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PRODUCTION AND APPLICATION OF LAYERS SENSITIVE TO LIGHT

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The present invention relates to improvements in the production and application of layers sensitive to light.

The production of pictures which are built up from single, similar or dissimilar, picture elements such as elements of different colour and/or size has been effected hitherto by the aid of screens and/or, for correct colour reproductions, by the preparation of several component negatives with the aid of different filters and printing the component pictures in the corresponding colours onto a common substratum. Homogeneous light-sensitive layers are always employed for this purpose. In many cases, however, these processes are very troublesome in operation.

We have now found that the same results can be obtained in a much more simple manner by preparing layers which consist of small articles which contain substances having an equal or a different sensitivity to the different rays of light, or of mixtures of such particles in which different portions of the particles contain substances of a different sensitivity to the different rays of the spectrum, and also substances which are not sensitive to light such as water-insoluble dyestuffs, pigments, resins and the like. These particles are produced by dispersing into fine globular particles, in the dry or wet way, organic colloidal substances such as gelatine, collodion and the like, or solutions of the same, in which globular particles light-sensitive substances, such as metal halides for example light-sensitive silver or mercury compounds and at the same time substances which are not sensitive to light, such as water-insoluble dyestuffs, substances acting as pigments and resinous substances and the like are dissolved or suspended. The dispersion may be effected in any known or suitable manner either by atomization with air or by emulsification in any inert liquid, and in either of these manners small globules are formed. These small more or less solid globules are then spread out by spraying or sedimentation besides each other to form an inhomogeneous layer on a supporting sheet which is previously rendered sticky with respect to the said globules.

Such layers may be employed for different photographic purposes. In particular they may be employed for the preparation of printing papers, or of plates, such as lantern slides, showing pictures in natural colours, by applying beside one another on a substratum in the manner described the globules which contain substances light-sensitive for the fundamental colours and which are correspondingly coloured in the aforesaid manner or which are intermingled with pigments of the same corresponding shades which should be particularly fast to light.

In a similar manner the process may be employed for the preparation of anaglyphs. For this purpose layers of two kinds of globules are employed, each of which is sensitive to light in a different range of the spectrum and each of which is coloured complementarily to the other. Thus for example the one kind of globules contains a red pigment, and the other kind of globules contains a blue green pigment. The red globules contain a substance which for example is particularly sensitive to red light and the blue green globules contain one which is particularly sensitive to blue green light. If the two component pictures of a stereoscopic photograph are then printed onto such a layer in a suitable manner, for example one behind a red filter and the other behind a green filter or with red and green light respectively, two stereoscopic pictures are obtained after suitable treatment which are on the same substratum, each picture being built up of individual points of the picture which lie in between those of the other picture.

Further the process may be employed for the production of layers which give pictures capable of being etched and suitable for the preparation of printing blocks without the employment of a screen, the layers being produced from globules of the same kind which contain a light-sensitive substance for example silver bromide and also a substance not attacked by normal etching agents for example a pigment or a resin and also asphaltum.

After exposure and development of the latent image the production of the final pic-

ture can be performed in various manners. The development can be performed in such a manner that either the single globules the light sensitive components of which have been influenced by the exposure, are wholly removed from the layer—or only a part thereof corresponding to the action of the light—or the globules, the light sensitive components of which have not been influenced by the exposure are removed. A further method consists in removing the colouring material and free metal formed from globules which have been influenced by the light during the exposure.

