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Arai et al.

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[54] **COPYING MATERIAL FOR USE IN ELECTROPHOTOGRAPHY**

[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**, Tokyo, Japan

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 830,252, June 4, 1969, Pat. No. 3,682,632.

[30] **Foreign Application Priority Data**

June 14, 1968	Japan	43/40585
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[52] **U.S. Cl.** ..... **96/1.8**, 96/1.5, 96/1 R, 101/454, 101/457, 101/462, 117/155 UA, 117/161 KP, 117/161 UN, 117/161 UC, 117/161 UB, 260/858, 260/859, 260/885, 260/883

[51] **Int. Cl.** **G03g 5/04**, G03g 5/08

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

[56] **References Cited**

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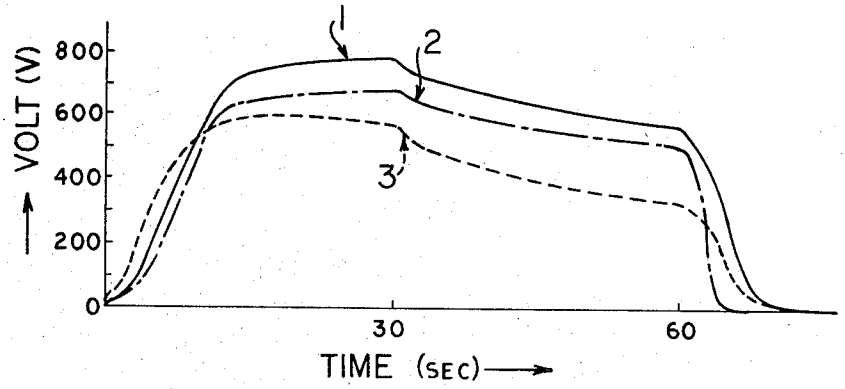
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Primary Examiner—Roland E. Martin, Jr.
Attorney—L. Martin Flynn

[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 the reaction product of vinyl polymer, polymer having urethane bonds and water-soluble amino resin.

2 Claims, 1 Drawing Figure


1
2
3
800
600
400
200
0
VOLT (V)
30
60
TIME (SEC)

COPYING MATERIAL FOR USE IN ELECTROPHOTOGRAPHY

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our co-pending application Ser. No. 830,252, filed June 4, 1969, now Pat. No. 3,682,632, issued Aug. 8, 1972.

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 the reaction product of vinyl polymer, polymer having urethane bonds and water-soluble amino resin.

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 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 polyvinylbenzyltrimethyl-ammoniumchloride 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 high volume printing. Therefore, varieties of proposals have so far been made with a view to remedying these defects. Typical proposals in this sphere include, for instance, a copying material having an adhesive layer sandwiched in between th intermediary layer and the photoconductive layer (Japanese Patent No. Showa 40-7332) or a copying material provided with an intermediary layer consisting of a reaction 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-blast) such as trimethylol melamine and the like (Japanese Patent No. Showa-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 comprising the reaction product of vinyl polymer, polymer

having urethane bonds and water-soluble amino resin.

Said vinyl polymer includes, for example, a polymer or a copolymer comprising monomers having a polymerizable vinyl radical such as acrylic ester, methacrylic ester, acrylonitrile, styrene, vinyl chloride, vinylidene chloride, vinylidene acetate, vinyl acetate, ethylene, butadiene, etc. or a polymer or a copolymer produced by the reaction between at least one member of the foregoing monomers having a polymerizable vinyl radical and at least one member of such monomers as acrylic acid, methacrylic acid, maleic acid, succinic acid, itaconic acid, glycidic acid, other carboxylic acids as well as acid anhydrides thereof, glycidyl methacrylic acid, hydroxyethylacrylic acid, hydroxypropylacrylic acid or esters thereof, acrylamide, vinyl amide formate and the group of amines such as primary amines, secondary amines, tertiary amines, etc., said polymer or copolymer having one or more radicals selected from carboxyl group, alkoxycarbonyl group, amino group, amido group, hydroxyl group, alkoxyl group, epoxy group and cyano group.

The aforesaid polymer having a urethane bond includes one or more polymers selected from methylol urethane polymers and other modified urethane polymers. Said methylol urethane polymer includes, for instance, a partial-methylolurethane polyvinylalcohol (manufactured by Toyo Koatsu Kogyo Co., Ltd. and sold under the name 'URAMINE-XP 72, URAMINE-T 1000, URAMINE-T 1050 and URAMINE-XP66') which is obtained by denaturing polyvinyl alcohol into urethane. There being some commercially available polymers containing water-soluble amino resin as above, it may be advisable to utilize them for the present invention. A partial-methylolurethane polyvinl alcohol has a methylol group bonded at the end of the polyvinyl alcohol moiety, so that it has plenty of reactivity as compared with an ordinary polyvinyl alcohol. It is not only provided with self-bridgemaking property but also is capable of readily reacting with vinyl polymer and water-soluble amino resin. Moreover, the reaction products thereof have complex network structures and, consequently, are excellent in water resistance as well as solvent resistance.

