline, binder-free silver halide layer lying on a subbed polyethylene terephthalate sheet to produce a visible dye layer of substantially uniform distribution at a concentration of approximately a microgram per 70 square mm. of silver halide surface. Exposure of a portion of the medium for 0.1 sec. to a lamp corrected to 5500° K. through a Wratten 25 filter and development in an internal developer produces no indication of red sensitivity. However, after wetting the dye surface of the unexposed portion of the medium with pure water and drying, upon the same exposure and development, the medium shows a red speed of the order of ASA 4×10^{-4} and a white light speed of the order of 1×10^{-2} .

This procedure is particularly effective to sensitize microcrystalline, binder-free silver halide media with appropriately vaporizable dyes that are poorly soluble or relatively insoluble in aqueous solution. The application of water in the last step either in pure form or mixed with an alcohol or other miscible fluid, is believed to provide the necessary aggregation of dye molecules adsorbed on the silver halide. Obviously, by this method, concentrations of some dyes can be applied to such media, which concentration could not be possibly achieved through application from aqueous or alcohol solutions.

In the preceding example, and in the preparation of the unsensitized evaporated film used therein, the highest purity materials obtainable were employed to insure that the effects noted were not due to unknown impurities.

The internal developer which is used as hereinbefore described is prepared and used as follows. Three stock solutions are prepared, preferably using triply-distilled water. These solutions are:

(a)		Grams
Metol	-----	0.50
Sodium sulphite (anhydr.)	-----	19.50
Hydroquinone	-----	1.87
in 250 cc. of water;		
(b)		Grams
Sodium carbonate (anhydr.)	-----	78.00
If monohydrate, use	-----	91.26
Potassium bromide	-----	2.0
in 1 liter of water		
(c)		grams
Gelatin	-----	1.25
Plus water to make 250 cc.		

Solution (a) decomposes with time, solution (b) keeps indefinitely, and solution (c) should be kept refrigerated to inhibit decomposition.

These solutions are used in equal proportions to make the developer. They are mixed by adding 20 ml. quantities of, first, solution (b) to solution (a), and then 20 ml. of solution (c) to the mixtures of solutions (a) and (b). To the mixture of (a), (b) and (c), 3 ml. of a 1% sodium thiosulfate solution is then added.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. A method of surface optical sensitization of microcrystalline binder-free silver halide photographic medium

comprising the steps of placing said medium in an evacuable region, reducing the ambient pressure in said region to a range of between approximately 1×10^{-1} to 1×10^{-6} mm. of mercury, vaporizing in said region a quantity of sensitizing dyestuff, condensing said vapor onto a surface of said medium, and applying water to the condensate on said surface.

2. A method of surface sensitizing as defined in claim 1 wherein said dyestuff is characterized by being vaporizable at temperatures substantially below 300° C. without substantial decomposition.

3. A method of surface sensitizing as defined in claim 1, wherein said dyestuff is a cyanine dye.

4. A method of surface sensitizing as defined in claim 1 wherein said dyestuff is pinacyanol.

5. A method of producing a photographic medium, comprising evaporating silver halide from a molten pool thereof and condensing the vapors upon the surface of a substrate material, under substantially stable conditions of temperature and pressure wherein said pressure is between about 10^{-1} and 10^{-6} mm. of mercury, to deposit a layer of silver halide to a thickness of a fraction of a micron, thereafter vaporizing a photographic sensitizing dyestuff and condensing the vapors thereof upon the surface of said layer of silver halide, and thereafter applying water to the surface having the dye deposited thereon.

6. A method as set forth in claim 5, wherein said thickness is between about 0.1 micron and 0.5 micron.

7. A method as set forth in claim 5, wherein said dyestuff is vaporizable at below 300° C. without substantial decomposition.

8. A method as set forth in claim 5, wherein said dyestuff is a cyanine dye.

9. A method as set forth in claim 5, wherein said dyestuff is pinacyanol.

10. A method of surface optical sensitization of a microcrystalline binder-free silver halide photographic medium comprising the steps of vapor depositing onto a surface of said medium a quantity of sensitizing dyestuff, and thereafter applying water to the deposit on said surface.

11. A method of producing a photographic medium, comprising evaporating silver halide from a molten pool thereof and condensing the vapors upon the surface of a substrate material, under substantially stable conditions of temperature and pressure, to deposit a layer of silver halide upon said substrate, thereafter vaporizing a photographic sensitizing dyestuff and condensing the vapors thereof upon the surface of said layer of silver halide, and thereafter applying water to the surface having the dye deposited thereon.

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