Thus, for example, in the case of employing for building up the picture, only those parts of the layer which have been developed in the usual manner, or those parts which contain free metal after reversal of the image by removal of the originally formed metal and subsequent conversion of the remaining metal halide into free metal, a suitable method consists in hardening the globules containing the free metal wholly or partially, depending on the quantity of free metal contained therein. After development and fixation, the unhardened particles are removed, for example, by washing out in a manner similar to that employed in making the so-called carbon prints; the hardening can be performed, for example, with a dilute bichromate or with the hardening solutions usually employed in the brom oil printing process. In order to avoid the formation of a halo i. e. the extension of the hardening effect onto particles which do not contain free metal, it is advantageous to work at the lowest suitable temperature. Quinone is for example a good hardening agent for the aforesaid purpose. After hardening, the layer is transferred to another support and developed in the manner usually employed in the carbon printing process and at the lowest suitable temperature. Free metal which may be still present in the particles remaining on the support, or their fragments, is removed by any of the well-known agents for dissolving silver and also metal halide which might be formed during the hardening is removed by one of the usual fixing agents. According to the method of working a picture consisting of single coloured particles is formed which picture shows the complementary colours when a single primary development has been applied, or a picture showing a correct colour reproduction when the metal formed by a primary development has been removed and the metal halide still present has been converted into free metal.

If, however, those particles of the layer which do not contain free metal are desired to build up the picture, the particles which after exposure and development contain free metal are removed by etching together with the colouring matter contained therein in a quantity corresponding to that of the free metal contained therein. A suitable bath for etching consists of hydrogen peroxide, sulphuric acid, copper sulphate and a small quantity of potassium bromide, the relative proportion of the said ingredients being varied according to the requirements.

Another method, which is particularly suitable for layers consisting of such single particles which contain a colouring material which, however, can be dissolved or decomposed by chemical agents, consists in developing in such a manner that the metal is formed and that either simultaneously, or by chemical aftertreatment, a removal or decomposition of the colouring matter in the particles, which have been influenced by the light, is performed without the removal of the whole particles. This effect can be obtained by suitable developers which produce a porosity of the single particles, so that the colouring matter can be washed out through the pores or decomposed by a suitable solution entering the particles through the pores.

The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples.

Example 1

For the preparation of layers which will serve for making copies of coloured transparent pictures, for example of pictures made with the so-called colour screen plates, or films, such as "Autochrom" or "Agfa" plates, the following emulsion of silver halide and gelatine is made up. A solution of 64 grams of silver nitrate in 640 cubic centimeters of distilled water is introduced at 20° C., while stirring, at dark red light, within about 1 minute, into a solution of 24.3 grams of potassium bromide, 16 grams of potassium chloride and 0.8 gram of gelatine in 400 cubic centimeters of distilled water and 5 cubic centimeters of an alcoholic 1/1000 solution of Pinaflavol (Colour Index, 1924, No. 808a). Stirring is continued for about 5 minutes at the said temperature. The whole is then allowed to settle, and the precipitate is then washed three times by decantation with 1 litre of distilled water each time. The precipitate is then warmed to about 50° C. and is then emulsified by stirring for about 5 minutes in a mixture of 90 grams of gelatine with 200 cubic centimeters of distilled water and 200 cubic centimeters of an aqueous solution of Naphthol yellow (Colour Index, 1924, No. 682) which is saturated at about 20° C. A mixture of 10 grams of gelatine with 200 cubic centimeters of Helio fast pink RL, paste (10 per cent) (Colour Index, 1924, page 355) and 400 cubic centimeters of water is then stirred into the emulsion at about 50° C. 5 cubic centimeters of a 10 per cent aqueous solution of chromium alum are then added to the emulsion and the whole is made

up to 2 liters by the addition of distilled water. The resulting emulsion is green sensitized and contains a red pigment fast to light.

A solution of 64 grams of silver nitrate in 640 cubic centimeters of distilled water is stirred in the course of 14 minutes at about 20° C. at dark green light, into a solution of 53.2 grams of potassium bromide and 0.5 gram of gelatine in 400 cubic centimeters of distilled water and 3 cubic centimeters of a 1/1000 alcoholic solution of Pinacyanol blue (Colour Index, 1924, No. 808). Stirring is continued for about 10 minutes at the said temperature. The precipitate is allowed to settle and is then washed three times by decantation with 1 liter of distilled water each time. The precipitate is then warmed at about 50° C. and is then stirred into a mixture of 70 grams of gelatine in 150 cubic centimeters of an aqueous solution of Naphthol yellow which is saturated at about 20° C. The mixture is then stirred at about 50° C. for 10 minutes, whereupon a mixture of 10 grams of gelatine with 75 cubic centimeters of a saturated aqueous solution of Naphthol yellow, 160 cubic centimeters of water and 270 cubic centimeters of an aqueous 9 per cent paste of Indanthren blue 8 GK (Colour Index, Supplement, page 43) is added at about 50° C. while stirring. 5 cubic centimeters of a 10 per cent aqueous solution of chromium alum are then added to the emulsion which is made up to 1.2 liters by means of water. This red-sensitized emulsion contains a blue pigment dyestuff.