The foregoing water-soluble amino resin includes alkylated melamine-formaldehyde resin such as melamine or dimethylol melamine, trimethylol melamine, etc., ureaformaldehyde resin, aniline-formaldehyde resin, cyanamide-formaldehyde resin or mixtures of these resins. According to the present invention, mixing of quite a small amount of said amino resin suffices to effect the object thereof, and will provide the intermediary layer with an appropriate flexibility as well as a satisfactory smoothness which could not be expected of any copying material in the prior art.

In case of forming an intermediary layer by employing the aforesaid vinyl polymer of water-dispersible quality, it is only necessary to take such steps that a film-formable dispersion is first prepared by dispersing a vinyl polymer, a polymer having a urethane bond and a water-soluble amino resin polymer in water, ammonium chloride or the like is then added to said dispersion as a bridge-making catalyzer, and the resultant solution is coated on a support and dried at 110°–140°C for 1–2 minutes subsequent thereto.

As for said dispersion for use in forming an intermediary layer, it comprises (a) 1 part by weight of vinyl polymer, (b) 0.1–5 parts by weight—preferably 0.1–2 parts by weight—of a polymer having a urethane bond, and (c) 0.05–0.5 parts by weight of a water-soluble amino resin per 1 part by weight of the sum of the foregoing two polymers (a) plus (b). Further, on the occasion of forming said intermediary layer, polyvinyl acetate, thermoplastic acrylic resin or the like may be jointly employed in order to further improve the flexibility as well as the adhesive property of said layer towards the photoconductive layer.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing is a graph showing the respective dark-decay properties of two copying materials according to the present invention and a control copying material for comparison's sake.

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:

- self-bridging type acrylic resin emulsion (a manufacture of Nippon Acryl Chemical Industries Co., Ltd. sold under the name 'HA 16', containing 45 wt. percent of resin) — 100 parts by weight
- acrylic ester emulsion (PRIMAL-AC 22, containing 45 wt. percent of resin) — 42 parts by weight
- partial-methylolurethane polyvinyl alcohol (a manufacture of Toyo Koatsu Industrial Co., Ltd. sold under the name 'URAMIN-XP 66', containing 10 wt. percent of resin) — 450 parts by weight
- urea-formaldehyde resin (a manufacture of Toyo Koatsu Industrial Co., Ltd., sold under the name 'URAMIN-P2200' containing 48 wt. percent of resin) — 19 parts by weight
- ammonium chloride — 1.1 parts by weight
- water — 300 parts by weight

was coated on the surface of a slick paper (pulp ratio of N/L being 50/50) by means of an air-doctor and was dried for 1 minute at 140°C, whereby an intermediary layer of 6μ thick was formed.

Subsequently, an electroconductive-layer-forming dispersion consisting of:

- self-bridging type acrylic resin emulsion — 100 parts by weight
- partial-methylolurethane polyvinyl alcohol (a manufacture of Toyo Koatsu Industrial Co., Ltd. sold under the name 'URAMIN-XP 66') — 90 parts by weight
- urea-formaldehyde resin (named 'URAMIN-P 2200') — 11 parts by weight
- polyvinylbenzyl-trimethylammonium chloride (containing 30 wt. percent of resin) — 10 parts by weight
- ammonium chloride — 1 parts by weight
- water — 300 parts by weight

was coated on the back of the foregoing slick paper support and was dried for 1 minute at 140°C, whereby an electroconductive layer was formed on said support. Both the intermediary layer and the electroconductive layer formed as above proved to be a perfect resin film having a smooth surface free of any flaw or pinhole.

Next, a photoconductive-layer formable acrylic resin was prepared by causing a mixture comprising 50 parts

by weight of styrene, 47 parts by weight of butyl acrylate, 3 parts by weight of acrylic acid and 100 parts by weight of toluene to react for 10 hours at 100°C. Then, a dispersion was prepared by dispersing 40 parts by weight of said acrylic resin, 100 parts by weight of zinc oxide and 2cc of 5 percent methanol solution of Rose Bengal in 150 parts by weight of toluene, and same was coated on the surface of the foregoing intermediary layer of the support and dried for 1 minute at 150°C to thereby form a photoconductive layer of 12μ thick, whereby a desired electrophotographic copying material was obtained.

