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3,015,562

RECEIVING SHEET FOR USE IN PHOTOGRAPHIC SILVER TRANSFER PROCESS

Clifford E. Herrick, Jr., Chenango Forks, Floyd J. Lafreniere, Johnson City, and Douglas Straw, Binghamton, N.Y., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware
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This invention relates to the reproduction of photographic images wherein a silver halide image is transferred imagewise to a receiving sheet for development and particularly to the constitution of such a receiving sheet.

The process whereby the residual silver halide in a negative silver image is utilized to form a positive image upon a transfer or receiving material is known as the diffusion-transfer process and is described in U.S. Patent 2,352,014. According to the method set forth in this patent, the material to be copied is used to form an image on a light sensitive silver halide emulsion which, for the sake of simplicity, can be designated as the negative material. In those areas of the negative material struck by light, a negative latent image is formed while those areas not struck by light contain a positive image of unexposed silver halide. The exposed negative material is then treated with a developer composition containing a silver halide solvent and a silver halide developing agent after which the wet, exposed negative material is contacted with a receiving material comprising a piece of paper or foil containing a fogging agent and silver halide solvents.

The developer composition causes the development of the negative latent image in the negative paper; the silver halide solvents in said developer composition react with the unexposed silver halide to form soluble silver complexes which are transferred by diffusion to the receiving material and are there acted upon by the fogging agent therein, whereupon said silver halide complexes are transformed to metallic silver or silver compounds of high optical density.

Although the diffusion-transfer process has found rather extensive application in the commercial market, it suffers from certain drawbacks and disadvantages, especially as regards the nature of the receiving material employed. Many commercial receiving materials, after processing, have a decided hazy or spotted appearance, a characteristic which is particularly objectionable when transparent receiving materials are used. Another drawback is a marked yellow discoloration of the background areas on ageing. In addition, these transfer foils have, after processing, a very tacky surface, such defect being particularly noticeable when the final copy is handled with damp fingers or under conditions of high humidity.

The receiving materials made in accordance with the above U.S. patent are prepared by coating gelatin from a water solution onto a base. This use of water, as the solvent, leads to problems such as long drying periods at fairly high temperatures and the tackiness so prevalent in such receiving materials is most likely due to its gelatin layer.

Another type of receiving material is described in U.S. Patent 2,579,587 to E. H. Land and the Polaroid Corporation. Although the receiving material described in this patent does not contain gelatin, the processing procedure and materials used are of such a nature as to be impractical for use in a simple office-type copying device.

We have now perfected a receiving material suitable for use in the diffusion-transfer copying system that is completely free of the defects associated with present commercial products and the provision of such a receiving

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material constitutes the objects and purposes of this invention.

According to our invention, a plastic foil base such as that from cellulose acetate, polystyrene, or the like, is coated with a solution comprising organic solvents together with a copolymer of maleic anhydride and an alkyl vinyl ether, a normally hydrophobic polymer such as cellulose acetate, vinyl acetate, or the like, a silver halide developing agent such as hydroquinone or p-aminophenol, a silver halide fogging agent such as 2-hydroxyethylallylthiourea, a water soluble silver salt such as silver nitrate, silver acetate, silver citrate, or the like, which, quite likely, aid in the nucleation needed to form dense images. Advantageously, traces of an acid corresponding to the anion of the H₂O soluble silver salt are included in our coating solution such as nitric, acetic, citric acids, or the like. The function of the acid is to prevent the silver ion from being reduced by the developing agent before the coated foil has been dried.

The polymer mixture used in coating the foil base is normally hydrophobic and, as such, will not be evenly wet with the aqueous developing solution used in processing. However, such hydrophobic coatings, when treated with certain hydrolytic agents, i.e., a moist nitrogen containing base, are transformed into hydrophilic films and, in this connection, reference is made to U.S. Patent 2,756,163 to Herrick and Amon. After the coating containing the copolymer of the alkyl vinyl ether and maleic anhydride has been rendered hydrophilic, the foil coating readily accepts the developer compositions used after exposure. The surface hydrolysis of the alkyl vinyl ether-maleic anhydride copolymer coating with a water soluble nitrogenous base also neutralizes any mineral acid present in the coating and allows the formation of minute silver grains required in nucleation.

