United States Patent Office

3,347,674

Patented Oct. 17, 1967

3,347,674

PROCESS OF FORMING IMAGES ACCORDING TO THE SILVER COMPLEX DIFFUSION TRANSFER PROCESS

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No Drawing. Filed Feb. 4, 1966, Ser. No. 525,127
4 Claims. (Cl. 96—29)

ABSTRACT OF THE DISCLOSURE

A method of making copies by diffusion transfer where the developing bath contains hydroquinone as developing agent and a sulfite preservative for the hydroquinone and is exposed to air as during repeated use, giving rise to formation by oxidation of colored quinone disulfonate. Additional hydroquinone plus sulfite preservative therefor is incorporated in the image-receiving material to reduce any quinone disulfonate absorbed from bath and produce copies free of undesirable coloration.

The present invention relates to an improved process for forming images according to the silver complex diffusion transfer process.

The present application is a continuation-in-part of the U.S. patent application Ser. No. 359,456.

According to the known silver complex diffusion transfer processes the principle of which is described in the U.S. patent specification 2,352,014 and in the British specifications 654,630 and 614,155, a light-sensitive silver halide material is image-wise exposed and then pressed into contact with an especially prepared receiving material in the presence of a developing substance and a solvent for silver halide. The silver halide of the image-wise exposed areas are developed and do not undergo any further change. The silver halide of the unexpected areas is dissolved by the solvent for silver halide which is present either in the developing liquid or in the receiving material, transferred by diffusion to the receiving layer and converted therein into metallic silver. This conversion occurs with the help of the catalytic action of development nuclei which are present in the receiving or silver precipitating layer and which consist of finely divided metal or metal sulfide. In this way an image appears in the receiving layer after separation of the image-receiving material from the silver halide material.

In the silver complex diffusion transfer process a developing liquid comprising hydroquinone as developing substance is very often used, which hydroquinone is most often used in combination with a sulfite such as sodium sulfite in an amount sufficient to normally preserve said liquid. In such circumstances quinone disulfonate is formed as an oxidation product during development because of, on the one hand, the developing action of hydroquinone disulfonate and, on the other hand, the regenerating action of hydroquinone disulfonate on the oxidised form of other developing substances e.g. on the oxidised 1-phenyl-3-pyrazolidone, which is often employed as developing substance in combination with hydroquinone. When the developing liquid is repeatedly used for the development of fresh material quinone disulfonate will form to such extent that the diffusion transfer copy will be orange-colored owing to the presence of a considerable amount of quinone disulfonate absorbed from the developing liquid into the image-receiving material.

It has now been found that the formation of such

orange-coloration on the image-receiving material can be avoided by using an image-receiving material incorporating an additional amount of hydroquinone together with a bisulfite compound to preserve said additional amount of hydroquinone, said bisulfite compound being selected from the group consisting of an alkali metabisulfite, a water-soluble inorganic bisulfite and a water-soluble organic bisulfite.

Very good results are attained when as alkali metabisulfite potassium metabisulfite is used.

As water-soluble inorganic bisulfites, sodium bisulfite and potassium bisulfite can be mentioned.

Very satisfying results are likewise attained when using water-soluble aldehyde bisulfites such as glyoxal bisulfite and benzaldehyde bisulfite.

The amounts of hydroquinone added to the receiving material may vary between 0.25 and 1.5 g./sq. m. The amounts of alkali metabisulfite, of water-soluble inorganic bisulfites or of water-soluble aldehyde bisulfites added to the receiving material is such as to preserve the hydroquinone present therein and may vary between 0.2 and 1.2 g./sq. m. The best results, however, are attained by addition of a mixture of 0.5 g. of hydroquinone and 0.4 g. of alkali metabisulfite per sq. m. wherein the alkali metabisulfite may be replaced by 0.4 g. of water-soluble inorganic bisulfite or 0.2 g. of water-soluble aldehyde bisulfite.

Under some circumstances it may be necessary, however, to increase the amounts of the above mentioned compounds above the limits just specified.

The developing solution for the silver halide comprises hydroquinone and a water-soluble sulfite, generally sodium sulfite, and as the case may be various necessary or usual ingredients for the application of the silver complex diffusion transfer process. Said solution comprises very often 1-phenyl-3-pyrazolidone as an additional developing agent and occasionally a solvent for the undeveloped silver halide, such as sodium thiosulfate, sodium thiocyanate or ammonia. The solvent for the silver halide may also be present in the image-receiving material.

As suitable emulsions for the application of the present process, any silver halide emulsion can be used which is characterized by sufficiently rapid development of the exposed silver salt and sufficiently rapid complexing of the non-exposed silver salt to meet the requirements of the diffusion transfer process. For this purpose preferably silver chloride emulsions are used which may contain definite amounts of silver bromide or silver iodide or to which other standard ingredients may be added for obtaining the emulsion characteristics desired.

The image-receiving layer may consist of a usual support or a water-permeable organic colloid layer applied to a support, which layer contains development nuclei for silver halide.

Development nuclei for silver halides suitable for obtaining the silver containing image in the image-receiving layer are: sulfides, selenides, polysulfides, polyselenides, thiourea, mercaptans, tin (II) halides, heavy metals or their salts and fogged silver halide. Sulfides of heavy metals such as of antimony, bismuth, cadmium, cobalt, lead, nickel, silver and zinc are also appropriate. The sulfides of lead and zinc as well as the complex salts thereof are particularly interesting to be used as such or mixed with thioacetamide, dithiobiuret and dithio-oxamide. Among the heavy metals silver, gold, platinum, palladium and mercury are to be mentioned, the noble metals thereof being the most active. The heavy metals are preferably used in colloidal form.

These development nuclei can be incorporated into the support material itself or they can be applied to a suitable support, such as paper, from solutions or dispersions

of such development nuclei in a colloid medium such as gelatine.

As to the application of this new process, the generally known processes of the silver salt diffusion transfer technique and the respective materials can be used such as described in "Progress in Photography," vol. III, 1955–1958, pages 24–36 and in the patent literature cited therein.

The following example illustrates the present invention without, however, limiting the scope thereof.

Example

A suspension of the following composition is prepared:

Water	cm.³	889
Gelatine	g.	30
0.2% aqueous suspension of colloidal silver	cm.³	45
Anhydrous sodium thiosulfate	g.	36

A 90 g./sq. m. paper support is coated with a thin layer by means of this suspension so that herewith 13 m.² of paper support are covered.

After drying, a second layer is applied thereto by means of the following solution:

Water	cm.³	975
Arabic gum	g.	6
Sodium salt of carboxymethylcellulose	g.	7
Hydroquinone	g.	7
Potassium metabisulfite	g.	5

whereafter the image-receiving material obtained is dried. A photographic material consisting of a paper support provided with a silver halide layer is image-wise exposed and after being brought into contact with the image-receiving material as described above carried through a diffusion transfer developing apparatus containing a developing solution having the following composition:

Water	cm.³	1000
Anhydrous sodium sulfite	g.	75
Sodium hydroxide	g.	10
Potassium bromide	g.	1
Hydroquinone	g.	16
1-phenyl-3-pyrazolidone	g.	1

After squeezing between the rubber rollers of the developing apparatus, and after a contact period of about 20 secs. both materials are separated from each other. The obtained positive print of the original has kept its complete white background even after many months of storing.

What we claim is:

1. In a process of forming images according to the silver complex diffusion transfer process by the steps comprising image-wise exposing a light-sensitive silver halide material, developing said material by means of a developing solution containing hydroquinone as a developing agent and a sulfite preservative compound in sufficient amount to normally preserve said hydroquinone, keeping the wet light-sensitive material in contact with an image-receiving material in the presence of a solvent for silver halide and separating the light-sensitive and image-receiving materials from each other, and in which process the said developing solution is repeatedly used for developing fresh material, the improvement of incorporating in said image-receiving material an additional amount of hydroquinone together with a bisulfite compound to preserve said additional hydroquinone, said bisulfite compound being selected from the group consisting of an alkali metabisulfite, a water-soluble inorganic bisulfite and a water-soluble organic bisulfite.

2. The process of claim **1** wherein said developing solution also contains a 3-pyrazolidone developing agent for co-operation with said hydroquinone.

3. The process of claim **2** wherein said 3-pyrazolidone developing agent is 1-phenyl-3-pyrazolidone.

4. The process of claim **1** wherein said sulfite preservative compound is sodium sulfite.

References Cited

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