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3,433,634

DIFFUSION TRANSFER PROCESS

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The present invention relates to an improved silver halide diffusion transfer process. Photographic materials and treating compositions which enable the said improved process will be described more in detail further in the description.

It is an object of the present invention to obtain diffusion transfer prints in an accelerated way.

It is another object of the present invention to reduce the treating liquid to a composition which is substantially free of developing agents.

It is a further object of the present invention to provide a method which enables obtaining several diffusion transfer prints from a same image-wise exposed light-sensitive silver halide material.

It is a still further object of the present invention to produce diffusion transfer prints which are practically immediately dry after they have been obtained.

It is another object to reduce the quantity of silver halide in the light-sensitive material.

It is still another object to simplify the composition of the support of the light-sensitive and/or the image-receiving material to a common paper support not specially intended for photographic purposes.

These and still other objects as well as advantages of this invention will appear hereinafter.

According to the present invention a diffusion transfer image is obtained by

image-wise exposing a light-sensitive material (a) comprising a support, a light-sensitive silver halide emulsion layer and a layer of a swellable colloid on top of said light-sensitive layer, and (b) containing hydroquinone and a 3-pyrazolidone developing compound, contacting said light-sensitive material, in the presence of an alkaline treating liquid which is substantially free of developing agents, with an image-receiving material containing development nuclei and/or substances capable of forming such nuclei in situ and separating the contacted materials from each other.

The support of the light-sensitive material is mostly a paper support such as of common paper.

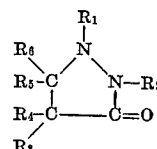
The composition of the silver halide emulsion layer may be as usual in the art of diffusion transfer. The emulsion composition is not critical provided its silver salt(s) is (are) capable of development and diffusion in the exposed and non-exposed areas respectively with the rapidity required in diffusion transfer processes. Gelatin silver chloride emulsions, which may contain silver bromide or silver iodide, and to which other ingredients have been added so as to impart the desired emulsion characteristics, are preferably used. The light-sensitive silver halide emulsion layer has to be hardened in a usual way by a suitable hardening agent such as formaldehyde. Preferably the silver halide emulsion layer contains per sq. m. of light-sensitive material an amount of silver halide equivalent to from 0.2 to 2 g. of silver nitrate. In the known diffusion transfer processes the optimum results are mostly obtained with a quantity of silver halide equivalent to about 1.5 g. of silver nitrate per sq. m. of light-sensitive material. According to the present invention, however, these optimum results may already be obtained with quantities of silver halide equivalent to about 0.5 g. of silver nitrate per sq. m. of light-sensitive material.

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This effect is probably due to the presence of the greater or all part of the developing agents in the light-sensitive material. The thickness of the light-sensitive layer is not very critical.

Suitable swellable colloids for the layer coated on top of the light-sensitive layer are a.o. the following water-permeable colloids: methylcellulose, hydroxyethylcellulose, hydroxyethyl-starch, hydroxypropyl-starch, sodium alginate, propylene glycol ester of alginic acid, gum tragacanth, starch, poly(vinylalcohol), poly(acrylic acid), poly(acryl amide), poly(vinyl pyrrolidone), poly(oxyethylene), copoly(methyl vinyl ether/maleic acid), etc. The thickness of this top layer varies among others according to the nature of the colloid chosen and the viscosity of the used colloid solution, but mostly the top layer is only a thin layer. Preferably it is not hardened. During separating the light-sensitive material and the image-receiving material from each other probably a thin stratum of said top layer is transferred to the image-receiving material.

The light-sensitive material comprises hydroquinone and a 3-pyrazolidone developing compound. Each of these compounds is preferably present in at least one water-permeable layer of the light-sensitive material such as the silver halide emulsion layer and the top layer on the silver halide emulsion layer. Hydroquinone as well as the 3-pyrazolidone developing compound preferably are present in an amount of from 0.1 to 5 g. per sq. m. of light-sensitive material. Specially suited 3-pyrazolidone developing compounds correspond to the following general formula:



wherein:

R₁ represents an aryl radical or a substituted aryl radical, R₂ represents a hydrogen atom or an acyl radical such as an acetyl radical, and each of R₃, R₄, R₅ and R₆ (the same or different) represents a hydrogen atom, an alkyl radical, a substituted alkyl radical, an aryl radical or a substituted aryl radical.