In order to reduce a tendency to curl and to prevent chemical spotting on the back, the foil base coated as above may also be coated on the back side with a solvent solution containing the alkyl vinyl ether-maleic anhydride copolymer and the hydrophobic polymer.

The alkyl vinyl ether-maleic anhydride copolymers contemplated for use are those described, for example, in U.S. Patent 2,772,972 and in U.S. application Serial No. 669,942, filed July 5, 1957, entitled "Positive Working and Photomechanical Printing Plates." Such copolymers include those from maleic anhydride, on the one hand, and methyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, 2-methoxyethyl vinyl ether, and the like, on the other hand.

In lieu of the cellulose acetate as the hydrophobic resin employed with the maleic anhydride copolymer, use may be made of the hydrophobic resins described in U.S. Patent 2,772,972. For example, the hydrophobic resin may be cellulose propionate, cellulose butyrate, mixed esters such as cellulose acetate propionate, cellulose acetate butyrate, polyvinyl acetals such as polyvinyl butyral, polymethyl acrylate, polymethylmethacrylate, and the like.

Alternates of the silver halide fogging agent may be employed and are described in U.S. Patent 2,755,185 and include N-allyl-4-morpholinethiocarbamate, 1-allyl-3-ethyl-2-thiourea, 1-benzyl-3-β-hydroxyethyl-2-thiourea, and the like.

Our new transfer foil produces, in a surprisingly short time, high contrast positive copies of originals with completely haze-free backgrounds free from yellow discoloration. After processing, the moist foil is completely tack free and dries in a few seconds to a copy very suitable for use in producing further reproductions by, for instance, the diazotype copying process or for use as a master for producing printing plates in a photomechanical repro-

duction process such as disclosed in U. S. Patent 2,772,972.

The use of the moist organic solvent system from which our transfer material is coated materially speeds up coating operation with a subsequent saving in cost.

In addition to the above new features and advantages, our new receiving material possesses all of the properties and uses of the receiving material of the prior art. Thus, the photographic images formed on our receiving material may be given any of the subsequent treatments employed in photography such as intensification, reduction, toning, color development, build up of color images by silver bleaching, and the like.

The invention is further illustrated by the following examples although it is to be understood that the invention is not limited thereto:

Example I

Solution A is made by dissolving 50 g. of polyvinyl methyl ether-maleic anhydride (PVM/MA) with a specific viscosity in 2-butanone at 20° C. of 1.0-1.5, and 25 g. of low viscosity cellulose acetate containing 56% combined acetic acid in a mixture of acetone (3000 ml.) and methyl cellosolve acetate (250 ml.).

Solution B contains methanol (1750 ml.), nitric acid (1.75 ml.), hydroquinone (5.0 g.) and 2-hydroxyethyl-allylthiourea (2.5 g.). To this is added silver nitrate (2.5 g.) dissolved in 5.0 ml. of water.

Solution B is added to solution A and the resulting mixture is applied by reverse roll bead coating to give a concentration of about 5 ml. per sq. ft. to a cellulose triacetate film base.

After drying, the foil is overcoated with a solution of monoethanolamine (10% in water) using the reverse roll bead method at a rate of 5.5 feet per minute and kept wet for about 1 minute before entering a drying chamber. The back side of the foil is now coated by reverse roll bead with a solution formulated as solution A but containing methanol (1750 ml.) in addition. This too is overcoated with 10% monoethanolamine as described above.

A piece of silver halide negative paper is exposed reflex-wise in a light box using an opaque original. After exposure, the negative paper and receiving foil described above are passed through a developing device. In the developing device, the exposed negative and receiving foil are pressed face to face in the presence of a developer solution containing a silver halide developing agent and a fixer such as hypo. A few seconds after emerging from the developing device, image transfer from the negative to the receiving material is complete and the two sheets are peeled apart. The receiving foil, only slightly damp, contains a completely clear black and white positive of the opaque original.

A developing composition suitable for use in the above developing device is as follows:

Hydroquinone	-----gram	13.0
Sodium sulfite	-----gram	40.9
Sodium thiosulfate	-----gram	21.5
Potassium bromide	-----gram	2.5
Phenidone	-----gram	1.0
Sodium hydroxide	-----gram	10.0
Water	-----ounces	26

Example II

A receiving foil was prepared according to Example I except that the low viscosity cellulose acetate used therein for solution A was replaced by a vinyl acetate resin. The particular vinyl acetate employed had an intrinsic viscosity in cyclohexanone of 0.11 at 20° C.

After exposing and processing as in Example I, excellent clear black and white positive images of the opaque copy material were obtained.

Example III

The same procedure was carried out as in Example I except that 50.0 g. of poly-2-chloroethyl vinyl ether-maleic anhydride was used in place of the PVM/MA.

Example IV

Using polyethyl vinyl ether-maleic anhydride in lieu of PVM/MA, the procedure in this example was carried out as given in Example I.

Example V

The procedure was the same as in Example I excepting that 25.0 g. of a vinyl acetate resin having an intrinsic viscosity in cyclohexanone at 20° C. of 0.11 was used as the hydrophobic resin in lieu of cellulose acetate. The resulting foil, when processed as in Example I, gave results parallel to those obtained in said Example I.

Example VI

Using 25.0 g. of a low viscosity, low hydroxyl polyvinyl butyral having a viscosity of 23 cps. (5% in ethanol) in lieu of the cellulose acetate, a cellulose acetate receiving foil was prepared, exposed and developed as in Example I. A clear black and white positive image of the opaque copy material was obtained.

Example VII

The procedure of Example I was carried out using polybutyl vinyl ether-maleic anhydride in lieu of PVM/MA. The results were parallel to those obtained in Example I.

Example VIII

The procedure of Example I was carried out using polyvinyl isobutyl ether-maleic anhydride in lieu of PVM/MA. The results were parallel to those obtained in Example I.

Example IX

The procedure of Example I was carried out using poly-2-methoxyethyl vinyl ether-maleic anhydride in lieu of PVM/MA. The results were parallel to those obtained in Example I.

We claim:

1. A receiving material for use in the photographic diffusion-transfer process comprising a support having thereon a water receptive layer comprising an alkali treated mixture of a polyalkyl vinyl ether-maleic anhydride co-polymer and a hydrophobic resin compatible therewith, a silver halide developing agent, a fogging agent capable of transforming a soluble silver halide image into an image of high optical opacity and a water soluble silver salt.

2. The product as defined in claim 1 wherein the alkali is a moist water soluble nitrogenous base.

3. The product as defined in claim 2 wherein the support is a transparent plastic.

4. The product as defined in claim 3 wherein the support is a cellulose triacetate.

5. The product as defined in claim 1 wherein the polyalkyl vinyl ether-maleic anhydride co-polymer is polyvinyl methyl ether-maleic anhydride co-polymer.

6. The product as defined in claim 1 wherein the hydrophobic resin is cellulose acetate.

7. The product as defined in claim 1 wherein the water soluble silver salt is silver nitrate.

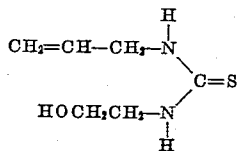
8. The product as defined in claim 1 wherein the fogging agent is a thiourea derivative, one nitrogen atom of which is joined through a methylene group to a grouping of carbon atoms containing a $>C=C<$ radical directly linked to said methylene group, and the other nitrogen atom of which is strongly basic by virtue of a chemical structure selected from the class consisting of those in which the nitrogen atom is substituted by an aliphatic radical and those in which the nitrogen atom forms part of a saturated heterocyclic ring.

9. In the process of producing a material for use in the photographic diffusion transfer process which comprises coating a support with a polyvinyl alkyl ether-maleic anhydride co-polymer, a hydrophobic resin compatible therewith, a silver halide developing agent, a fogging agent capable of transforming a soluble silver halide

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image into an image of high optical opacity, and a water soluble silver salt, the improvement of which comprises adding to the coating, an acid, the anion of which is identical with the anion of said water soluble silver salt, said layer being rendered water receptive by treatment with an alkali.

10. The product as defined in claim 8 wherein the thiourea derivative has the following formula:



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References Cited in the file of this patent

UNITED STATES PATENTS

2,704,721	Land	Mar. 22, 1955
2,751,300	James et al.	June 19, 1956
2,756,163	Herrick et al.	July 24, 1956
2,882,151	Yutzy et al.	Apr. 14, 1959

OTHER REFERENCES

- 10 Morrell et al.: Synthetic Resins and Allied Plastics, 3rd ed. 1951, pp. 9 and 10.