

# United States Patent

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## [54] VINYL-AMINO RESIN INTERLAYER FOR ELECTROPHOTOGRAPHIC MEMBER USED IN OFFSET PRINTING

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101/462

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### ABSTRACT

An electrophotographic material for offset printing having an interlayer, which comprises a reaction product of vinyl resin and amino resin, between a support and a photoconductive layer, said vinyl resin being vinyl polymer having hydroxyl group in the terminal of the long side chain thereof and said amino resin being melamine resin, urea resin, aniline-aldehyde resin, polyacrylamide, polymethylolacrylamide or their derivatives such as methylated-ethylated- or butylated-methylolmelamine, polymethacrylamide or polymethylol-methacrylamide is disclosed.

1 Claims, No Drawings

# VINYL-AMINO RESIN INTERLAYER FOR ELECTROPHOTOGRAPHIC MEMBER USED IN OFFSET PRINTING

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to an electrophotographic material for offset printing having an interlayer between a support and photoconductive layer, said interlayer comprising a reaction product of vinyl resin and amino resin.

### 2. Description of the Prior Art

In general, electrophotographic materials are made by applying a mixture of photoconductive substance and insulating resin (insulating binder) to a surface of a support (e.g., paper) and providing an electroconductive layer on the reverse side of the support. Such an electrophotographic material can not be utilized as a plate for offset printing, as it is. The reasons are as follows. The electrophotographic material for offset printing must have a high-water-resisting quality besides the good electrostatic property, since said material is treated with a specific aqueous solution (hydrophobic-hydrophilic-changing solution) in order to change the nonimage area of said material from hydrophobic (oleophilic) to hydrophilic (oleophobic).

Furthermore, said material requires that the peeling of the photoconductive layer from the support does not occur on running. For those reasons, there have been proposed various electrophotographic materials for offset printing, but the materials having satisfactory properties, i.e., high printability and running faculty, have not been obtained. (The running faculty means the number of sheets of the printed matter given by one sheet of the electrophotographic material for offset printing.)

It is, therefore, an object of the present invention to provide an improved electrophotographic material for offset printing having a superior printability and running faculty.

## SUMMARY OF THE INVENTION

The present invention relates to an improved electrophotographic material for offset printing, and more particularly to an electrophotographic material having an improved printability and running faculty.

The electrophotographic material for offset printing of this invention comprises a support (e.g., paper), a photoconductive layer on the support, an interlayer between said photoconductive layer and support, and an electroconductive layer.

The properties such as printability and running faculty of the electrophotographic material for offset printing depend on a quality of the interlayer formed between the photoconductive layer and the support of the material. The interlayer having a good quality is that having an improved water-resisting quality and adhesive property, a high flexibility and an adequate electric resistance.

We have found that such an interlayer may be formed by applying an interlayer-forming solution comprising a mixture of vinyl resin and amino resin to the support and heating to a temperature between 100° and 150° C., said vinyl resin is vinyl polymer having a functional group such as hydroxyl group, for example, hydroxyethyl or hydroxylpropyl group in the terminal of the long side chain of the molecule.

Said vinyl polymer may be obtained by copolymerization of at least one monomer selected from the group consisting of hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, hydroxy acrylate and 5-hydroxy-pentyl-vinyl ether, and at least one vinyl monomer selected from the group consisting of styrene, acrylic ester, methacrylic ester, vinyl chloride, vinyl acetate and vinylidene chloride. This copolymerization is a solution polymerization carried out in an organic solvent such as alcohol or toluene.

An aqueous solution of said vinyl polymer, which is applied to the support in the form of the aqueous solution, may be obtained by carrying out the copolymerization of each of the above-mentioned two types of monomers and at least one un-

saturated carboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid, and then mutualizing the carboxylic acid with basic substances such as ammonium hydroxide or amines.

The aforementioned properties of the interlayer may be optionally varied by the selection of the above-mentioned monomers.

The other constituents, i.e., amino resins are preferably melamine resin, urea resin, aniline-aldehyde resin, polyacrylamide, polymethylolacrylamide or their derivatives. The preferred commercial amino resins include Uramine T-350, Uramine T-33, Uramine T-36, Uramine 560 and Uramine 561 (trademark; made by Toyo Koatsu Co.), Sumirez-Resin (trademark; made by Sumitomo Chemical Co.).

The aforementioned interlayer-forming solution hardens by making to react vinyl polymer with amino resin at a temperature between 100° and 150° C. It seems that this hardening is caused by linkage of OH group of vinyl polymer and OH, NH<sub>2</sub> or NHCH<sub>2</sub>OH group of amino resin under dehydration.

The high-sized support may be prepared by sizing a support (e.g., paper) with usual sizing agents, such as cationized polyvinyl resin, water-soluble cellulose or water-soluble acrylic resin. Alternatively, the interlayer-forming solution may be utilized for sizing. The photoconductive layer comprises, for example, a mixture of zinc oxide and insulating binder such as alkyl resin or acrylic resin.

The adhesion between the photoconductive layer and the support through the medium of the interlayer of this invention is very firm, and consequently the electrophotographic material having such an interlayer may give more than 5,000 sheets of printed matter without peeling of the photoconductive layer by means of a conventional offset printing machine.

The details of utilizing the electrophotographic material having an interlayer of this invention for offset printing, will be described in the following examples.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is further illustrated by the following nonlimitative examples.

