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HEATED DIFFUSION TRANSFER USING LEUCOPHTHALOCYANINES

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9 Claims. (Cl. 96—29)

The invention relates to a process and materials for the production of non-laterally reversed images, using a supported photosensitive silver halide emulsion layer which contains developer substances and which is subjected to heat development while in contact with a transfer material.

It is known from German Patent No. 888,045 to develop exposed silver halide emulsion layers containing reducing substances, by heating. In accordance with German Patent No. 895,101, this dry developing process can be combined with a transfer process in which silver salts or, in particular, developer substances are transferred to a transfer material in contact therewith. The transfer layer contains substances which are insensitive to light and which produce colored compounds by reaction with the developer. Since only the unexposed areas of the exposed light-sensitive material contain unused developing agents which are transferred, the resulting print is a non-laterally reversed positive image of the original. These known processes have limited utility because of the depth of color and the stability to light of the resulting copies are unsatisfactory.

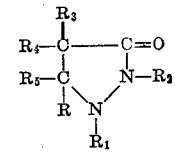
The principal object of the present invention is to provide photographic processes for the production of photographic images which are deeply colored and are stable to light by development with heat and photographic materials for use in such processes. Other objects and advantages of the process, some of which are referred to specifically hereinafter, will be evident to those skilled in the art to which this invention pertains.

This object has been achieved by employing light-sensitive materials, which contain a light-sensitive silver halide emulsion layer containing one or more developing agents of the 3-pyrazolidone series. After imagewise exposure the light-sensitive material is brought into contact with a transfer material which contains a leucophthalocyanine. Both materials while maintained in intimate contact are subjected to a temperature between 80 and 200° C., preferably between 110 and 170° C., for a period of time between ½ second and 3 minutes, preferably between 1 and 30 seconds. During this treatment the silver halide in the exposed areas of the light-sensitive layer is developed to form a negative silver image and the 3-pyrazolidone developing agent of the unexposed areas of the light-sensitive layer, which remained unused, is transferred into the adjacent areas of the transfer material. The transferred 3-pyrazolidone reduces the leucophthalocyanine that is present in the transfer material thereby forming a deeply colored, positive phthalocyanine dye image, which does not fade even if exposed to sunlight.

In some cases it has proved to be advantageous to develop the light-sensitive material alone by application of heat and to bring it into contact with the transfer material and a second processing.

All diffusible substances of the 3-pyrazolidone series which are active as developers on heating and at a relatively low pH-value between 4.5 and 6.5 preferably 4.9 and 5.6 can be used as developing agents for the process according to the invention. The properties of the developing agent can be modified within certain limits by substituents on the pyrazolidone ring, thereby obtaining the

most suitable compound for the particular reproduction process in which the light-sensitive material containing that developing agent is to be used. 3-pyrazolidones of the following formula exhibit particular utility:



wherein R_1 represents hydrogen, alkyl having up to 5 carbon atoms, or aryl, preferably a phenyl radical which may be substituted, for example, with lower alkyl or alkoxy groups having up to 3 carbon atoms or halogen such as chlorine or bromine; R_2 represents hydrogen or an acyl group, preferably a lower aliphatic acyl group such as acetyl or propionyl; R_3, R_4, R_5 and R_6 represent hydrogen, an alkyl having up to 5 carbon atoms, aryl preferably a phenyl radical which can be substituted with alkyl or alkoxy having up to 3 carbon atoms or halogen such as chlorine or bromine.

The following are in particular suitable:

1-phenyl-3-pyrazolidone,
1-m-toluyl-3-pyrazolidone,
1-p-toluyl-3-pyrazolidone,
1-phenyl-4-methyl-3-pyrazolidone,
1-phenyl-5-methyl-3-pyrazolidone,
1,4-dimethyl-3-pyrazolidone,
4-methyl-3-pyrazolidone,
4,4-dimethyl-3-pyrazolidone,
1-phenyl-2-acetyl-3-pyrazolidone,
1-phenyl-4,4-dimethyl-3-pyrazolidone,
1(4-bromophenyl)-3-pyrazolidone.