A solution of 64 grams of silver nitrate in 640 cubic centimeters of distilled water is quickly stirred at 20° C., at dark red light, into a solution of 53.2 grams of potassium bromide and 0.4 gram of gelatine in 425 cubic centimeters of distilled water. The mixture is stirred at 20° C. for about 10 minutes. The precipitate is then allowed to settle and it is washed three times by decantation with 1 liter of distilled water each time, whereupon the precipitate is warmed to 50° C., mixed with a solution of 4 grams of potassium bromide in 20 cubic centimeters of distilled water and then emulsified with a solution of 60 grams of gelatine in 400 cubic centimeters of distilled water. The whole is then stirred at about 50° C. for half an hour. A mixture of 10 grams of gelatine with 200 cubic centimeters of a 9 per cent aqueous paste of Algol yellow GC paste (Schultz, Farbstofftabellen, 7th Ed., No. 1249) and 100 cubic centimeters of water is then added while stirring at 50° C. 6 cubic centimeters of a 10 per cent aqueous solution of chromium alum is then added to the emulsion and the whole is made up to 1.2 liters by means of water. The resulting emulsion contains a yellow pigment dyestuff. One after another these three emulsions are sprayed at about 40° C. in the form of very fine droplets by means of an atomizing apparatus into a tower of about 3 or 4 meters height wherein the droplets are dried at about 80° C. by a stream of hot air while still in flight. The powders thus obtained which consist of globules of from 0.01 to 0.05 millimetre in diameter are mixed in such proportions that a colour as near as possible to a dark, neutral grey is obtained, and the mixture is then spread out to a uniform layer on a sticky substratum, such as caoutchouc applied to the surface of paper, glass, celluloid acetyl cellulose or the like, which latter may be provided with a superficial layer of barytes. Instead of Helio fast pink, carmine (Colour Index 1924, No. 1239) may be employed. Instead of Indanthren blue 8 GK, Brilliant indigo 4 G (Colour Index, No. 1189) or Indanthren brilliant blue 3 G (Colour Index, supplement, page 43) may be used, and instead of Algol yellow GC, Indanthren yellow G (Colour Index, 1924, No. 1118) may be employed.

Example 2

In a similar manner, globules which have been prepared from pigment and silver bromide and gelatine for example as described in Example 1 may be employed for the preparation of anaglyphs. Silver halide collodion emulsions may, however, also be employed. A silver bromide collodion emulsion which has been rendered sensitive to red in any known or suitable manner for example with Pinacyanol blue (Colour Index, 1924, No. 809) and the blue sensitivity of which has been repressed, if desired by a yellow dyestuff, for example Naphthol yellow, is coloured red with the aid of a red pigment or the like. Likewise an emulsion which has been rendered sensitive to green with pinaflavol is coloured blue green with the aid of a blue green pigment or the like. The two emulsions are atomized and the powders obtained are mixed in equal proportions and the mixture is spread out on a substratum.

Example 3

For the preparation of a layer to be used for the manufacture of printing blocks, a silver bromide gelatine emulsion is very intimately mixed with very fine asphalt powder and atomized in any known or suitable manner. The powder obtained is applied onto the substratum as described in Example 1.