Good results can be obtained with the following compounds corresponding to the above formula:

1-phenyl-3-pyrazolidone
1-(m-tolyl)-3-pyrazolidone
1-phenyl-2-acetyl-3-pyrazolidone
1-phenyl-4-methyl-3-pyrazolidone
1-phenyl-5-methyl-3-pyrazolidone
1-phenyl-4,4-dimethyl-3-pyrazolidone
1-phenyl-5,5-dimethyl-3-pyrazolidone
1,5-diphenyl-3-pyrazolidone
1-(m-tolyl)-5-phenyl-3-pyrazolidone
1-(p-tolyl)-5-phenyl-3-pyrazolidone

Into the light-sensitive emulsion layer and/or into a water-permeable layer situated at the same side of the support as the light-sensitive emulsion layer usual substances beneficial or essential to the process may be incorporated, for instance softening agents, stabilizing agents, black-toning agents and the like.

The image-receiving material for being used in the present process may comprise a support of for instance paper, film, textile, ceramic metal etc. Mostly a paper support is used. The image-receiving material comprises

development nuclei and/or substances capable of forming such nuclei in situ. These nuclei and/or substances capable of forming such nuclei in situ may be incorporated in the support itself, e.g. in the sizing layer of a paper sheet, or in a separate layer applied to the support, such as a baryta layer coated on a paper support or another layer e.g. of gelatin applied to a support, such as a paper support which may be baryta-coated. In case the image-receiving material is not entirely soaked in the treating liquid, but is only moistened by the wetted light-sensitive material at the nuclei side, it is often advantageous to have the rear side of the image-receiving material provided too with one or more layers preventing curling of the image-receiving material in this way. One of these layers may be a nuclei-containing layer too, so that a material may be obtained suited for producing a diffusion transfer image on each side.

Development nuclei for silver halide complexes suitable for promoting the formation of the silver containing diffusion transfer image are the sulphides of heavy metals e.g. of antimony, bismuth, cadmium, cobalt, lead, nickel, silver and zinc. Selenides, polysulphides, polyselenides, mercaptanes, stannous halides, heavy metals or their salts and fogged silver halides are also suitable for this purpose. The complex salts of lead sulphide and zinc sulphide are effective either in themselves or mixed with thioacetamide, dithiobiuret and dithiooxamide. Among the heavy metals, silver, gold, platinum, palladium and mercury, preferably in their colloidal form, are to be mentioned. The noble metals among them are the most active. The substances capable of forming development nuclei in situ do so by reacting with a compound or compounds present in the light-sensitive or image-receiving material, e.g., by reacting with diffusing complexed silver halide.

The image-receiving material may also comprise in at least one of its layers usual ingredients for the diffusion transfer process such as sodium sulphite, a complexing agent for silver halide such as sodium thiosulphate and black-toning agents. It is specially interesting to have present in the image-receiving material, e.g. in the nuclei-containing layer, a quantity of hydroquinone and occasionally at least one compound selected from the group consisting of alkali metabisulphites such as potassium metabisulphite, water-soluble inorganic bisulphites and water-soluble aldehyde bisulphites as a preservative for hydroquinone and in order to obtain diffusion transfer copies keeping a white background in aging. Such an image-receiving material containing hydroquinone and the said bisulphites is described in the German patent specification 1,129,052. The hydroquinone is mostly present in an amount of from 0.1 to 5 g. per sq. m. and the water-soluble bisulphite in an amount of from 0.2 to 2 g. per sq. m.

The treating liquid for carrying out the process of the present invention is an alkaline, preferably aqueous, liquid which is substantially free of developing agents. For alkalinizing the treating liquid basic compounds are added such as sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, sodium carbonate, sodium phosphate, etc. For a compound which is weak in this respect, e.g. sodium phosphate, it is appropriate to use an amount of the anhydrous salt of from 50 to 200 g. per liter. In the case of a compound which imparts a high degree of alkalinity, e.g. sodium hydroxide, an amount of from 5 to 20 g. will suffice.

