United States Patent Office

3,761,259
Patented Sept. 25, 1973

3,761,259

ELECTROPHOTOGRAPHIC ELEMENT CONTAINING AN INTERMEDIATE LAYER

Fumiaki Arai, Tokyo, Wasaburo Ohta and Junji Kurokawa, Yokohama-shi, Noriyuki Usui, Kawasaki-shi, Sakae Shimizu, Tokyo, and Tetsuo Tanaka, Kasukabe-shi, Japan, assignors to Kabushiki Kaisha Ricoh, Tokyo, Japan

No Drawing. Original application June 4, 1969, Ser. No. 830,252, now Patent No. 3,682,632. Divided and this application July 5, 1972, Ser. No. 269,122

Claims priority, application Japan, June 14, 1968, 43/40,585; Sept. 9, 1968, 43/64,277; Oct. 2, 1968, 43/71,153; Oct. 9, 1968, 43/73,174; Oct. 12, 1968, 43/74,449

Int. Cl. G03g 5/06

U.S. Cl. 96—1.8 2 Claims

ABSTRACT OF THE DISCLOSURE

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 (A) at least one member of film forming and water soluble high molecular weight substances, (B) at least one member of ethylene-type vinyl resins, and (C) N-methylol acrylamide.

CROSS REFERENCE TO RELATED APPLICATION

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

BACKGROUND OF THE INVENTION

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 (A) at least one member of film forming and water soluble high molecular substances, (B) at least one member of ethylene-type vinyl resins and (C) N-methylol acrylamide.

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 has been previously processed for electroconductivity, and which is provided with an intermediary layer formed by coating the opposite side thereof with a resin solution such as polyvinyl alcohol, polyvinyl acetate, etc. The surface of the 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 acrylic resin, alkyd resin and the like, and a sensitizer, thereby forming a photo-

conductive 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 the 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 the 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 the 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 intermediary 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 producing large numbers of copies. 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 Patent No. Showa 40/7,332) or a copy-

ing 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-plast) such as trimethylol melamine and the like (Japanese patent No. Showa 40/18,708). 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 is apt to give rise to lack of uniformity of efficiency, while, in case of the latter, it has the 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 eletcrostatic properties as well as printing endurance suitable for the offset printing plate.

The intermediary layer according to the present invention comprises a composition consisting essentially of the reaction product of (A) at least one member of film forming and water soluble high molecular substances, (B) at least one member of ethylene type vinyl resins, and (C) N-methylol acrylamide. The film forming and water soluble high molecular substances include, for example, polyvinyl alcohol, a derivative of cellulose such as methyl cellulose, carboxymethyl-cellulose, ethyl cellulose and hydroxyethyl cellulose, starch, casein, sodium polyacrylate, sodium polymethacryalte, ammonium polyacrylate and ammonium polymethacrylate.

The above stated vinyl resins include, for example, a homopolymer or a copolymer produced by a reaction between at least one member of such monomers having a polymerizable vinyl radical as acrylic ester, methacrylic ester, acrylonitrile, styrene, vinyl chloride, vinylidene chloride, vinyl acetate, vinylidene acetate, ethylene, butadiene, acrylic acid, methacrylic acid, maleic acid, succinic acid, itaconic acid, glycidic acid, glycidyl methacrylic acid, hydroxyethyl acrylic acid, hydroxyethyl methacrylic acid, hydroxypropyl acrylic acid, hydroxypropyl methacrylic acid or esters thereof. These polymers or copolymers are used in the state of emulsion.

In case of forming an intermediary layer by employing the aforesaid materials, upon dissolving or dispersing a film-formable high molecular substance and a vinyl resin in water, N-methylol acrylamide is added to the solution or dispersion thus prepared and is stirred thoroughly to achieve homogenization. Subsequently, an aqueous solution comprising a polymerization catalyzer such as hydrogen peroxide, potassium persulfate, ammonium persulfate, etc. and a condensation catalyzer such as an acidic salt like ammonium chloride or an organic amine salt is added, as occasion demands, to the foregoing dispersion, whereby there is prepared a dispersion for use in forming an intermediary layer. The ethylene type vinyl resin and N-methylol acrylamide within the intermediary layer preferably are 20~150 parts by weight and 10~150 parts by weight based on 100 parts by weight of the high molecular substance, respectively. The resultant dispersion for use in forming an intermediary layer is coated on the non-electroconductive side of a support, whose surface has been processed for electroconductivity, by such a conventional means as the so-called air-doctor, and then dried for 1–2 minutes at a temperature in the range of 130–150° C. to thereby form said intermediary layer.

It seems that, in forming the intermediary layer, there occurs condensation or radical polymerisation between the reactive functonal groups contained in N-methylol acrylamide and the high molecular substance and/or the vinyl resin as well as polymerization of N-methylol acrylamide to thereby produce a reaction product having complicated net-work structures.

Subsequently, a dispersion for use in photoconductive layer consisting of such well known materials in the art as zinc oxide, a resinous binder, a sensitizer etc. is coated on the surface of the thus prepared intermediatry layer in order to form a photoconductive layer, whereby an electrophotographic copying material is obtained.

In the case of using a support which is not yet electroconductive-processed, the aforesaid intermediary layer-forming dispersion added can have thereto an electroconducting agent and, if necessary, a surface-smoothing agent is coated on one side of the support to form an electroconductive layer thereon.

As the resulting copying material according to the present invention has an intermediary layer provided with the net-work structures above-mentioned, it is not only improved in resistivity against water and solvents and in durability but also forms a clear copied image due to its good dark decay property. Thus, should the copying material be employed for offset printing, a number of acceptable prints will be obtained because of its excellent durability.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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

EXAMPLE 1

A mixture consisting of:

	Parts by weight
50 wt. percent emulsion of polyvinyl acetate (a manufacture of Hoechst Gosei Co., Ltd. sold under the name "Movinyl 114")	67
10 wt. percent aqueous solution of polyvinyl alcohol	500
50 wt. percent aqueous solution of N-methylol acrylamide (a manufacture of Toyo Koatsu Industrial Co., Ltd. sold under the name "Uramin-T 80")	100
Condensation catalyzer (a manufacture of Toyo Koatsu Industrial Co., Ltd. sold under the name "Uramin Catalyst P)	28
5 wt. percent aqueous solution of potassium persulfate	20

was dispersed in 100 parts by weight of water and was stirred for about 10 minutes, whereby an intermediary-layer-forming dispersion was prepared. The thus obtained dispersion was then coated, by means of an air-doctor, on the non-electroconductive surface of a slick paper (pulp ratio of N/L:50/50, thickness: 100μ) whose back had been processed for electroconductivity, and was dried for 1 minute at 150° C., whereby an intermediary layer of about 6μ thick was formed. After that, a photoconductive-layer-forming dispersion prepared by stirring and homogenizing a composition comprising 100 parts by weight of zinc oxide, 40 parts by weight of 50% toluene solution of acrylic resin, 2 cc. of 5% methanol solution of Rose Bengal and 150 parts by weight of toluene was coated on the surface of said intermediary layer and was dried for 1 minute at 130° C., whereby an electrophotographic copying material provided with a photoconductive layer of 10μ thick was obtained.

The thus obtained copying material proved to have superior durability, water-resisting quality, solvent-resisting quality and inter-layer adhesive quality, and the copied

image thereof formed through dry development as well as wet development was quite clear. Besides, there was observed no influence at all on the liquid developer. Further, in case where a copy 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 more than 4,000 prints.

EXAMPLE 2

A mixture consisting of:

	Parts by weight
45 wt. percent emulsion of self-bridging type acrylic resin (a manufacture of Nippon Acryl Chemical Co., Ltd. sold under the name 'Primal-HA 16")	90
45 wt. percent emulsion of polyvinyl acetate	67
10 wt. percent aqueous solution of methyl cellulose (a manufacture of Shin-Etsu Chemical Co., Ltd. sold under the name "Metolose-SM")	500
50 wt. percent aqueous solution of N-methylol acrylamide	140
Uramin Catalyst-P	30
5 wt. percent aqueous solution of potassium persulfate	34

was dispersed in 100 parts by weight of water and was stirred for about 10 minutes, whereby an intermediary-layer-forming dispersion was prepared. Then, said dispersion was coated on the same slick paper as that of Example 1 in the same way as in case of forming the intermediary layer of Example 1, whereby an intermediary layer was formed. Subsequently, the same photoconductive-layer-forming dispersion as that of Example 1 was coated on said intermediary layer, whereby an electrophotographic copying material was obtained. The efficiency of the thus prepared copying material proved equivalent to that of Example 1, and in case where said copying material was employed for printing as an offset printing plate, it could produce more than 6,000 acceptable prints.

EXAMPLE 3

A composition comprising:

	Parts by weight
45 wt. percent emulsion of self-bridging type acrylic resin (Primal-HA–16)	90
45 wt. percent emulsion of acrylic ester resin (a manufacture of Nippon Acryl Chemical Co., Ltd., sold under the name of Primal-AC–22)	20
20 wt. percent aqueous solution of starch	300
50 wt. percent aqueous solution of N-methylol acrylamide	70
Clay	80
Water	700
NH_4Cl	1

was stirred for about 10 minutes, whereby an intermediary-layer-forming dispersion was prepared. Then, said dispersion was coated on the same slick paper as that of Example 1 in the same way as in case of forming the intermediary layer of Example 1, whereby there was formed an intermediary layer. Subsequently, the same photoconductive-layer-forming dispersion as employed in Example 1 was coated on the surface of said intermediary layer, and was dried for 1 minute at 135° C. whereby an electrophotographic copying material provided with a photoconductive layer of 10μ thick was obtained. The copying material demonstrated characteristics equivalent to that of the preceding examples, and in case where said copying material was empolyed for printing as an offset-printing plate, more than 4,000 acceptable prints were obtained.

EXAMPLE 4

An electrophotographic copying material was prepared by the same method as said Example 1 except that the following intermediary-layer-forming dispersion was used.

	Parts by weight
50 wt. percent emulsion of styrene~butadiene copolymer (a manufacture of Dow Chemical Corp., sold under the name of "Dow Latex 636")	100
10 wt. percent aqueous solution of hydroxyethyl cellulose	500
50 wt. percent aqueous solution of N-methylol acrylamide	100
Clay	100
NH_4Cl	1
Water	500

The thus prepared copying material demonstrated characteristics equivalent to that of the preceding examples, and in case where said copying material was employed for printing as an offset-printing plate, more than 4,000 acceptable prints were obained.

EXAMPLE 5

An electrophotographic copying material was prepared by the same method as said Example 1 except that the following intermediary-layer-forming composition was used.

	Parts by weight
50 wt. percent emulsion of acrylonitrile~butadiene copolymer	100
30 wt. percent aqueous solution of sodium polymethacrylate	70
10 wt. percent aqueous solution of polyvinyl alcohol	300
Clay	100
NH_4Cl	1
Water	500
50 wt. percent aqueous solution of N-methylol acrylamide	100

The thus prepared copying material demonstrated characteristics equivalent to that of Example 1, and in case where said copying material was employed for printing as an offset-printing plate, more than 4,000 acceptable prints were obtained.

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 (A) at least one member of film forming and water soluble high molecular weight substances selected from the group consisting of polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose, ethyl cellulose, hydroxyethyl cellulose, starch, casein, sodium polyacrylate, sodium polymethacrylate, ammonium polyacrylate and ammonium polymethacrylate, (B) at least one member of ethylene type vinyl resins selected from the group consisting of homopolymers and copolymers of acrylonitrile, styrene, vinyl chloride, vinylidene chloride, vinyl acetate, vinylidene acetate, ethylene, butadiene, acrylic acid, methacrylic acid, maleic acid, succinic acid, itaconic acid, glycidic acid, glycidyl methacrylic acid, hydroxyethyl arylic acid, hydroxyethyl methacrylic acid, hydroxypropyl acrylic acid and esters of the foregoing acids, and (C) N-methylol acrylamide.

2. An electrophotographic copying material as claimed in claim 1, in which said intermediate layer contains from 20 to 150 parts by weight of said ethylene-type vinyl resin and from 10 to 150 parts by weight of N-methylol acrylamide per 100 parts by weight of said high molecular weight substance, respectively.

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ROLAND E. MARTIN, JR., Primary Examiner

U.S. Cl. X.R.

96—1 R, 1.5; 101—454, 457, 461, 462; 117—157, 161 C, 161 UN, 161 UA, 218