The above compounds can be prepared by the processes described in British Patents Nos. 679,677 and 679,678 in which the "phenimines," which can be prepared by reacting acrylonitrile derivatives with the corresponding hydrazine compounds, are saponified to the 3-pyrazolidone.

3-pyrazolidones may also be prepared by the process described in British Patent No. 703,669, in which the final products are obtained by condensation of esters of acrylic acid or their derivatives with hydrazines. This process is particularly suitable for reaction with unsubstituted hydrazine. The resulting 3-pyrazolidones, which are oily materials, can be obtained as crystalline compounds by converting them into the hydrochlorides.

The preparation of 4,4-dialkyl-3-pyrazolidone is described in U.S. Patent No. 2,772,282. In this process, 2,2-dialkyl-beta-chloropropionic acid chloride is reacted with hydrazines.

The 3-pyrazolidones are added to the casting solution for the light-sensitive silver halide emulsion layer, in the form of free bases or in the form of their salts, with preferably inorganic acids such as hydrochloric acid or sulfuric acid. If salts are employed, the 3-pyrazolidone is liberated by the sodium acetate present in the layers and is enabled to develop exposed silver halide.

The developer is added to the silver halide emulsion layers in concentrations of about 2.5 to 20 g. per liter of casting solution, which corresponds to a concentration of between 0.1 and 2.0 g. per square meter of the dried light-sensitive layer.

By the term "leucophthalocyanines" is to be understood in this connection colorless or only slightly colored compounds which are composed of four isoindolenine units arranged in a true phthalocyanine structure and which produce on reduction a phthalocyanine dye. The leucophthalocyanines according to the foregoing definition can be used in the metal-free form or in the form of com-

plexes with metals that form phthalocyanine complexes, such as cobalt, nickel, copper or zinc. The metal complexes in particular those with cobalt are preferred. This term includes compounds which are known as "phthalocyanine-precursors," a term which has been used by B. R. A. Brooks, J. G. Burt, B. F. Skiles and M. S. Whelen, J. Org. Chem., vol 24, page 383 (1959), for those leucophthalocyanines which are not prepared from phthalocyanines. In Ullmanns Encyklopaedie der Technischen Chemie, third edition, vol. 13, the term "phthalocyanine-metal-complexes" is used to designate the same compounds which are referred to herein as "leucophthalocyanines." In U.S. Patent No. 2,772,285, R. A. Brooks uses the term "leucophthalocyanine" to refer in a restricted sense to the copper complexes of leucophthalocyanines, which are described therein.

The leucophthalocyanines can be produced, for example, by first preparing a phthalocyanine, e.g., a phthalocyanine containing no metal or containing cobalt, nickel, copper or zinc, and then attaching additional groups thereto under oxidizing conditions or by heating a reaction mixture which is suitable for the preparation of a phthalocyanine to a temperature below that required for forming the phthalocyanine, or by eliminating the reduction potential required for the formation of a phthalocyanine.

Combined processes have also been described, in which a phthalocyanine is first formed which is then further converted, within the same reaction mixture, to the leuco stage. Alternatively, a complex-forming metal atom can be introduced into a leucophthalocyanine containing no metal, or a metallic leucophthalocyanine can be prepared from a phthalocyanine free from metal. The leucophthalocyanines can be modified in their structure or solubility by subsequent treatments without thereby losing their essential property of being convertible into a phthalocyanine by reduction. In principle, all leucophthalocyanines, regardless of the method by which they have been prepared, are suitable for the copying process according to the invention.

Cobalt leucophthalocyanines are particularly suitable because they are only very slightly colored. Copper or nickel leucophthalocyanines have a yellowish or brownish tinge. Particularly to be mentioned are cobalt leucophthalocyanines of the type Phthalogen Blue IB (trade name of the Farbenfabriken Bayer AG) which has been described in the Zeitschrift für Angewandte Chemie, vol. 68, page 145 (1956), and which is regarded as a leucophthalocyanine-cobalt-ethylenediamine complex.