Example 4

A latent image obtained with a layer prepared in accordance with Examples 1 or 2 and consisting of a mixture of single particles of gelatine containing silver bromide the chromatic sensitivity of which is different, and which contain besides the silver bromide fragments, a corresponding different colouring matter is developed with a suitable non-

tanning developer, for example, with iron oxalate or amidol-sulphite after the layer has been superficially hardened in a bath of ethyl alcohol. After fixation in a weakly acid bath and rinsing, the gelatine particles containing free silver, are hardened in a bath consisting of 2 grams of quinone, 10 grams of potassium bromide and 300 cubic centimetres of distilled water. The layer is then transferred onto a suitable support in the manner usually employed in carbon printing and developed on the said support with water at the lowest suitable temperature, which depends on the nature, i. e. on the flow-point, of the gelatine employed.

Example 5

If the particles which are free from metallic silver in a layer as described in the foregoing example and exposed, are to be employed for building up the final picture the development can be performed in the following manner. After bathing the layer containing the latent image for about 20 seconds in pure 96 per cent ethyl alcohol and carefully drying the latent image is developed by means of a developer which, however, must not give a picture by itself other than the silver picture as is the case with pyro, a usual developer solution of glycin or iron oxalate being applicable. After short rinsing a bath consisting of a weakly acid 10 per cent thiosulphate solution to which have been added each 10 cubic centimetres of a 10 per cent chromium alum solution per each 1000 cubic centimetres, is applied for about 5 minutes for fixation, whereupon the layer is rinsed again for from 5 to 10 minutes in running water or in fresh water for several times. After carefully drying an etching solution is applied consisting of 30 cubic centimetres of water, 15 cubic centimetres of a 10 per cent solution of copper sulphate, 5 cubic centimetres of 10 per cent sulphuric acid, 10 cubic centimetres of a 3 per cent solution of hydrogen peroxide and 2 drops of a 10 per cent solution of potassium bromide, while slightly moving the etching liquid to and fro. Silver, gelatine and pigment are dissolved from the particles or the parts thereof containing free silver. After etching is finished the layer is rinsed for a short time and silver bromide which may be formed by the action of the etching solution is removed by fixation with the above mentioned fixing bath. After rinsing for about 10 minutes the picture can be dried.

Example 6

In the development of a latent image from a layer prepared in the aforedescribed manner, the single particles of which consist, however, of collodion instead of gelatine and which contain a colouring matter, which is insoluble in water, but soluble for example in alcohol, the following method can be employed. The latent image is developed with a caustic developer, for example, with a developer containing pyrocatechin and caustic soda, whereby the collodion becomes porous of those particles or the parts thereof in which metallic silver has been produced by the development. The porosity can be increased by conversion of the silver, for example, into silver sulphide in the usual manner. The colouring material contained in the porous particles or in the porous parts thereof, is then washed out from the particles in a proportion corresponding to the quantity of metallic silver or silver sulphide present by means of suitable agents which do not dissolve collodion for example with commercial ethyl alcohol. The metallic silver sulphide is then removed in the usual manner.

Example 7

For the preparation of printing blocks a layer is prepared consisting of particles of an emulsion containing silver bromide, gelatine and very finely dispersed asphaltum. The layer is exposed and developed and then etched in the manner described in Example 5. After transferring the picture onto a metal sheet, such as zinc, it is dried and slightly heated until it sticks uniformly to the metal sheet. The picture thereon consists of single small particles of asphaltum and the etching of the metal sheet can be performed in any convenient method usually applied for such purposes.

What we claim is:

1. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance, each with a light-sensitive silver halide which is differently and particularly sensitive to the different rays of light for each portion of the colloidal substance, thus forming a plurality of photographic emulsions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules.

2. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance each with a light-sensitive silver halide which is differently and particularly sensitive to the different rays of the spectrum for each portion of the colloidal substance, thus forming a plurality of photographic emulsions, in-

corporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules.

3. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance each with a light-sensitive silver halide which is differently and particularly sensitive to a certain spectral range for each portion of the colloidal substance, thus forming a plurality of photographic emulsions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules.

4. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance each with a light-sensitive silver halide which is differently and particularly sensitive to a certain spectral range for each portion of the colloidal substance, thus forming a plurality of photographic emulsions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, said colouring matter having a shade complementary in each case to each of the said spectral ranges, respectively, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules.

5. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance each with a light-sensitive silver halide which is differently and particularly sensitive to a particular colour, complementary in at least two of said portions of the colloidal substance, thus forming a plurality of photographic emulsions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules.

6. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance each with a light-sensitive silver halide which is differently and particularly sensitive to a particular colour complementary in at least two of said portions of the colloidal substance, thus forming a plurality of photographic emulsions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, said colouring matter having a shade complementary in each case to each of the said complementary colours, respectively, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules.

7. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance each with a light-sensitive silver halide which is differently and particularly sensitive to the different rays of light for each portion of the colloidal substance, thus forming a plurality of photographic emulsions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules, exposing said layer to the action of light, developing the latent image, thereby forming particles containing free silver and particles containing unaltered silver halide, and removing one of these groups of particles.

8. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance, each with a light-sensitive silver halide which is differently and particularly sensitive to the different rays of light for each portion of the colloidal substance, thus forming a plurality of photographic emul-

sions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules, exposing said layer to the action of light through a coloured transparent picture, developing the latent image, thereby forming particles containing free silver and particles containing unaltered silver halide, and removing one of these groups of particles.

9. The process for the production and application of layers sensitive to light, which comprises incorporating a plurality of portions of a liquefied organic colloidal substance each with a light-sensitive silver halide which is differently and particularly sensitive to the different rays of light for each portion of the colloidal substance, thus forming a plurality of photographic emulsions, incorporating each of the said photographic emulsions with a different, finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, dispersing each of the said photographic emulsions separately into fine globular particles and spreading the resulting globules to form an inhomogeneous light-sensitive layer onto a substratum having a superficial layer which is sticky with respect to the said globules, exposing said layer to the action of light, developing the latent image, thereby forming particles containing free silver and particles containing unaltered silver halide, and removing the portion of the said particles which contains free silver by treatment with an agent dissolving the said metal.

10. As a new article of manufacture, an inhomogeneous, light-sensitive layer comprising, on a substratum which is sticky to the said layer, single globules of an organic colloidal substance, part of said globules containing a silver halide particularly sensitive to certain rays of light and a finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, and at least one other part of the said globules containing a silver halide which is particularly sensitive to other rays of light and another finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, and having a shade different from that of the other colouring matter.

11. As a new article of manufacture, an inhomogeneous, light-sensitive layer comprising, on a substratum which is sticky to the said layer, single globules of an organic colloidal substance, part of said globules containing a silver halide particularly sensitive to a certain spectral range and a finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, and at least one other part of the said globules containing a silver halide which is particularly sensitive to another spectral range and another finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, and having a shade different from that of the other colouring matter.

12. As a new article of manufacture, an inhomogeneous, light-sensitive layer comprising, on a substratum which is sticky to the said layer, single globules of an organic colloidal substance, part of said globules containing a silver halide particularly sensitive to a certain spectral range, and a finely divided water-insoluble colouring matter indifferent to light and practically insert to the said silver halide, said colouring matter having a shade complementary to the said spectral range, and at least one other part of the said globules containing a silver halide which is particularly sensitive to another spectral range and another finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, which latter colouring matter has a shade complementary to the spectral range to which the silver halide contained in this other part of globules is particularly sensitive.

13. As a new article of manufacture, an inhomogeneous, light-sensitive layer comprising, on a substratum which is sticky to the said layer, single globules of an organic colloidal substance, part of said globules containing a silver halide particularly sensitive to a certain spectral range, and a finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, said colouring matter having a shade complementary to the said spectral range, and at least one other part of the said globules containing a silver halide which is particularly sensitive to another spectral range and another finely divided water-insoluble colouring matter indifferent to light and practically inert to the said silver halide, which latter colouring matter has a shade complementary to the spectral range to which the silver halide contained in this other part of globules is particularly sensitive, the particular sensibilities of the different silver halides and the shades of the colouring matters covering at least the blue, green and red ranges of the spectrum.

In testimony whereof we have hereunto set our hands.

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