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[54] **ZINC OXIDE PHOTOCONDUCTIVE ELEMENT WITH STARCH REACTION PRODUCT INTERLAYER**

[75] Inventors: **Fumiaki Arai,** Tokyo; **Wasaburo Ohta; Junji Kurokawa,** both of Yokohama; **Noriyuki Usui,** Kawasaki; **Sakae Shimizu,** Tokyo; **Tetsuo Tanaka,** Kasukabe, all of Japan

[73] Assignee: **Kabushiki Kaisha Ricoh,** Ota-ku, Tokyo, Japan

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[58] **Field of Search** ..... 96/1 R, 1.5, 1.6–1.8; 101/454, 457, 462; 117/161 C, 165

[56] **References Cited**

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Primary Examiner—Roland E. Martin, Jr.
Attorney—Woodhams, Blanchard and Flynn

[57] **ABSTRACT**

An electrophotographic copying material having a photoconductive layer formed on the surface of a support, whose back is pre-coated with an electroconductive layer, with an intermediary layer between said photoconductive layer and the support, said intermediary layer comprising a printing-durable polymer consisting of methylol starch or a mixture of methylol starch and vinyl polymer.

2 Claims, No Drawings

ZINC OXIDE PHOTOCONDUCTIVE ELEMENT WITH STARCH REACTION PRODUCT INTERLAYER

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our copending application Ser. No. 830,252, filed June 4, 1969, now U.S. Pat. No. 3,682,632.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an electrophotographic copying material suitable for both the wet-developing process and the dry-developing process, which has a photoconductive layer formed on the surface of a support, whose back is precoated with an electroconductive layer, with an intermediary layer between said photoconductive layer and the support, said intermediary layer comprising a printing-durable polymer consisting of methylol starch or a mixture of methylol starch and vinyl polymer.

2. Description of the Prior Art

The conventional electrophotographic copying material employed for an offset printing plate in the prior art has been prepared using a paper or fibrous support, one side of which is previously processed for electroconductivity, which is provided with an intermediary layer formed by means of coating the opposite side thereof with a resin solution such as polyvinyl alcohol, polyvinyl acetate, etc., and the surface of thus formed intermediary layer is further coated with a dispersion consisting of a photoconductive substance such as zinc oxide and the like, a resinous binder such as acryl resin, alkyd resin and the like, and a sensitizer, thereby forming a photoconductive layer. In order to obtain an offset printing plate by employing a copying material as above, the surface of said photoconductive layer is first electrified with corona discharge, and then an original optical image is exposed onto thus electrified surface to thereby form an electrostatic latent image, and subsequently a copied image is formed through either a dry-developing process or a wet-developing process, and lastly the non-image areas are made hydrophilic by means of a treating solution containing inorganic and organic ions.

During the foregoing copying process, the electric potential impressed on the photoconductive layer is required not to easily decay by virtue of conduction by an intermediary layer as well as the support. Such phenomenon of the potential decay, that is, the so-called 'dark decay' is much influenced by the electric efficiency of the intermediary layer—such as electric insulating property, ion property, etc.—as well as physical and chemical efficiency such as hydroscopicity and the like, while, at the time of exposure said electric potential is required to decay rapidly. The characteristic curve of said dark decay is desired to be almost constant under normal humidity or a high humidity and deterioration thereof under a high humidity should be as little as possible. Therefore, the back of the copying material is coated with an electroconductive substance such as polyvinylbenzyltrimethylammoniumchloride or other surfactant so as to facilitate the escape of electric charge therefrom. As to the process of making the copying material hydrophilic, inasmuch as a treating solution can easily permeate through the photoconductive layer up to the intermediary layer, said intermediary layer is required to have a sufficient water-resisting property as well as interlayer- or wet-adhesive property. Should a photoconductive layer fail to meet these requirements, it will result in easy exfoliation in the course of offset printing. As to the manufacturing process of a copying material on the other hand, inasmuch as the surface of an intermediary layer is to be coated with a photoconductive-layer-forming dispersion (which employs water or an organic solvent such as toluene, etc., as a dispersion medium), said intermediary layer is required to have an adequate solvent-resisting property and smoothness of the surface thereof (clay is ordinarily employed as surface-smoothing agent). Since the copying efficiency (viz, image formability) of a copying material provided with an intermediary layer and the printability of said material when employed for an offset printing plate need to meet such requirements as stated above, selection of a material suitable for said inter-layer is a matter of great importance.

However, none of the conventional electrophotographic copying materials has been provided with an intermediary layer capable of satisfying all of these requirements. That is, for instance, a copying material employing such a resin as polyvinyl alcohol, polyvinyl acetate, etc. has been attended with defects in respect of water-resisting property, solvent-resisting property, adhesive property or printing endurance thereof and, consequently, has been inadequate as an offset printing plate for use in voluminous printing. Therefore, varieties of proposals have so far been made with a view to remedying these defects. Typical proposals in this sphere are relevant to for instance, a copying material having an adhesive layer sandwiched in between the intermediary layer and the photoconductive layer (Japanese Pat. No. 40-7332) or a copying material provided with an intermediary layer consisting of a reactio product between a polymer having a reactive functional group such as a hydroxyl group, carboxyl group, etc., and an initial-stage condensate of amino resin (viz, amino-plast) such as trimethylol melamine and the like (Japanese Pat. No. 40-18708). However, in case of the former of the above cited proposals, the printability is admittedly improved to some extent, but it requires provision of three layers, to wit, an intermediary layer, an adhesive layer and a photoconductive layer and, therefore, it is not only uneconomical but also apt to give rise to lack of uniformity of efficiency, while, in case of the latter, it has such a drawback that the residual formaldehyde within the intermediary layer is apt to volatilize to thereby decompose the sensitizer (viz, a dye) contained in the photoconductive layer or give rise to a change of quality of said photoconductive layer with the lapse of time to thereby cause deterioration of preservability as well as degeneration of the electrostatic properties and printability thereof.

SUMMARY OF THE INVENTION

The present invention provides an electrophotographic copying material having an improved intermediary layer, with a view to elimination of the above stated shortcomings of the copying materials in the prior art and also the provision of a copying material having superb electrostatic properties as well as printing endurance suitable for the offset printing plate.

As for the intermediary layer according to the present invention, there is employed a composition com-

prising methylol starch or a mixture of methylol starch and vinyl polymer.

As for said methylol-starch, one prepared according to a method comprising for example, mixing an aqueous solution of starch with 0.1–5 weight percent of a basic catalyst based on the water in the starch solution to adjust the pH to 7, adding 1–40 weight percent of N-methylol acrylamide into the mixture, maintaining the mixture at 20°–60°C for 0.5–2 hours and neutralizing the product with an acid, is applicable, but the invention is not necessarily limited thereto. As to the commercially available methylol-starch, a manufacture of SOKEN Chemical Co. Ltd. sold under the name 'WS–120' is suitable.

Methylol-starch has a superb water-resisting property. To take an illustration, a coating film formed through the steps of adding 0.1 part by weight of ammonium chloride per 10 parts by weight of methylol-starch to prepare an aqueous solution, coating the thus obtained aqueous solution on a paper support and drying thereafter for 3 minutes at a temperature of 130°C, proves to be no longer water-soluble. Not only that, the coating film thus formed is also excellent in its flexibility.

Furthermore, for the sake of accelerating the bridge-making reaction, a bridge-making catalyzer such as ammonium chloride, salts of organic amine or the like may also be added to the intermediary-layer-forming solution.

Besides, in order to improve the adhesive property of the present composition to the photoconductive layer, an emulsion containing a vinyl polymer may be added to said methylol-starch to the extent of 10–100 parts by weight, per 100 parts by weight of methylol starch. As for such vinyl polymer emulsion, either a non-reactive emulsion or a reactive emulsion having a reactive functional group will do. Such vinyl polymer emulsion includes, for example, acrylic resin, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, etc.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention will be further described with reference to the following illustrative examples.

EXAMPLE 1

An intermediary-layer-forming dispersion consisting of 100 parts by weight of 20 wt. percent aqueous solution of methylol starch (viz, a manufacture of Soken Chemical Co., Ltd. sold under the name 'WS–120') and 0.2 part by weight of ammonium chloride added thereto and stirred well, was coated to the extent of 13g/m² in terms of resin on one side of a paper support, whose opposite side has been processed for electroconductivity, and then was dried for 3 minutes at 140°C to thereby provide an intermediary layer. Subsequently, a photoconductive-layer-forming dispersion consisting of

photoconductive zinc oxide — 500 g
silicone resin (a manufacture of Shin-Etsu Kagaku Co., Ltd. sold under the name 'KR 211') — 50 g
acrylic resin (a manufacture of Toa Gosei Co., Ltd. sold under the name 'Aron 1003') — 50 g
fluoroscene — 0.01 g
Rose Bengal — 0.01 g
toluene — 600 g

was coated on the surface of said intermediary layer and was dried to thereby prepare an electrophotographic copying paper. The thus obtained electrophotographic copying papery produced an excellent image having a good contrast, and, in case where it was employed for preparing an offset-printing plate, said plate produced more than 2,000 acceptable prints.

