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PROCESS FOR THE PRODUCTION OF NON-LATERALLY REVERSED POSITIVE COPIES BY HEAT DEVELOPMENT

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8 Claims. (Cl. 96—29)

The present invention relates to a process for the production of non-laterally reversed positive copies and more especially to a process in which a silver halide layer is developed with a silver halide developing substance and in which the developer substance contained in the unexposed areas of the silver halide layer is transferred to a second layer, which is brought in contact with the first layer and which contains one or more substances which are insensitive to light and which produce colored compounds with the said developer substances preferably at elevated temperatures.

It has been found that the image in the transfer layer can be obtained by producing sulphur dyestuffs. For forming the sulphur dyestuffs, it is possible to employ all processes which are known for this purpose and which operate at temperatures such as those usually employed in the heat development. The color shades of the resulting images vary according to the developer substance which is used. The depth of color and tone of the dyestuffs can be influenced by adding heavy metal salts, such as copper sulphate, zince sulphate, ferric nitrate, alum, cerium nitrate, uranium nitrate, Reinecke salt

$$[Cr(NH_3)_2(SCN)_4].NH_4.H_2O$$

and others or amines, such as aromatic mono- and polyamines, which may be substituted as for instance aniline, toluidine, xylidine, m-phenylendiamine, m-toluylendiamine, asym. dimethyl-p-phenylendiamine, 4,4'-diaminodiphenyl, 3,3'-dimethoxy-4,4'-diaminodiphenyl, 1,4-naphthylendiaminesulfat, 2,6-naphthylen-diamine. For the production of the negative layer, it is possible to use any silver halide emulsion, such as for example silver chloride, silver bromide and silver iodide emulsions, even admixed as desired with one another, of high or low sensitivity, with any desired gradations and also with normal, high or low silver content. Added to these negative emulsion layers to serve as developer substances are aromatic amino or hydroxy compounds or aminohydroxy compounds, and also amino or hydroxy compounds or aminohydroxy compounds of diphenylamines, and diphenyls.

The transfer layer contains compounds which easily split off sulfur at temperatures of about 80–150° C., such as ammoniumsulfide, metal sulfides as for instance alkali and alkaline earth sulfides (sodiumsulfide, calciumsulfide), ironsulfide, zincsulfide, cadmiumsulfide, aluminiumsulfide (that is to say such metal sulfides are of special advantage which are soluble in mineral acids, such as 10% hydrochloric acid), ammoniumpolysulfides, sodiumpolysulfides, calciumpolysulfides (Na_2S_2, Na_2S_7, CaS_2, CaS_7) or other alkali or alkaline earth polysulfides, polythionates, such as sodium trithionate, bariumtrithionates, Wackenroder's solution and salts derived from said solution, such as potassium tetrathionate and pentathionate, and furthermore organic compounds such as thioamides, especially thiourea, thiobenzamide, and thioacetamide. In order to accelerate the decomposition there may be added basic or acid substances to the layer. The sulfur

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compounds are preferably applied in quantities amounting to about 15 and 50 g. per litre of solution of binding agent for the transfer layer.

As a binding agent for the transfer layer and for the silver halide layer there may be used gelatine, polyvinylalcohol, polyvinylpyrrolidone, celluose derivatives, alginates, mixtures of said substances or other natural or synthetic film forming substances which are swellable in water. To the solutions which are used for the preparation of the transfer layers there are added with advantage compounds which are capable of forming water-containing crystals, such as sodiumacetate, trisodiumphosphate, sodiumsulfate. In this case the solutions must contain sufficient water so that after evaporation the transfer layer contains a certain quantity of crystal water. The compounds may also be added to the silver halide emulsion layer. Instead of or together with the above compounds there may be added glycerine, glycols or corresponding hygroscopic substances to the transfer layer and/or to the silver halide emulsion layer. The quantities of said compounds may vary within wide limits according to the nature of the substances actually used. Sodium acetate may for instance be used in quantities of about 5–150 g. per litre of silver halide emulsion or solution for the preparation of the transfer layer. The glycerine and the other compounds may be applied in corresponding quantities.

The heavy metal salts are preferably applied in quantities of about 5–20% by weight as calculated on the sulfur compounds. The developing substance is added to the silver halide layer preferably in quantities of about 8–20 g. per litre of silver halide emulsion. The pH of the emulsion is preferably kept between 5.0 and 6.5.

For certain purposes, it can be advantageous for the transfer paper to be coated on both sides, it being possible for the positive paper to be arranged between two negative papers during the heat development, so that a double-sided copy is obtained in a single operation.

For carrying out the process the silver halide layer is exposed to an object to be reproduced and thereafter brought in contact with the transfer layer. The combined layers are then heated for about 10–60 seconds to a temperature of about 80–150° C., preferably 110–135° C., whereby the transfer layer may be heated to a somewhat lower temperature than the negative layer, such as 90–110° C. Hot presses, high-glaze presses which can be heated electrically, drying drums and the like are suitable for the development and simultaneous image transfer. After separating the two layers a laterally correct color reproduction of the original to be reproduced is obtained.

EXAMPLE 1

Negative material

10 g. of the hydrochloric acid salt of 4-aminophenol, 100 g. of sodium acetate and 150 cc. of water are added to 1 litre of any desired silver halide emulsion. Other additives known in the emulsion art can be used. The emulsion is cast on to paper or any other conventional support and dried.

Positive (Transfer) material

20 g. of sodium sulphide are dissolved in 500 cc. of water and made up with a 10% aqueous solution of polyvinyl alcohol to 1000 cc. The solution is cast on to paper or any other suitable layer support and dried.

After exposure, the negative paper is brought into contact with the positive paper. The two papers are then subjected for 10 to 60 seconds to a temperature of 135 to 150° by means of a glazing press or two flat-irons. The positive paper can be heated to a lower temperature.

A reddish-brown image is obtained in the positive layer when the two layers are separated.

EXAMPLE 2

Negative material

The additives referred to in Example 1 can be used for the negative material.

Positive material

20 g. of sodium trithionate, 10 g. of sodium acetate and 2 g. of Reinecke salt are dissolved in 600 cc. of water, and 300 cc. of a 10% aqueous solution of polyvinyl alcohol and 100 cc. of glycerine are added thereto. The solution is cast on to a suitable support and dried.

The processing takes place as indicated in Example 1 and a positive image of brown to brownish-violet color is obtained.

EXAMPLE 3

Negative material

10 g. of p-methylaminophenol sulphate and 100 g. of sodium acetate dissolved in water are added to 1000 cc. of a silver halide emulsion. Other additives can be used. A silver halide layer is cast from said emulsion on a paper support.

Positive material

40 g. of sodium trithionate are dissolved in 600 cc. of water and 300 cc. of a 10% aqueous solution of polyvinyl alcohol and 100 cc. of glycerine are added thereto.

After proceeding as described in Example 1, a light brown image is obtained.

EXAMPLE 4

Negative material

10 g. of p-phenylene diamine dissolved in water, 100 g. of sodium acetate, 10 cc. of 40% citric acid and 20 cc. of 5% benztriazole or the corresponding amount of another stabilizer are added to 1 litre of a silver halide emulsion. A layer is cast from said emulsion onto a paper support.

Positive material

The layers described in Example 1, 2 or 3 can be used.

After processing as described in Example 1, a violet to dark blue image is obtained, depending on the conditions.

EXAMPLE 5

Negative material

10 g. of 5-amino-2-cresol are dissolved in water and added to 1000 cc. of a silver halide emulsion, to which are then added 200 g. of sodium acetate. This emulsion is coated on a paper support and dried.

Positive material

As described in Example 1, 2 or 3. The positive obtained after processing as described in Example 1 is light brown in color.

EXAMPLE 6

Negative material

10 g. of 3-chloro-4-aminophenol are added to 1000 cc. of a silver halide emulsion. 100 g. of sodium acetate dissolved in a little water are added thereto. This emulsion is cast on a paper support and dried.

Positive material

As in Example 1, 2 or 3.

A greyish brown image is obtained after processing as in Example 1.

EXAMPLE 7

Negative material

10 g. of 2,5-toluylene diamine are dissolved in water and added to 1000 cc. of a silver halide emulsion. 150 g. of sodium acetate, 10 cc. of 40% citric acid and 20 cc. of 5% benztriazole are added thereto. This emulsion is cast on a paper support and dried.

Positive material

As described in Examples 1, 2 and 3. A red dyestuff image is obtained after processing as described in Example 1.

EXAMPLE 8

Negative material

10 g. of 2,5-diaminoanisole are dissolved in water and added to 1000 cc. of a silver halide emulsion, to which are then added 100 cc. of sodium acetate and 20 g. of benztriazole. This emulsion is cast on a paper support and dried.

Positive material

As in Example 1, 2 or 3.

A bright red image dyestuff is obtained after the processing as described in Example 1.

EXAMPLE 9

Negative material

10 g. of 4-4-diaminodiphenylamine hydrochloride are dissolved in water and added to 1000 cc. of any desired silver halide emulsion. 100 g. of sodium acetate, 10 cc. of 40% citric acid and 20 cc. of 5% benztriazole are then added to the emulsion. This emulsion is coated on a paper support and dried.

Positive material

As in Example 1, 2 or 3.

A bluish-violet dyestuff image is produced after processing as in Example 1.

EXAMPLE 10

Negative material

As described in Example 3.

Positive material

A solution is prepared containing 40 g. of sodium trithionate, 5 g. of 1,3-phenylene diamine, 1 g. of ferric chloride, 600 cc. of polyvinyl alcohol and 100 cc. of glycerine. This solution is coated on a paper support and dried.

After processing as described in Example 1, a violet dyestuff image is obtained.

EXAMPLE 11

Negative material

8 g. of pyrocatechol dissolved in water, 200 g. of hydrated sodium acetate crystals and 15 cc. of benztriazole (5%) or other stabilizers are added to one liter of silver halide emulsion. This emulsion is cast on a paper support and dried.

Positive material

30 g. of thiourea are dissolved in water and added to 500 cc. of an aqueous polyvinyl alcohol solution (10%). Thereupon 10 g. of sodium carbonate and 100 cc. of glycerine are added.

After processing as in Example 1 a laterally non-reversed dyestuff image of the original is obtained.

EXAMPLE 12

Negative material

10 g. of 3-hydroxy-4-aminidiphenylamine hydrochloride are dissolved in water and added to 1000 cc. of a silver halide emulsion. 115 g. of sodium acetate and 15 cc. of benzotriazol (5%) or the equivalent amount of another stabilizer are added to the emulsion. This emulsion is cast on a paper support and dried.

Positive material

A solution of 15 g. of thioacetamide, 1 g. of copper sulfate and 100 cc. of glycerine are added to 700 cc. of polyvinyl alcohol.

After proceeding as described in Example 1 a dark colored positive image is obtained.

What we claim is:

1. Process for the production of non-laterally reversed photographic sulfur-dyestuff images without the use of treating baths, said process being characterized by the steps of providing a light-sensitive solid silver halide emulsion layer that contains an organic silver halide developer selected from the class consisting of aromatic amino and aromatic hydroxy developers which forms a sulfur-dyestuff when heated to from 80 to 150° C. with a compound splitting off sulfur, providing a separating supported transfer layer containing a compound which splits off sulfur at a temperature of about 80 to 150° C., at least one of said layers containing hydrated material that liberates sufficient moisture on heating to 80 to 150° C. to facilitate transfer between the layers, photographically exposing the emulsion layer, contacting the exposed emulsion layer with the transfer layer, and subjecting said combined layers to a heat treatment at a temperature of about 80 to 150° C., to cause only said organic developer to transfer from the unexposed places of said silver halide layer into said transfer layer and react in the transfer layer to form a positive sulfur-dyestuff image of the original to which the silver halide layer was exposed, and thereafter separating said two layers.

2. Process according to claim 1, wherein the hydrated material is a hydroscopic substance.

3. Process according to claim 1, wherein the hydrated material has molecules of water of crystallization therein.

4. Process according to claim 1, wherein the transfer

layer contains a heavy metal salt that changes the color of the sulfur-dyestuff image.

5. Process according to claim 1 wherein the heat treatment takes place at a temperature of between about 110 and 135° C. and is maintained for a period of between about 10 and 60 seconds.

6. Process according to claim 1 wherein the pH of the silver halide emulsion layer is about 5 to 6.5.

7. Process according to claim 1 wherein said silver halide developer is present in the silver halide emulsion in an amount corresponding to 8 to 20 g. per liter of that emulsion.

8. Process according to claim 1 wherein the transfer layer contains an amine selected from the class consisting of aniline, toluidine, xylidine, m-phenylenediamine, m-toluylendiamine, asym. dimethyl-p-phenylendiamine, 4,4'-diaminodiphenyl, 3,3'-dimethoxy-4,4'-diaminodiphenyl, 1,4-naphthylendiaminesulfat, 2,6-naphthylen-diamine.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,971,840 February 14, 1961

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It is hereby certified that error appears in the above numbered pat-
nt requiring correction and that the said Letters Patent should read as
orrected below.

Column 4, line 26, for "4-4-diaminodiphenylamine" read -- 4,4'-diaminodiphenylamine --.

Signed and sealed this 3rd day of October 1961.

SEAL)

ttest:

RNEST W. SWIDER
ttesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC