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PHOTOGRAPHIC IMAGE-RECEIVING MATERIAL

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4 Claims. (Cl. 96—76)

The present application is a continuation-in-part of the United States application Serial No. 131,426, now abandoned.

The present invention relates to an improved photographic material to be employed in the silver complex diffusion transfer process.

According to the known silver complex diffusion transfer processes, the operation of which is described in United States patent specification 2,352,014, in British specifications 614,155 and 654,630 and in German patent specification 887,733, a light-sensitive silver halide material is exposed to an image and then pressed into contact with a specially prepared receiving material in the presence of a developer and a silver halide solvent. In the exposed areas the silver halide is developed and does not undergo any further change. In the unexposed areas the silver halide is complexed by a complexing agent for silver halide which is present either in the developer or in the receiving material, whereupon the complexed silver halide is transferred by diffusion onto the receiving layer and converted thereon by development into metallic silver. The conversion is effected by the catalytic action of the developing nuclei present in the receiving, or silver precipitating, layer. These nuclei consist of finely divided metal or metal sulfide. In this way, an image is formed on the receiving layer after separation of the image-receiving material from the light-sensitive material.

In order to obtain a uniform diffusion of the complexed silver halide, a temporary close contact of emulsion layer and receiving layer is necessary. If, however, both layers contain hardened or unhardened gelatin, the adhesion power is too strong on separation. Attempts have been made to avoid this difficulty by substituting other binding agents for the gelatin.

Thus, it is known, as shown in German patent specification 869,008, that the separation of emulsion and receiving layers is facilitated by wholly or partly replacing the gelatin in at least one of these layers with other layer-forming substances such as cellulose derivatives, polyamides, polesters, polyvinyl alcohols, polyvinyl acetates, partially hydrolyzed polyvinyl acetates, polyvinyl acetals, or other synthetic or natural resins.

It is also known, as shown in British patent specification 748,892, to incorporate starch into the emulsion and image-receiving layers.

It is further known, as shown in British patent specification 814,154, that the separation of emulsion and image-receiving layers can be effected even after practically complete drying if starch ether or galacto-mannan is incorporated into at least one of these two layers.

Another method of facilitating the separation of the emulsion layer from the image-receiving layer consists in applying a thin auxiliary layer onto the emulsion layer and/or onto the image-receiving layer. It is known, as shown in the German patent specification 1,055,953 that starch or starch derivatives can be used for this purpose.

The layers manufactured according to the processes described in the above-mentioned patent literature can, however, be easily damaged during the squeezing of the emulsion layer and image-receiving layer between the rollers of the developing apparatus, so that poorly defined images are formed. This difficulty is very often experienced when the emulsion and image-receiving layers are quickly separated from each other.

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It has now been found that even when the emulsion and image-receiving layers are left in contact with each other for only a short time after the silver complex diffusion transfer, sharply defined images can be obtained if the image-receiving material comprises a surface layer of the chromium salt of carboxymethylcellulose. The chromium salt of carboxymethylcellulose is formed in situ during the coating stage by reaction of a water-soluble carboxymethylcellulose, applied to the image-receiving material, with a water-soluble chromium salt.

Any water-soluble chromium salt is suitable, including salts of both organic and inorganic acids such as, e.g., chromium (III) acetate, chromium (III) chloride, chromium (III) fluoride, chromium (III) iodide, chromium (III) nitrate, chromium (III) sulfate, potassium chromium (III) sulfate, potassium chromate, potassium dichromate, sodium chromate, sodium dichromate, chromyl, chloride stearate, etc.

These water-soluble chromium salts are preferably added to the carboxymethylcellulose layer itself. The amounts of added chromium salts may vary widely but are preferably chosen between 0.8 and 5.0%, based on the weight of the water-soluble carboxymethylcellulose. At any rate the concentration of chromium salt in the layer-forming solution must be chosen in such a way that the increase of viscosity in this solution does not hinder the casting.

The water-soluble carboxymethylcellulose salt may previously be admixed with a water-soluble alginate salt which, in its turn, is hardened by a water-soluble strontium salt present in a subjacent water-permeable layer. This water-soluble alginate salt may be used in concentrations which vary between 40 and 70%, based on the weight of water-soluble carboxymethylcellulose salt.

More particulars regarding the use and the preparation of water-soluble alginate salts can be found in our Continuation-in-Part Application Serial No. 359,455, filed April 13, 1964.

The carboxymethylcellulose used according to the method of this invention must be soluble in water. Its viscosity may vary between 25 and 2200 cp. A suitable carboxymethylcellulose product for this purpose is, e.g., the sodium salt of carboxymethylcellulose, which may be prepared according to the processes described in the United States patent specifications 2,618,609, 2,607,772 and 2,667,480. It is used in aqueous solution in concentrations which may vary between 3 and 20 g. per liter of casting composition. These amounts, however, are not at all critical, and if it is convenient may be varied outside these limits. Obviously, other water-soluble salts of carboxymethylcellulose, such as ammonium or other alkali metal salts, may also be used.

The required adhesion of the carboxymethylcellulose layer thus obtained to a subjacent gelatin layer strongly improves when a known hardner for gelatin, e.g. formaldehyde or glyoxal, is present in the carboxymethylcellulose layer. Such a substance superficially hardens the adjacent gelatin layer by diffusion.

An important advantage in the use of the image-receiving material according to this invention is the greater range of manipulation conferred to the silver complex diffusion transfer process. Indeed, due to the short contact times of light-sensitive material and image-receiving material, the same light-sensitive material can successfully be used for the manufacture of a second, a third, etc. diffusion transfer print. Also, for use in developing apparatus that operates at a developing speed of 7.5 cm./sec., the quick bath treatment can now be coupled with a quick separation of the light-sensitive and image-receiving material so that the diffusion transfer process is speeded up considerably. Moreover, due to the strongly improved mutual adhesive properties, the image-receiving material can be separated from the light-sensitive material after a long contact time and even after complete drying without the risk of tearing these materials.

As to the use of this new process, it can be employed generally with the known processes of the silver complex diffusion transfer technique and the respective known materials such as are described in "Process in Photography," vol. I, 1940–1950, pages 76–77 and 140; vol. II, 1951–1954, pages 156–7; vol. III, 1955–1958, pages 24–36, and in the patent literature cited therein.

Any silver halide emulsion can be used in the process of this invention, provided only that its exposed silver salt is sufficiently rapidly developed during the diffusion transfer process and its non-exposed silver salt is sufficiently rapidly complexed. For this purpose, silver chloride emulsions, which may contain silver bromide or silver iodide, to which other ingredients have been added so as to impart the desired emulsion characteristics, are preferably used.

The image-receiving layer may be composed of a support alone or of a water-permeable organic colloid layer applied to a support, said colloid layer containing development nuclei.

Development nuclei for silver halides suitable for obtaining the silver-containing image in the image-receiving layer are the sulfides of heavy metals e.g. of antimony bismuth, cadmium, cobalt, lead, nickel, silver and zinc. Selenides, polysulfides, polyselenides, mercaptans, tin (II) halides, heavy metals or their salts and fogged silver halides are also suitable for this purpose. The complex salts of lead sulfide and zinc sulfide are effective either in themselves or mixed with thioacetamide, dithiobiuret or dithio-oxamide. Among the heavy metals, silver, gold, platinum, palladium and mercury are particularly worthy of mention, especially in their colloidal form. The precious metals among them are the most active.

These development nuclei can be incorporated into the support material itself, or they can be applied onto a suitable support such as paper from their solutions or dispersions in colloid media, such as gelatin.

The composition of the developing solution for the silver halide is that of the conventional developing solution for the silver complex diffusion transfer; it contains the necessary ingredients for the development of the exposed silver halide such as hydroquinone and 1-phenyl-3-pyrazolidone and sometimes a solvent for the undeveloped silver halide, e.g., sodium thiosulphate, sodium thiocyanate or ammonia. The solvent for silver halide may, of course, be present in the image-receiving material as well as in the developer.

More particulars on the composition of the silver halide emulsion layer, the image-receiving material and the baths, and for the exposing and developing apparatus are given in the last cited literature and in the patent specifications mentioned therein.

The following examples illustrate the present invention without limiting, however, the scope thereof.

Example 1

A 90 g./sq. m. paper support is coated with a receiving layer from a suspension of the following composition:

Water, cc.	925
Gelatin, g.	33
Sodium thiosulphate, g.	40
Sodium sulfide, g.	0.2
Cobalt (II) nitrate (6% aqueous), g.	1

This suspension is cast in such a way that 1 l. thereof covers 13 sq. m. of paper. After drying, a second layer is applied from the following solution:

Sodium salt of carboxymethylcellulose, g.	1
Water, cc.	300
10% aqueous solution of potassium chromium (III) sulfate, cc.	0.25
25% aqueous saponine solution, cc.	1.5

in such a way that with 1 l. thereof, 8 sq. m. of paper are covered, whereupon this layer is dried. The image-receiving material obtained, in close contact with the silver halide emulsion layer of an image-wise exposed light-sensitive material, is passed through a developing bath of the following composition:

	G.
Sodium hydroxide	11
Sodium sulphite (anhydrous)	100
Potassium bromide	1.5
Hydroquinone	9
1-phenyl-3-pyrazolidone	1.5
Water to 1000 cc.	

After squeezing the image-receiving layer and the light-sensitive layer between the rubber rollers of the developing apparatus, the image-receiving material and the light-sensitive material are separated from each other and a positive image of the original is obtained in the receiving layer.

Examples 2–6

When chromium (III) chloride, chromium (III) fluoride, chromium (III) acetate, chromyl chloride stearate or chromium (III) nitrate was substituted for potassium chromium (III) sulfate in the above example, identical results were obtained.

Examples 7 and 8

Example 1 was repeated twice, substituting potassium and ammonium carboxymethylcellulose salts, respectively, for sodium carboxymethylcellulose. Very satisfactory results were obtained in each instance.

Example 9

A 90 g./sq. m. paper support is coated with a receiving layer from a suspension of the following composition:

Water, cc.	675
Gelatin, g.	68
0.1% aqueous colloidal silver, cc.	25
Sodium thiosulfate, g.	122
Sorbitol, g.	100
Strontium chloride, g.	10

This suspension is cast in such a way at 40° C. that 1 l. thereof covers 40 sq. m. of paper. After drying, a second layer is applied at 60° C. from the following solution:

Water, cc.	1000
Ammonium alginate, g.	8
Sodium salt of carboxymethylcellulose, g.	15
40% aqueous formaldehyde, cc.	10
10% aqueous potassium chrominum (III) sulfate, cc.	1

in such a way that with 1 l. thereof 60 sq. m. of paper are covered, whereupon this layer is dried. The image-receiving material obtained is then brought in close contact with the silver halide emulsion layer of an exposed light-sensitive material and further treated as in Example 1. A positive image of the original is obtained in the receiving layer.

Examples 10–14

Example 9 was repeated, substituting chromium (III) iodide, potassium dichromate, sodium dichromate, sodium chromate and chromium (III) sulfate for the potassium chromium (III) sulfate. All results obtained were highly satisfactory.

Example 15

Example 9 was repeated, substituting potassium alginate for the ammonium salt and ammonium carboxymethylcellulose for its sodium salt. The result, again, was highly satisfactory.

Examples 16–18

Example 9 was repeated, substituting strontium acetate, strontium nitrate and strontium bromide for strontium chloride. Identical results were obtained.

I claim:

1. An image-receiving material for use in the silver complex diffusion transfer process comprising successively a support, a silver precipitating layer containing development nuclei and as a separate layer, a surface layer of carboxymethylcellulose hardened by reaction with a water-soluble chromium salt provided substantially only in said surface layer.

2. An image-receiving material for use in the silver complex diffusion transfer process comprising successively a support, a silver precipitating layer containing development nuclei and as a separate layer, a surface layer of strontium alginate and carboxymethylcellulose hardened

by reaction with a water-soluble chromium salt provided substantially only in said surface layer.

3. An image-receiving material according to claim **1**, wherein the silver precipitating layer is a superficially hardened gelatin layer containing development nuclei.

4. An image-receiving material according to claim **2**, wherein the silver precipitating layer is a superficially hardened gelatin layer containing development nuclei.

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