EXAMPLE 2

An intermediary-layer-forming dispersion was prepared by means of adding 100 parts by weight of a polyvinyl acetate emulsion manufactured by HOECHST GOSEI Co., Ltd. and sold under the name 'MOVINYL 144' (which contains 45 wt. percent resin), 200 parts by weight of 50 wt. percent aqueous solution of methylol starch (a manufacture of SOKEN Chemical Co., Ltd. sold under the name 'WS–120') and 14 parts by weight of 10 wt. percent aqueous solution of ammonium chloride to 200 parts by weight of water and thoroughly stirring the mixture to form homogeneous dispersion. The thus prepared intermediary-layer-forming dispersion was then coated on the surface of a support consisting of a slick paper (pulp ratio of N/L being 50/50), the back of which has been processed for electroconductivity, by means of an air-doctor, and, subsequent to drying for 1 minute at 150°C, was subjected to supercalendering, whereby there was formed an intermediary layer on said support. The amount of adhesion of the resultant intermediary layer was about 10g/m² in terms of the solid matter.

Meanwhile, a photoconductive-layer-forming dispersion was prepared by means of adding 100 parts by weight of zinc oxide, 30 parts by weight of acrylic resin (containing 50 wt. percent of resin), 10 parts by weight of silicone resin (containing 50 wt. percent of resin) and 2.5 parts by weight of methanol solution containing 50 wt. percent of Rose Bengal to 140 parts by weight of toluene and thoroughly dispersing them to effect homogenization. Subsequently, the thus obtained dispersion was coated on the surface of the foregoing intermediary layer formed on the support and was dried for 2 minutes at 120°C to thereby form a photoconductive layer of 12μ thick, whereby an electrophotographic copying material was obtained.

An electrophotographic copying material thus prepared demonstrated a superb electrification property and, in particular, the dark decay under high humidity was small, so that in case of either dry development or wet development the image produced thereby displayed a superb contrast and had a superior durability. Besides, said electrophotographic copying material did not show any cracks or exfoliation of its photoconductive layer even though it was bent or folded. And, a copy obtained through dry developing a copying material under the present invention, when employed as an offset-printing plate, was not eroded by etching liquid or immersion water, nor did it exhibit any deformation or damage even after producing 4,000 prints.

EXAMPLE 3

An intermediary-layer-forming dispersion was prepared by means of adding 100 parts by weight of a self-bridging type acrylic emulsion (viz, a manufacture of Nippon Acryl Chemical Co., Ltd. sold under the name 'PRIMAL-HA 16' containing 45 wt. percent of resin), 44 parts by weight of polyvinyl acetate emulsion (containing 45 wt. percent of resin), 130 parts by weight of 50 wt. percent aqueous solution of methylol starch which is the same as that employed in Example 1

above, 5 parts by weight of 40 wt. percent aqueous solution of macromolecular quarternary ammonium salt (viz, a manufacture of Cargon Corporation, sold under the name 'Conductive Polymer 261') and 14 parts by weight of 10 wt. percent aqueous solution of ammonium chloride to 25 parts by weight of water and thoroughly stirring for dispersion. Subsequently, the thus obtained intermediary-layer-forming dispersion was coated on the surface of a support which is the same as that employed in Example 1 above and, upon drying for 1 minute at 150°C, was subjected to super-calendering, whereby an intermediary layer was formed on said support. Then, a photoconductive-layer-forming dispersant having the same composition as that of Example 2 was coated on said intermediary layer formed on the support and was dried to form a photoconductive layer of 11μ thick, whereby there was prepared an electrophotographic copying material. The efficiency of the thus obtained copying material proved equivalent to that of the copying material obtained in the foregoing Example 2. Besides, said electrophotographic copying material, when applied to an offset-printing plate, did not show any deformation nor damages even after producing 5,000 prints.

Meanwhile, in case of an electrophotographic copying material prepared for the sake of comparison through quite the same operations as in the present example, except for the replacement of methylol starch by corn starch, an offset-printing plate prepared by employing said control copying material showed the occurrence of cracks and exfoliation of the photoconductive layer after producing about 500 prints and it proved unsuitable for mass-printing.

We claim:

1. In an electrophotographic copying material comprised of an electroconductive paper support, an intermediate layer and a photoconductive layer containing photoconductive zinc oxide, the improvement wherein said intermediate layer consists essentially of a material selected from the group consisting of (a) methylol starch reaction product obtained by reacting starch with N-methylol acrylamide and (b) mixture of said reaction product (a) and a vinyl polymer selected from the group consisting of arcylic resin, polyvinyl acetate, polyvinyl chloride and polyvinylidene chloride.

2. An electrophotographic copying material as claimed in claim **1**, in which said intermediate layer (b) contains from 10 to 100 parts by weight of vinyl polymer per 100 parts by weight of said reaction product (a).

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