### EXAMPLE 1

An interlayer-forming solution was prepared from the following ingredients:

ethyl alcohol solution of methyl methacrylate-butyl acrylate-hydroxyethyl methacrylate copolymer (solid 50%)	60 parts by weight
melamine resin (trademark, Uramine T-350, solid 50%)	40 parts by weight
denatured alcohol	200 parts by weight

This solution was applied on a surface of a reinforced paper subjected to surface sizing with a sizing agent containing polyvinyl alcohol as a main constituent by air-knife and then dried off at a temperature of 130° C. for 3 minutes to form an interlayer having thickness of about 2-5μ.

The above-mentioned methyl methacrylate-butyl acrylate-hydroxyethyl methacrylate copolymer may be produced by solution polymerization of the following monomers in ethyl alcohol under an atmosphere of nitrogen.

methyl methacrylate	50 parts by weight
butyl acrylate	40 parts by weight
hydroxyethyl methacrylate	10 parts by weight

A photoconductive layer-forming solution was prepared from the following ingredients:

zinc oxide (photoconductive type)	100 parts by weight
acrylic resin	10 parts by weight
alkyl resin	10 parts by weight
manganese naphthenate and cobalt naphthenate	very small quantities

sensitizer (Rose Bengale,  
Fluoresceine)  
toluene

0.05 part by weight  
100 parts by weight

This solution was applied on the surface of said paper having the interlayer and dried off in the same manner as above described. Thus, an electrophotographic material for offset printing was obtained.

A desired printed image was formed on said material by commercial printer. The excellent image was obtained electrophotographically even when the formation of the image has been carried out in an atmosphere of relative humidity of 30-85 percent.

The property of nonimaged area of said material was changed from hydrophobic (oleophilic) to hydrophilic (oleophobic) and then this material was employed for offset printing. Ten thousand sheets of the printed matter carrying a clear image was obtained without peeling of the photoconductive layer.

Commercial electrophotographic material having only polyvinyl alcohol as a main constituent of the interlayer was compared with the material of this invention. Said commercial material gave only 1,000 sheets of the printed matter before the peeling of the photoconductive layer occurred.

#### EXAMPLE 2

A copolymer was obtained from ethyl alcohol solution (solid 50 percent) of 50 parts by weight of methyl methacrylate, 40 parts by weight of butyl acrylate, 5 parts by weight of acrylic acid and 5 parts by weight of hydroxyethyl acrylate. An aqueous solution (solid 25 percent) of said copolymer was obtained by addition of triethylamine and water. A mixture of 60 parts by weight (calculated in solid constituent) of said aqueous solution of the copolymer and 40 parts by weight of Sumirez-Resin were diluted with water to give 10 percent aqueous interlayer-forming solution. This solution was applied on a surface of a reinforced paper of thickness of 0.1 mm. in the same manner as that of example 1 and a mixture of electroconducting agent (sold by Calgon Inc. under the trademark "Calgon Conductive Polymer 261") and waterproof cationic latex was applied on the other side of the paper and dried off at a temperature between 110° and 150° C. to complete the interlayer and electroconductive layer.

The photoconductive layer-forming solution of example 1 was applied on the surface of said paper having the interlayer and dried off at 110° to 150° C. to give an electrophotographic material for offset printing. The electrophotographic material thus obtained, possessed the same properties as that of example 1.

The printing test was repeated five times and each test gave more than 5,000 sheets of the printed matter, said printed matter carrying a good image. On the contrary, commercial electrophotographic material offset printing gave only 800 sheets of the printed matter carrying a good image.

#### EXAMPLE 3

A mixture of the interlayer-forming solution of example 2 and a small quantity of cationic latex was applied on the surface of a paper and then the interlayer-forming solution prepared as in example 1 was applied on the surface of said paper and dried off. Then, the electroconductive layer was formed on the other side of the paper by the procedure of example 2. The paper thus treated was remarkably waterproof and the adhesion between the paper and the interlayer is very firm.

A photoconductive layer-forming solution was prepared from the following ingredients:

zinc oxide	100 parts by weight
acrylic resin	18 parts by weight
silicone resin	2 parts by weight
sensitizer (Rose Bengale, Fluoresceine)	0.05 parts by weight
toluene	100 parts by weight

This solution was applied on the surface of the interlayer of said paper in coating speed of 30 m./min. by means of wire bar and dried off at 130° C. Thus, electrographic material for offset printing was obtained.

This material gave more than 10,000 sheets of the printed matter without peeling of the photoconductive layer and the printed image was very clear.

We claim:

1. An electrophotographic material for offset printing comprising a paper support, a zinc oxide photoconductive layer on said support, an interlayer between said photoconductive layer and support and an electroconductive layer characterized in that said interlayer comprises a vinyl polymer obtained by copolymerizing at least one monomer selected from the group consisting of hydroxyethylmethacrylate, hydroxyethylacrylate, hydroxypropylmethacrylate, hydroxyacrylate, and 5-hydroxy-pentylvinylether and a vinyl monomer selected from the group consisting of styrene, acrylic ester, methacrylic ester, vinylchloride, vinylacetate and vinylidene chloride, and an amino resin selected from the group consisting of melamine resin, urea resin, aniline-aldehyde resin, polyacrylamide, and polymethylolacrylamide, said interlayer being hardened by reacting the vinyl polymer and the amino resin at a temperature of about 100° to 150° C.

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