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3,257,206

## PHOTOGRAPHIC MATERIAL

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2 Claims. (Cl. 96—29)

This invention relates to an improved material for being applied in the silver complex diffusion transfer process and to a process wherein this material is used.

The principle of the silver complex diffusion transfer process is described in the United States patent specification 2,352,014 and the German patent specification 887,733. According to this process the silver complex which is transferred by diffusion from the silver halide emulsion layer to the image-receiving layer is developed by the action of the developing nuclei which are present in the receiving layer.

With regard to the deposition of the silver in the image-receiving layer there can be mentioned that a high density of the silver deposition can be promoted by a rapid development of the silver complex so that this complex does not have an opportunity to be distributed laterally in the nuclei-containing or image-receiving layer. Such lateral distribution tends to result in a less dense and more diffuse diffusion transfer image.

The rapidity of the deposition of the silver and consequently the density of the diffusion transfer image depend to a high degree on the nature and concentration of the developing nuclei used.

Although the rate of deposition of the metallic silver depends on the nature and concentration of the used developing nuclei, it can still be accelerated according to the United States patent specification 2,698,237 by incorporating colloidal silica in the nuclei-containing layer.

It has now been found that by adding colloidal silica to a water-permeable covering layer of the image-receiving material, the reduction of the diffusing silver complex is to say initiated, so that a more rapid and more complete reduction of the silver complex in the image-receiving material is obtained. In this way, a sharp dense image is obtained which is probably due to the fact that by the initiating action of the colloidal silica a vertical trace of silver nuclei is formed in the water-permeable covering layer. Moreover, a favourable matting effect arises when using a material according to the invention.

Any water-permeable layer which enables the diffusing complexed silver halide to penetrate into the image-receiving material and which makes it possible to obtain a good separation between the image-receiving material and the light-sensitive material after the formation of the diffusion transfer image, can be used as water-permeable covering layer. Suitable covering layers are among others described in the French patent specifications 1,304,279 and 1,304,280.

Colloidal silica used in the material and the process according to the present invention is, e.g., Santocel C (tradename of Monsanto Chemical Company, St. Louis, Mo., U.S.A.) and dispersions of hydrated silica are, e.g., Ludox LS (tradename of E. I. du Pont de Nemours & Co. (Inc.) Wilmington, Del., U.S.A., for a 30% aqueous dispersion of silica) and Syton 2X (tradename of Monsanto Chemical Company, St. Louis, Mo., U.S.A., for a 30% aqueous dispersion of silica particles having an average size of 0.025 $\mu$ ). According to the desired matting effect these silica compositions can be dispersed in the coating composition of the water-permeable layer in an amount mostly varying from 5 to 50 g. per liter. More details about the thickness of a water-permeable covering layer are

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given in the patent specifications dealing with such covering layers, among others the two above mentioned French patent specifications.

The image-receiving material may consist of a support or of a support carrying a water-permeable colloid layer which contains developing nuclei for complexed silver halide. Physical as well as chemical developing nuclei are suited.

Developing nuclei suitable for promoting the formation of the silver-containing image in the image-receiving layer are the sulfides of heavy metals, e.g., antimony, bismuth, cadmium, cobalt, nickel, iron, tin, thallium, copper, lead, silver and zinc. The selenides, polysulfides, polyselenides, mercaptans, stannous halides, heavy metals or their salts and fogged silver halide are also suited for this purpose. The complex salts of lead sulfide and zinc sulfide either in themselves or mixed with thioacetamide, dithiobiuret or dithio-oxamide are especially effective. Among the heavy metals: silver, gold, platinum, palladium and mercury are particularly worthy of mention, especially in their colloidal form. The noble metals among them are the most active.

These developing nuclei for silver can be incorporated in the support material itself or they can be applied onto a suitable support such as paper, from solutions or dispersions of such developing nuclei in a colloid medium such as gelatin.

The image-receiving layer and/or the hydrophilic covering layer can still contain all kinds of other ingredients such as developing substances, complexing agents for silver halide, optical bleaching agents, softening agents, black-toning agents etc.

Suitable black-toning agents are described in the Belgian patent specification 605,802, the French patent specifications 1,305,068 and 1,140,526 and the United States patent specification 2,699,393.

Particularly good results are obtained when using black-toning agents, according to the last patent specification, in combination with metal sulfide nuclei to the exclusion of silver sulfide nuclei.

Any silver halide emulsion, the exposed silver halide of which is sufficiently rapidly developed during the diffusion transfer process and the non-exposed silver halide is at the same time sufficiently rapidly complexed for allowing the formation of the diffusion transfer images, is suited for being used in combination with the image-receiving material according to this invention. Silver chloride emulsions which may also contain silver bromide or silver iodide or to which some ingredients may be added so as to impart the desired emulsion characteristics are preferably used. Some materials playing a part in the diffusion transfer image formation may also be incorporated in the light-sensitive material.

The composition of the developing liquid is the one usually used in the silver complex diffusion transfer process: it contains among others the ingredients necessary for the development of the exposed silver halide such as hydroquinone and 1-phenyl-3-pyrazolidone, a complexing agent for silver halide etc. Some of these ingredients can be wholly or partially incorporated in the light-sensitive or image-receiving material.

Concerning the diffusion transfer process in general, there can be referred to "Progress 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 the patent literature cited therein.

For more details concerning the composition of the silver halide emulsion layers, the image-receiving material, the baths and the exposing and development apparatus there can also be referred thereto.

The following examples illustrate the present invention.

*Example 1*

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

|   |                  |     |
|---|------------------|-----|
| Water   | cm. <sup>3</sup> | 100 |
| Sodium thiosulfate  | g.               | 1.2 |
| Gelatin   | g.               | 8   |
| 10% aqueous solution of sodium sulfide                          | g.               | 0.2 |
| 10% aqueous solution of cobaltous nitrate                       | cm. <sup>3</sup> | 0.8 |
| 1% solution in ethanol of 1-phenyl-5-mercapto-1,2,3,4-tetrazole | cm. <sup>3</sup> | 1   |

After drying, a second layer is applied from the following suspension:

|  |                  |      |
|--|------------------|------|
| Water  | cm. <sup>3</sup> | 100  |
| The sodium salt of carboxymethyl cellulose         | g.               | 0.75 |
| 10% aqueous solution of potassium chromium sulfate | g.               | 0.20 |
| 30% aqueous dispersion of silica                   | cm. <sup>3</sup> | 10   |

The obtained image-receiving material is dried and together with an image-wise exposed silver chloride emulsion material containing 1.3 g. of silver chloride per sq. m. passed through a developing bath of the following composition:

|                          |                  |      |
|--------------------------|------------------|------|
| Sodium hydroxide         | g.               | 11   |
| Anhydrous sodium sulfite | g.               | 100  |
| Potassium bromide        | g.               | 1.5  |
| Hydroquinone             | g.               | 9    |
| 1-phenyl-3-pyrazolidone  | g.               | 1.5  |
| Water up to              | cm. <sup>3</sup> | 1000 |

After squeezing the image-receiving layer and the light-sensitive layer between the rubber rollers of the developing apparatus and after a contact time of about 20 sec. the image-receiving material and the light-sensitive material are separated.

In the receiving layer a sharp image with good covering and neutral image-tone is obtained.

*Example 2*

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

|  |                  |     |
|--|------------------|-----|
| Water                                  | cm. <sup>3</sup> | 898 |
| Gelatin                                | g.               | 80  |
| Sodium thiosulfate                     | g.               | 12  |
| 10% aqueous solution of sodium sulfide | cm. <sup>3</sup> | 2   |
| 10% aqueous solution of cobalt nitrate | cm. <sup>3</sup> | 8   |

After drying a second layer is applied from the following suspension:

|   |                  |      |
|---|------------------|------|
| Water   | cm. <sup>3</sup> | 100  |
| Sodium salt of carboxymethyl cellulose                          | g.               | 0.75 |
| 1% solution in ethanol of 1-phenyl-5-mercapto-1,2,3,4-tetrazole | cm. <sup>3</sup> | 5    |
| 30% aqueous dispersion of silica                                | cm. <sup>3</sup> | 10   |

The obtained image-receiving material is dried and together with an image-wise exposed silver chloride emulsion material containing 1.3 g. of silver chloride per sq. m. passed through the developing bath of Example 1.

After squeezing the image-receiving layer and the light-sensitive layer between the rubber rollers of the developing apparatus and after a contact time of about 20 sec. the image-receiving material and the light-sensitive material are separated.

In the receiving layer a sharp image with good covering and neutral image-tone is obtained.

I claim:

1. A photographic image-receiving material for forming prints thereon according to the silver complex diffusion transfer process by precipitating the silver of image-wise distributed soluble silver complexes of an exposed photosensitive element, including a support and a silver halide emulsion layer, brought into contact therewith, said material comprising a support, a water-permeable image-receiving layer containing development nuclei and a hydrophilic, water-permeable surface layer on said image-receiving layer, said surface layer containing colloidal silica and being free of silver precipitating agent.

2. A process of forming transfer images comprising the steps of exposing a light-sensitive material comprising a support and a silver halide emulsion layer, contacting said exposed material with an image-receiving material comprising a support, a water-permeable image-receiving layer containing development nuclei and a hydrophilic water-permeable surface layer on said image-receiving layer, said surface layer containing colloidal silica and being free of silver precipitating agent, separating the light-sensitive material from the image-receiving material containing the transfer image, the transfer being effected in the presence of a developing substance and a solvent for silver halide.

## References Cited by the Examiner

## UNITED STATES PATENTS

|           |         |         |       |
|-----------|---------|---------|-------|
| 2,563,342 | 8/1951  | Land    | 96—29 |
| 2,653,527 | 9/1953  | Land    | 96—29 |
| 2,686,716 | 8/1954  | Land    | 96—29 |
| 2,698,237 | 12/1954 | Land    | 96—29 |
| 2,834,676 | 5/1958  | Stanley | 96—29 |
| 2,878,121 | 3/1959  | Gray    | 96—29 |

## FOREIGN PATENTS

|         |        |                |
|---------|--------|----------------|
| 597,904 | 6/1961 | Belgium.       |
| 874,046 | 8/1961 | Great Britain. |

## OTHER REFERENCES

Photographic Age, February 1949, pp. 45—6.

NORMAN G. TORCHIN, *Primary Examiner*.

G. H. Bjorge, A. E. Tanenholtz, *Assistant Examiners*.