After that, the surface of the thus formed photoconductive layer of said copying material was subjected to corona discharge under the conditions of 32°C and a relative humidity of 80 percent to impart a saturated potential, and, after 30 seconds, the electrified surface was exposed to light and the dark-decay characteristic curve was sought.

On the other hand, a control electrophotographic copying material for use in comparison was prepared in just the same way as the present example except that the principal components of the intermediary layer and electroconductive layer thereof were replaced by the reaction products between the initial-stage condensate consisting of dimethyl-trimethylol melamine resin and styrene-hexyl acrylate-acrylonitrile, and the dark decay characteristic curve was sought under the same conditions. The results of experiments as above were as shown in the accompanying drawing. In said drawing, curve 1 shows the characteristic in case of the present example, while curve 3 shows the characteristic in case of the comparative material. (Curve 2 shows the characteristic in case of Example 2). As may be understood from said diagram, the copying material according to the present invention is provided with a saturated potential higher than that of said material employed for comparison's sake, the decrement of the dark decay characteristic curve thereof is slight, and the sensitivity thereof is very high. Accordingly, the copied image obtained through dry development as well as wet development of a copying material of the present invention was very clear. Furthermore, in case where the copied image obtained through dry development was employed for an offset-printing plate, it was not eroded by etching liquid or immersion water, and could turn out quite acceptable prints even after more than 10,000 prints were produced.

EXAMPLE 2

a. A mixture comprising:
methyl methacrylate — 60 parts by weight
ethyl acrylate — 45 parts by weight
acrylamide — 2 parts by weight
glycidyl methacrylate — 3 parts by weight
ammonium persulfate — 0.2 parts by weight
sodium laurylbenzenesulfonate — 1.0 parts by weight
hydroxyethyl cellulose —0.5 parts by weight
water —100 parts by weight

was caused to react for 6 hours at 120°C, whereby a vinyl-polymer emulsion was prepared. Subsequently, a dispersion was prepared by dispersing 100 parts by weight of said emulsion, 500 parts by weight of partial-methylolurethane polyvinyl alcohol solution (a manufacture sold under the name 'URAMIN-T 1000', containing 10 wt. percent of resin), 40 parts by weight of thermoplastic acryl resin emulsion (a manufacture sold under the name 'PRIMAL-AC 22', containing 50 wt. percent of resin), 8 parts by weight of melamine-formaldehyde resin (a manufacture of Sumitomo Chemical Co., Ltd., sold under the name 'SUMIREZ Resin 613' containing 80 wt. percent of resin) and 1.4 parts by weight of ammonium chloride to 100 parts by weight of water. The thus prepared dispersion was then coated on one side of a slick paper (pulp ratio of N/L: 50/50, thickness: 120μ) by means of an air-doctor and was dried for 1 minute at 140°C, whereby there was formed an intermediary layer of 6μ thick.

Next, another dispersion was prepared by dispersing 100 parts by weight of the emulsion obtained through the process as set forth under (a) above, 90 parts by weight of the foregoing partial-methylolurethane polyvinyl alcohol solution, 5 parts by weight of the foregoing thermoplastic acryl resin emulsion, 17 parts by weight of 30 percent aqueous solution of polyvinylbenzyl-trimethylammonium chloride, 1.4 parts by weight of ammonium chloride, 80 parts by weight of clay and 0.3 part by weight of sodium hexametaphosphate to 200 parts by weight of water, and the thus prepared dispersion was coated on the other side (viz. uncoated side) of said slick paper support in the same way as in the case of forming the aforesaid intermediary layer and was dried for 1 minute at 140°C, whereby an electroconductive layer was formed. Then, the surface of said intermediary layer formed on the support was dipped for 1 hour in toluene to be employed on the occasion of forming a photoconductive layer subsequent thereto, but there was observed no change at all.

Subsequently, by means of employing the same electrophotoconductive-layer-formable dispersion and in the same way as in Example 1, a photoconductive layer of 12μ thick was formed and a desired electrophotographic copying material was prepared therefrom.

The surface of the photoconductive layer of the thus obtained electrophotographic copying material was subjected to corona discharge at 32°C under the conditions of 32°C and 80 percent R.H. as in the case of Example 1 to seek its dark decay characteristic curve (See curve 2 of the accompanying drawing), and the thus obtained characteristic curve was compared with the curve 3 pertaining to the control copying material employed for comparison's sake. As a result, it was found that the copying material of the present example could be provided with such a high saturated potential as in the case of Example 1 and the decrement of its dark decay characteristic curve was slight and the sensitivity thereof was high. Accordingly, a copied image obtained through dry development as well as wet development of the copying material under the present invention had no stained texture and was quite clear.