Other suitable diamines or polyamines such as:

1,2-propylenediamine,
1,3-propylenediamine,
N-monoethyl-1,3-propylenediamine,
N-(2-hydroxyethyl)ethylenediamine,
N-methyl-N-(2-hydroxyethyl)propylenediamine,
N,N-diethyl ethylenediamine,
N,N-di(2-aminoethyl)ethylenediamine,
N,N'-di(2-aminoethyl)ethylenediamine, or
N,N-di(2-(2-aminoethyl)aminoethyl)amine,

or monoamines such as:

n-octadecylamine
NH_3
N-propylamine
N-butylamine
iso-butylamine
dodecylamine
tetradecylamine
hexadecylamine
octadecylamine
N-diethylstearylamine
allylamine
diallylamine
diethylamine
di-N-propylamine
di-N-butylamine
N,N-dimethyl-ethylendiamine, or
tetramethylethylendiamine
1-amino-3-methylaminopropan
di-(2-aminoethyl)-amine
3-dimethylaminopropylamine
3-diethylaminopropylamine
tetramethylendiamine
hexamethylendiamine
tetraethylenpentamine
di(3-amino-propyl)-amine
1-diethylamino-4-amino-pentane
di(3-amino-propyl)-methylamine
N-methyl-N-(2-hydroxy-ethyl)-propylendiamine(1,3)
3-(2-ethylhexoxy)-propylamine-(1)
2-aminoethanol
N-methyl-aminoethanol
diethanolamine
3-methoxypropylamine-(1)
3-butoxypropylamine-(1)
1-aminobutanol-(3)
1-aminobutanol-(4)
2-amino-2-methyl-propandiol-(3)

may be used as ligands instead of ethylenediamine in the foregoing leuco complex. Especially suitable are, for example,

stearylamine
N-methyl-N-(2-hydroxyethyl)-1,3-propylenediamine

NH_3
dodecylamine
tetradecylamine
hexadecylamine
octadecylamine
3-(2-ethylhexoxy)-propylamine-(1)
1-aminobutanol-(4).

The solubility of the metal leucophthalocyanine, for instance, of cobalt leucophthalocyanine, depends on the type of amine used.

In the reduction of the leucophthalocyanines constituents, for example, the constitutents referred to hereinbefore can be split off.

Suitable solvents for the leucophthalocyanine are inorganic or organic acids such as amidosulfonic acid, orthophosphoric acid, acetic acid, propionic acid, lactic acid amides such as dimethylformamide, pyrrolidone and N-methylpyrrolidone, alcohols such as methanol, propanol, benzyl alcohol ethylene glycol, ethylene glycol ethyl ether (ethoxy ethanol), polyethylenglycols, esters such as ethoxyethyl acetate, hydrocarbons such as benzene, toluene, chlorobenzene, cyclohexane and n-hexane, and mixtures of these solvents.

The transfer material may be saturated with these solutions or the solutions may be added to suitable solutions of film-forming binding agents with which the transfer material is then coated on one or both sides. The leucophthalocyanines may be emulsified in the solutions of binding agents using emulsifiers such as dinaphthylmethansulfonate, oleylalcoholglycolether, using mixing apparatus, vibrating mills and the like. The casting solutions may contain approximately 0.2 to 20 g. per liter of the leucophthalocyanine compound which corresponds to a concentration in the dried transfer material of between 0.01 and 1.0 g. per square meter. Particularly suitable as binding agents for these layers are cellulose derivatives, e.g., carboxymethyl cellulose, methyl cellulose, methylhydroxyethyl cellulose, polysaccharides and derivatives such as starch ethers, e.g., carboxymethyl starch, gallactomannan, alkali-metal salts of alginic acid, alginic acid esters, polyvinyl alcohol, polyvinyl acetate and gelatine, or mixtures of these binding agents.

The adhesion of the positive layer to the negative layer can be modified by the addition of suitable matting agents to the positive or negative layer so that the layers will

adhere firmly together without sticking. The following products exhibit particular utility: Kieselgur such as Superfloss (trade name of the firm Johns-Mansville International Co., New York), finely dispersed silicon dioxide, and silica aerogels such as Aerosil (trade name of the firm Degussa), Vulkasil (trade name of the firm Farbenfabriken Bayer AG) or hydrosols of silicic acids such as Syntharesin (trade name of the Farbenfabriken Bayer AG) and finely dispersed aluminum oxide and titanium dioxide. The addition of these products at the same time improves the whiteness of the image.

It has been found particularly advantageous to employ additional substances which provide a desired amount of moisture in the light-sensitive layer or the transfer layer during the heat development step. Such substances are compounds which split off water on heating or compounds which increase the residual moisture content of the layer. Compounds of the first mentioned type are urea, salts containing water of crystallization such as sodium citrate or preferably sodium acetate; compounds of the second mentioned type are, for example, polyhydric alcohols such as sorbitol, glycerol or polyethylene glycols. These compounds may be added in such quantities to the casting solution for the negative layer, that the dried layer contain between 0.1 and 25 g. per square meter thereof.

The negative and the transfer layers can be applied on any suitable support which is stable at the temperatures of heat development, e.g., paper, baryta-coated paper, film-forming synthetic polymers, such as polycarbonates, in particular of bis-hydroxyphenyl-alkanes, or polyesters of terephthalic acid and ethylene glycol, and also cellulose esters, textile fabrics or metal foils.

The light-sensitive silver halide emulsion layer may contain as light-sensitive silver salts silver chloride, silver bromide or mixtures thereof, if desired with an additional content of up to 5% of silver iodide. The concentration of silver is between 0.5 and 5.0 preferably between 1 and 2 g. per square meter of the dried layer. The light-sensitive layer may contain further additives normally used, such as sensitizing dyes or stabilizers.

According to a preferred embodiment of the instant invention antioxidants are added to the light-sensitive layers which contain the 3-pyrazolidene developing agents. Suitable antioxidants are, for example: alkali-metal sulfites or metabisulfites such as potassium metabisulfite or sodium sulfite, bisulfite compounds of ketones or aldehydes such as cyclohexanone bisulfite, or salts of hydroxylamine hydrochloride.

The light-sensitive layer has a pH-value between about 4.5 and 6.5, preferably between 4.9 and 5.6.

It has been found advantageous to heat the two materials during the heat development to different temperatures, so that the transfer material has a slightly higher temperature than the light-sensitive material.

EXAMPLE 1

Production of the light-sensitive material

30 g. of crystallized sodium acetate

($NaOOCCH_3 3H_2O$)

20 ml. of a 30% hydrosol of silicic acid with a surface of 200 square meters per gram, 0.5 g. of hydroxylamine hydrochloride and 8 g. of 1-phenyl-3-pyrazolidone are added to 1 liter of a silver halide emulsion, the silver halide of which consists of silver chloride. The pH is adjusted to 5.2 by the addition of acetic acid. The emulsion is applied in known manner to a support such as paper or a foil of a polymeric product and dried.

Production of the transfer material

15 g. of a cobalt leucophthalocyanine (the preparation of which is described at the end of this example) are dissolved in 100 ml. of a polyethyleneglycol having an average molecular weight of about 400, 10 ml. of acetic acid and 890 ml. of ethyl alcohol. A paper sheet is impregnated with this solution and dried.

After imagewise exposure to actinic light, the light-sensitive layer is brought into contact with the transfer material. Both layers are heated, while maintained in intimate contact, to a temperature between 110 and 170° C. for ½ to 10 seconds by means of a developing apparatus as described in Belgian Patent No. 628,174 or by means of a high gloss press or a drying drum. After separation of the papers, a blue image is obtained on a pale yellow background.

The cobalt leucophthalocyanine was prepared as follows:

50 g. of a crude product prepared according to Example 1 of German Patent No. 855,710 were converted into the nitrate by treatment with concentrated nitric acid, as described in German Patent No. 839,939. 16 g. of the dried nitrate were refluxed for 20 minutes with 15 g. stearylamine in 50 ml. of a benzine fraction having a boiling range from 100 to 150° C. Thereafter, the mixture was diluted with 750 ml. of the same benzine fraction, the resulting solution was filtered at 100° C. and stirred in the cold for several hours. The crystallized product was filtered by suction and dried. The reaction product, of which 27 g. were obtained, was dissolved in boiling ethanol, the solution was stirred in the cold, the crystalline product was filtered by suction and dried. 12 g. of an orange cobalt leucophthalocyanine were obtained.

EXAMPLE 2

Production of the light-sensitive material

30 mg. of 1-phenyl-5-mercaptotetrazole (as a 1% solution in ethyl alcohol), 25 g. of crystalline sodium acetate, 2 g. of potassium metabisulfite and 10 g. of 1-phenyl-4-methyl-3-pyrazolidone were added to 1 liter of a silver halide emulsion, the silver halide of which consists of 0.35 mol/l. of silver chloride, containing 0.1% of silver iodide. The pH is adjusted to 4.9 by the addition of sulfuric acid.

Transfer material

10 g. of Phthalogen Blue I.B. (trade name of Farbenfabriken Bayer AG) prepared according to Example 1 of DBP 940,164 are dissolved in 1 liter of a 6% aqueous solution of acetic acid. After the addition of 12 ml. of a 30% hydrosol of a silicic acid with a surface of 200 square meter per g., a paper is impregnated with this solution and dried.

The materials are processed as described in Example 1. A blue image of a pale yellow ground is obtained.

EXAMPLE 3

Production of the light-sensitive material

0.5 g. of benzotriazole (as a 5% solution in ethyl alcohol), 100 ml. of a 15% hydrosol of a silicic acid having a surface of 100 square meter per g., 15 g. of crystalline sodium acetate, 5 g. of potassium metabisulfite and 10 g. of p-toluene-3-pyrazolidone are added to 1 liter of a silver chloride emulsion. The pH is adjusted to 5.5 by the addition of citric acid. This emulsion is applied on a paper support and dried.

Transfer material

1 g. of a cobalt leucophthalocyanine, prepared as described below, dissolved in 30 ml. of a polyethylene glycol having an average molecular weight of about 400, 2 ml. of lactic acid, 3 g. of tartaric acid and 5 ml. of a 30% aqueous solution of saponine are added to 1 liter of a 0.7% aqueous solution of gallactomannan, for example, Guar CSAA (trade name of Meypro A.G., Kreuzlingen, Switzerland). This solution is applied in known manner on a paper or a foil of a polymeric product and dried.

The materials are processed as described in Example 1. A blue image is obtained.

The cobalt leucophthalocyanine was prepared from the nitrate referred to in Example 1. 12 g. of this compound

were refluxed with 10 ml. N-methyl-N-(2-hydroxyethyl)-1,3-propylenediamine in 100 ml. of methanol until, after about 15 minutes, the reaction product was uniformly crystallized. The reaction mixture was filtered by suction and the residue washed with methanol and dried. 12 g. of orange yellow crystals were obtained.

EXAMPLE 4

0.5 g. of 4-hydroxy-6-methyl-1,2,3,a,7-tetraazaindene (as a 1% solution in ethyl alcohol), 50 g. of crystalline sodium acetate, 2 g. of potassium metabisulfite, 5 g. of cyclopentanone-bisulfite, 10 g. m-toluyl-3-pyrazolidone and 200 ml. of a 15% hydrosol of a silicic acid having a surface of 200 square meter per g. were added to 1 liter of a silver chloride emulsion. The pH was adjusted to 5.2 by addition of sulfuric acid. The emulsion is cast onto a paper support and dried.

Transfer material

4 g. of a cobalt leucophthalocyanine prepared according to Example 1 are dissolved in 40 ml. of a polyethylene glycol having an average molecular weight of about 400, 24 ml. of a 30% hydrosol of a silicic acid with a surface of 200 square meter per g., and 5 ml. of a 30% aqueous solution of saponine were added to 1 liter of a 5% aqueous solution of carboxy-methylcellulose. A paper is impregnated with this solution in known manner and dried. The materials are processed as described in Example 1. A blue image is obtained.

We claim:

1. A process for the production of a non-laterally reversed photographic image which comprises:

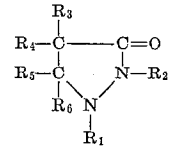
(a) exposing a light-sensitive silver halide emulsion layer upon a support to an original to be reproduced, said light-sensitive layer contains a 3-pyrazolidone developing agent in an amount between 0.1 and 2.0 g. per square meter of the light-sensitive layer;

(b) contacting the exposed layer with a light-sensitive transfer material which contains, in an amount between 0.01 and 1.0 g. per square meter of the transfer material, a leucophthalocyanine that is at most only slightly colored and is composed of 4 isoindolenine units which are arranged in a true phthalocyanine structure and which produce on reduction a phthalocyanine dye;

(c) heating the exposed layer and the transfer material while in intimate contact with each other to a temperature between 100 and 200° C. to cause the exposed portions of the light-sensitive layer to be developed to form a silver image, while the developer compound at the unexposed portions of the light-sensitive layer is transferred into the transfer material to produce a non-laterally reversed visible phthalocyanine dye image by reduction of the leucophthalocyanine in the transfer material;

(d) separating the developed layer from the transfer material.

2. A process as defined in claim **1** in which 3-pyrazolidone developing agent has the following formula:



in which R_1 is a radical of the group consisting of hydrogen, alkyl containing up to 5 carbon atoms and phenyl; R_2 is a radical of the group consisting of hydrogen and lower aliphatic acyl radicals having up to 5 carbon atoms; and R_3, R_4, R_5 and R_6 are each a radical of the group consisting of hydrogen and alkyl having up to 5 carbon atoms and phenyl.

3. A process as defined in claim **1** in which the light-sensitive silver halide emulsion layer contains 1-phenyl-3-pyrazolidone as developing agent.

4. A process as defined in claim **1** in which the light-sensitive silver halide emulsion layer contains 1-phenyl-4-methyl-3-pyrazolidone as developing agent.

5. A process as defined in claim **1** in which the light-sensitive silver halide emulsion layer contains 1-para-tolyl-3-pyrazolidone as developing agent.

6. A process as defined in claim **1** in which the light-sensitive silver halide emulsion layer contains 1-m-tolyl-3-pyrazolidone as developing agent.

7. A process as defined in claim **1** in which the transfer material contains a leucophthalocyanine having a central metal atom of the group consisting of cobalt, copper, nickel and zinc.

8. A process as defined in claim **3** in which the transfer material contains a cobalt leucophthalocyanine.

9. A process according to claim **1**, wherein the exposed light-sensitive silver halide emulsion layer is first heated, then contacted with the transfer material, then again heated, and then separated from the transfer material layer.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,335,006 August 8, 1967

Anita Von König et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 5 to 10, for the left-hand portion of the formula reading "R" read -- R_6 --; column 3, line 64, for "N-propylamine" read -- n-propylamine --; line 65, for "N-butylamine" read -- n-butylamine --; line 75, for "di-N-propylamine" read -- di-n-propylamine --; column 4, line 1, for "di-N-butylamine" read -- di-n-butylamine --; line 23, for "-propandiol-(3)" read -- -propandiol-(1,3) --; lines 46 and 47, for "lactic acid" read -- lactic acid, succinic acid, tartaric acid, p-toluene-sulfonic acid, acid --; column 5, line 43, for "3-pyrazolidene" read -- 3-pyrazolidone --.

Signed and sealed this 28th day of January 1969.

(SEAL)

Attest:

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