The treating liquid may further contain other usual ingredients such as sodium sulphite, e.g. in the amount of from 10 to 40 g. per liter, sodium bromide, a complexing agent for silver halide, a calcium sequestering compound and a black-toning agent e.g. 1-phenyl-5-mercapto-tetrazole or similar products such as those described in the British patent specification 561,875 and the Belgian patent specification 502,525.

Since the treating liquid is substantially free of developing substances it cannot be exhausted by aerial ox-

dation and consequently may be used for fairly a long time before being replaced. This is one of the great advantages of the present process.

According to the present invention, both the light-sensitive and the image-receiving material may be moistened with treating liquid, whereupon they are brought in contact with each other. It is, however, a preferred embodiment of the present invention to moisten only one of the materials used, preferably the light-sensitive material, and to bring this moistened material in contact with the other dry one. The moistening of at least one of the materials used may occur by means of wetted rollers e.g. as fully described in the Dutch patent application 288,817 (filed Feb. 11, 1963). In this way only one side e.g. the emulsion side of the light-sensitive material may be wetted. In this patent application also an interesting method is described of separating the light-sensitive and the image-receiving material from each other. The great advantage of wetting the sole light-sensitive material, preferably by means of wetted rollers, is that the obtained diffusion transfer copy is practically immediately dry and keeps its white background during storage, for only a very little quantity of the treating liquid has been absorbed.

Another advantage of the present diffusion transfer process is the rapidity at which the prints may be obtained. Indeed, a moistening time of the light-sensitive material with treating liquid of about 3 seconds and a contact time between the light-sensitive and the image-receiving material of about 5 to 15 seconds mostly may suffice to obtain a diffusion transfer print of good quality.

In order to facilitate the separation of the light-sensitive from the image-receiving material and to obtain a completely dry diffusion transfer print, the pressed sandwich of light-sensitive and image-receiving materials may be subjected to heat.

Finally, according to the invention, it is also possible to obtain several diffusion transfer prints from a same image-wise exposed light-sensitive material by bringing it, in the presence of the treating liquid, successively in contact with a second, a third, etc. image-receiving material.

The following examples illustrate the present invention.

Example 1

A gelatino silver chloride emulsion (gelatin/silver nitrate=1.67), hardened in the usual way with formaldehyde is applied at 45° C. to a common paper support of 90 g./sq. m. in such a way that an amount of silver chloride equivalent to 1.6 g. of silver nitrate is present per sq. m.

Onto this silver chloride emulsion layer a top layer is coated in a proportion of 1 liter per 20 sq. m. from the following solution at 45° C.

Water	-----cm. ³ ---	800
Hydroxyethyl starch having a substitution degree of 0.27 hydroxyethyl groups	-----g--	40
Ethanol	-----cm. ³ ---	200
1-phenyl-3-pyrazolidone	-----g--	5
Hydroquinone	-----g--	10
Aqueous formaldehyde, 20%	-----cm. ³ ---	10

This light-sensitive material is image-wise exposed and then moistened with the following treating liquid:

Water	-----cm. ³ ---	1000
Sodium phosphate	-----g--	75
Anhydrous sodium sulfite	-----g--	40
Anhydrous sodium thiosulfate	-----g--	10

This light-sensitive material is then brought in contact with a dry image-receiving material consisting of a paper support of 90 g./sq. m. to which a layer from the fol-

lowing composition has been applied at 45° C. in a proportion of 1 liter per 40 sq. m.:

Water	cm. ³	140
Gelatin	g	10
Aqueous suspension of barium sulfate, 56%	g	700
Dispersion of cobalt (II) sulfide nuclei as defined hereinafter	cm. ³	35
1-phenyl-5-mercaptotetrazole in ethanol, 1% solution	cm. ³	25

The dispersion of cobalt (II) sulfide is prepared at 45° C. from:

Water	cm. ³	78
Gelatin	g	2
Aqueous sodium sulfide, 10%	cm. ³	12
Aqueous cobalt (II) nitrate, 10%	cm. ³	11

After a contact time of about 10 seconds the light-sensitive and the image-receiving material are separated from each other. A practically completely dry diffusion transfer print of excellent quality is obtained.

Example 2

A light-sensitive material as described in Example 1 is prepared with the difference, however, that the silver halide emulsion layer is applied in such a way that an amount of silver chloride equivalent to 0.6 g. of silver nitrate is present per sq. m.

This light-sensitive material is image-wise exposed and then moistened, at the emulsion side only, with a treating liquid as described in Example 1. After 3 to 5 seconds the light-sensitive material is brought in contact with an image-receiving material for about 8 seconds. This material may be prepared by coating a paper support of 90 g. per sq. m. in a proportion of 1 liter per 25 sq. m. with the following composition:

Water	cm. ³	812.5
Gelatin	g	30
Dispersion of cobalt (II) sulfide nuclei as described in Example 1	cm. ³	7.5
1-phenyl-5-mercapto-tetrazole in ethanol, 1% solution	cm. ³	15
Hydroquinone	g	37.5
Anhydrous potassium metabisulfite	g	37.5
Aqueous formaldehyde 20%	cm. ³	60

After separating the light-sensitive and image-receiving material from each other, an excellent, dry positive print of the original is obtained.

Example 3

A light-sensitive material is prepared as described in Example 2, with the difference, however, that the hydroquinone and the 1-phenyl-3-pyrazolidone, instead of being incorporated in the layer on top of the silver halide emulsion layer, are incorporated in the silver halide emulsion layer itself in a concentration of 1 g. and 0.5 g. respectively per sq. m. of light-sensitive material.

This light-sensitive material is image-wise exposed and, together with an image-receiving material as described in Example 2, moistened with the treating liquid of Example 1. The light-sensitive and the image-receiving material are pressed against each other, subjected to a heat treatment and separated from each other. A dry positive print of good quality is obtained.

I claim:

1. A process for obtaining photographic images according to the silver halide diffusion transfer process, which comprises:

image-wise exposing a light-sensitive material, (a) com-

prising a support, a light-sensitive silver halide emulsion layer and a layer of a swellable colloid on top of said light-sensitive layer, and (b) containing hydroquinone and a 3-pyrazolidone developing compound,

contacting said light-sensitive material, in the presence of an alkaline treating liquid which is substantially free of developing agents, with an image-receiving material containing hydroquinone and a member selected from the group consisting of development nuclei and substances capable of forming such nuclei in situ, and

separating the contacted materials from each other.

2. The process of claim 1, wherein the light-sensitive silver halide emulsion layer contains per per sq. m. an amount of silver halide which is equivalent with from 0.2 to 2 g. of silver nitrate.

3. The process of claim 1, wherein the image-receiving material contains from 0.1 to 5 g. per sq. m. of hydroquinone and said light-sensitive material contains from 0.1 to 5 g. per sq. m. of hydroquinone and said 3-pyrazolidone developing compound.

4. The process of claim 1 wherein said light-sensitive material is wetted with said alkaline treating liquid and is thereafter contacted while wet with dry image-receiving material.

5. The process of claim 4, wherein the sole emulsion side of the light-sensitive material is wetted with the alkaline treating liquid.

6. A process for obtaining photographic images according to the silver halide diffusion transfer process, which comprises:

image-wise exposing a light-sensitive material (a) comprising a support, a light-sensitive silver halide emulsion layer and a layer of a swellable colloid on top of said light-sensitive layer, and (b) containing hydroquinone and a 3-pyrazolidone developing compound,

contacting said light-sensitive material in the presence of an alkaline treating liquid which is substantially free of developing agents, with an image-receiving material containing hydroquinone, at least one compound selected from the group consisting of alkali metabisulphites, water-soluble inorganic bisulphites and water-soluble aldehyde bisulphites, and a member selected from the group consisting of development nuclei and substances capable of forming such nuclei in situ, and

separating the contacted materials from each other.

7. The process of claim 6, wherein the said at least one compound is present in the image-receiving material in an amount of from 0.2 to 2 g. per sq. m.

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