Further, in case where a copied image obtained through dry development was employed for an offset-printing plate, there was observed no erosion by etching liquid or immersion water, nor any deformation or damage even after producing 10,000 prints.

EXAMPLE 3

b. A mixture comprising:
methyl methacrylate — 60 parts by weight
butyl acrylate — 30 parts by weight
hydroxyethyl acrylate — 10 parts by weight
ammonium persulfate — 0.2 parts by weight
sodium laurylbenzene sulfonate — 1.0 parts by weight

hydroxyethyl cellulose — 0.5 parts by weight
water — 100 parts by weight

was caused to react for 6 hours at 120°C, whereby a film-coating copolymer emulsion was prepared. Next, a dispersion was prepared by dispersing 100 parts by weight of said emulsion, 40 parts by weight of vinyl acetate emulsion (containing 50 wt. percent of resin), 180 parts by weight of partial-methylolurethane polyvinyl alcohol solution (viz. a solution comprising 25 wt. percent of resin, and named 'URAMIN-XP 72') which contains 10 wt. percent of urea-formaldehyde resin and 1.4 parts by weight of ammonium chloride to 100 parts by weight of water. The thus prepared dispersion was then coated on a slick paper (pulp ratio of N/L: 50/50, thickness: 120) in the same way as in Example 1 and was dried, whereby an intermediary layer of 6μ thick was formed. After that, another dispersion was prepared by dispersing 100 parts by weight of the emulsion obtained through the process as set forth under (b) above, 40 parts by weight of the foregoing partial-methylolurethane polyvinyl alcohol solution containing said urea-formaldehyde resin, 117 parts by weight of 30 percent aqueous solution of polyvinylbenzyltrimethylammonium chloride, 1.4 parts by weight of ammonium chloride, 80 parts by weight of clay and 0.3 part by weight of sodium hexametaphosphate to 200 parts by weight of water, and the thus prepared dispersion was coated on the other side (viz. non-coated side) of said slick paper support and was dried for 1 minute at 140°C, whereby an electroconductive layer was formed.

Then, the surface of said intermediary layer formed on the support was coated with the same photoconductive dispersion as in the case of Example 1 and was dried for 1 minute at 130°C, whereby a desired electrophotographic copying material provided with a photoconductive layer of 10μ thick was obtained.

The thus prepared copying material demonstrated almost the same characteristics as that of Example 1 and, when employed for an offset-printing plate, was stable against etching liquid as well as immersion water, and showed no deformation or damage even after producing more than 10,000 prints.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

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 the reaction product of (1) vinyl polymer selected from the group consisting of (A) a polymer or copolymer of at least one monomer selected from the group consisting of acrylic ester; methacrylic ester; acrylonitrile; styrene; vinyl chloride; vinylidene chloride; vinylidene acetate; vinyl acetate; ethylene; and butadiene, and (B) a copolymer of at least one of said monomers with at least one comonomer selected from the group consisting of maleic acid, succinic acid, itaconic acid, glycidic acid and acid anhydrides of the foregoing acids; gylcidyl methacrylic acid, hydroxyethyl-acrylic acid, hydroxypropylacrylic acid and esters thereof; acrylic acid; methacrylic acid; acrylamide; vinyl amide formate; primary amines; secondary amines; and tertiary amines, (2) partial methylolurethane polyvinyl alcohol and (3) at least one water-soluble amino resin selected from the group consisting of melamine, dimethylol melamine, trimethylol melamine, urea-formaldehyde resin, aniline-formaldehyde resin and cyanamide-formaldehyde.

2. An electrophotographic copying material as claimed in claim 1 in which said intermediate layer consists essentially of

a. one part by weight of vinyl polymer,
b. from 0.1 to 5 parts by weight of partial methylolurethane polyvinyl alcohol, and
c. from 0.05 to 0.5 parts by weight of water-soluble amino resin, per 1 part by weight of the sum of (a) plus (b).

* * * * *

PRINTER'S TRIM L

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3 775 108 Dated November 27, 1973

Inventor(s) Fumiaki Arai, Wasaburo Ohta, Junji Kurokawa, Noriyuki Usui, Sakae Shimizu and Tetsuo Tanaka

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Under the heading "Foreign Application Priority Data" change

"Sept. 9, 1968 Japan ..... 43/64271" to

---Sept. 9, 1968 Japan ..... 43/64277---.

Signed and sealed this 23rd day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents