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ELECTROPHOTOGRAPHIC RECORDING PLATE FOR LITHOGRAPHY

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5 Claims

ABSTRACT OF THE DISCLOSURE

An electrophotographic copying paper which is comprised of a support sheet, an intermediate layer formed on one surface of said support sheet with a water-soluble thermo-setting resin containing a hydroxymethyl radical, a photoconductive layer consisting of a photoconductive substance securely adhered to the upper surface of said intermediate layer by the use of a thermosetting resin having a hydroxyethyl radical and a carboxyl radical, and a layer of low electric resistance provided on the reverse surface of said support sheet, serves as a highly satisfactory recording plate for lithography.

BACKGROUND OF THE INVENTION

(a) Field of the invention

The present invention is concerned with an electrophotographic recording plate for lithography.

(b) Description of the prior art

An electrophotographic recording plate for lithography, in general, is of a structure comprising a support sheet, an intermediate layer provided on one surface of said support sheet, a photoconductive layer formed on the upper surface of said intermediate layer, and a further layer provided on the reverse surface of said support sheet. The intermediate layer normally is made with a hydrophilic colloid. Conventional electrophotographic recording plates for lithography were such that their aforesaid intermediate layers and the layers formed on the reverse side of the support sheets both lacked sufficient water-proofness and that their photoconductive layers also were insufficient in their mechanical strengths. Therefore, the conventional electrophotographic recording plate had various drawbacks such that their photoconductive layers caused cracks or exfoliation during the process of planographic printing, or there arose the staining of prints by the printing ink owing to local damages in the photoconductive layers. For the foregoing reasons, the conventional electrophotographic recording plates for lithography were not sufficient in their stability which is one of the important properties of the printing plates required in the process of printing, and moreover, they were durable for a limited number of runs which was of the order of only 2000 to 3000 prints at most.

SUMMARY OF THE INVENTION

The present invention has been worked out as a result of an overall review of the various drawbacks and inconveniences of the conventional electrophotographic record-

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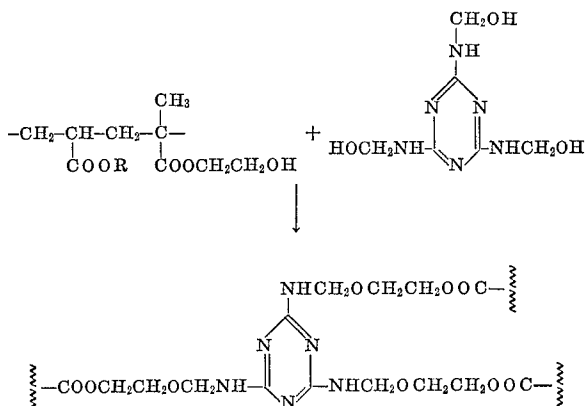
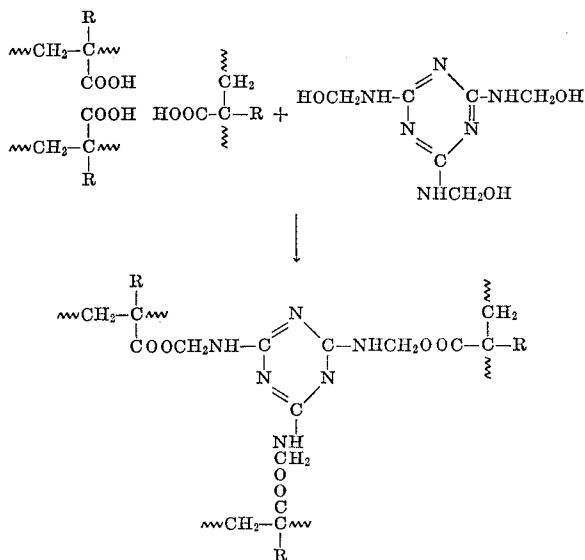
ing plates for lithography and as a result of a large number of experiments conducted from various angles with respect to the individual materials constituting the electrophotographic recording plates for lithography.

The present invention has for its object the provision of a novel electrophotographic recording plate for lithography which is free of all of the drawbacks and inconveniences of the conventional electrophotographic recording plates.

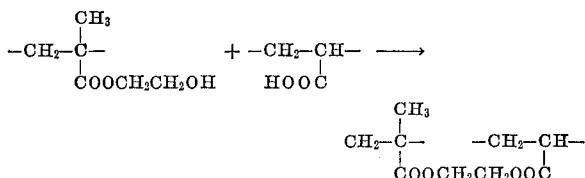
As has been stated above, an electrophotographic recording plate is provided, on the reverse surface thereof, with a layer having a low electric resistance. This layer formed on the reverse surface of the recording plate is required to have a sufficient waterproofness in addition to the low electric resistance. According to the present invention, there is produced, on the reverse surface of the recording plate, a layer which most desirably satisfies these requirements by applying onto said surface a solution of a ureaformaldehyde resin or an acetal resin prepared by condensing melamine glycol and formaldehyde, or by applying thereto a mixed solution consisting of the aforesaid resin and a substance such as vinylbenzyl-trimethyl ammonium chloride having a high molecular weight and having a relatively high electroconductivity, and then drying the same. The layer which is formed on the reverse side of the support sheet of the electrophotographic recording plate for lithography in such a way as described above is featured by a highly improved water-proofness and also by a surface resistance of 10^{10} Ω -cm. or smaller. On the upper surface of the support sheet, on the other hand, there are formed an intermediate layer and also a photoconductive layer. As the material for use in the formation of the intermediate layer, there is employed, as the principal component, a water-soluble thermo-setting resin having a hydroxymethyl radical in each of their molecules, such as a cation-modified urea-formaldehyde resin, a melamine-formaldehyde resin and a polymethylol-acrylamide. It is needless to say that a urea-formaldehyde resin which has undergone a two-step modification can also be effectively used as the resin for use in the formation of the intermediate layer. An intermediate layer which is formed with such a resin will, after the resin solution has been dried by the application of heat, have a surface resistance of 10^{12} Ω -cm. or smaller, and furthermore, the layer will have a sufficient water-proofness. The resin for use in the formation of the intermediate layer is applied, in the form of an aqueous solution, onto one surface of a support sheet and the same is dried briefly at 100° C. for a period of the order of 2 minutes and then a solution in which particles of the resin for the formation of the photoconductive layer is dispersed is applied onto the upper face of said intermediate layer. As the resin for binding the photoconductive layer to the intermediate layer, there is used a thermo-setting acryl resin containing a hydroxyethyl radical and a carboxyl radical. The layer on the reverse surface of the support sheet, the intermediate layer and the photoconductive layer are formed, respectively, by applying the individual layer-forming resins on a support sheet and then drying them by the application of heat at a temperature in the vicinity of 100° C. for a period of time of the order of about 30 to 60 minutes. It should be understood, however, that these conditions for drying the resins do not constitute an element which restricts the present invention. During the aforesaid process

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of the heat treatment, there takes place a linkage (see the following chemical formulas):



between the carboxyl radicals contained in the resin for binding the photoconductive layer and the hydroxymethyl radicals contained in the resin of the intermediate layer due to the ester bonding therebetween, and as a result, the photoconductive layer is made to adhere very firmly to the intermediate layer. It is presumed that the resin contained in the intermediate layer is thermally set in the presence of an acid catalyst and that the hydroxyethyl radicals and the carboxyl radicals of the resin for binding the photoconductive layer perform ester bonding between the molecules of the resin (see the following chemical formulas):



It has been confirmed that particularly in case a copolymer acrylic synthetic resin having hydroxyethyl radicals and carboxyl radicals is mixed with an acryl resin having carboxyl radicals, the carboxyl radicals contained in the acryl resin will act as an acid catalyst so that the mixture can be sufficiently thermoset by a heat treatment which is conducted at 100° C. for 30 minutes.

While it has been stated above that the layer on the reverse side of the recording plate for lithography, the intermediate layer and the photoconductive layer of the present invention are laminated on an appropriate support sheet, it is to be understood that in case it is in-

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tended to use a support sheet made of paper, it is preferred to use a paper made from the pulp of needle-leaved trees.

As has been described in detail, the layer formed on the reverse side of a support sheet, the intermediate layer and the photoconductive layer of the present invention are comprised of specific resins, respectively, so that the intermediate layer and the layer formed on the reverse side of the recording plate both have a highly enhanced water-proofness and in addition, the intermediate layer is firmly adhered, by being thermally set, to the photoconductive layer in the form of ester bonding. For this reason, the electrophotographic recording plate for lithography of the present invention is capable of markedly increasing the number of runs due to the highly durable printing face of the plate. At the end of the runs amounting to over 10,000 prints in number, there is noted no appreciable amount of deterioration of the photoconductive layer. The printing plate of the present invention brings about a good result with respect also to the resolving power.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Resin solutions having the following compositions and for use in the formation of the layer on the reverse surface of the support sheet, the intermediate layer and the photoconductive layer, respectively, were prepared. The hydroxyethyl acrylic synthetic resin and the carboxyl acrylic synthetic resin which were used in the preparation of the resin solution for forming the photoconductive layer were obtained according to the following procedures, respectively:

Hydroxyethyl acryl resin.—To 120 gr. of a mixed solvent consisting of toluene, xylene and butanol were added 60 gr. of butyl acrylate, 10 gr. of hydroxyethyl methacrylate and 40 gr. of ethyl acrylate. They were polymerized at 100° C. for 8 hours in a reaction vessel containing an atmosphere which was replaced by nitrogen and in the presence of 2 gr. of benzoyl peroxide.

Carboxyl acrylic synthetic resin.—50 gr. of ethyl acrylate, 48.5 gr. of n-butyl methacrylate and 1.5 gr. of itaconic acid were subjected to polymerization under the conditions similar to those stated above.

Composition of Solution A (intended for forming the layer on the reverse side of the support sheet):

	Gr.
Acetal resin (Aoba Resin AR 750, a product of Aoba Kagaku K. K. of Japan)	30
Zinc nitrate	5
Methanol	50
Water	200

Composition of Solution B (intended for forming the intermediate layer)

	Gr.
Urea resin (using Uramin 1500 HV, a product of Toyo Koatsu Industries, Inc. of Japan)	30
Hardening catalyst (ammonium chloride)	0.5
Methanol	80
Water	170

Composition of Solution C (for forming the photoconductive layer)

	Gr.
Hydroxyethyl acryl resin	70
Carboxyl acrylic synthetic resin	30
Zinc oxide	500
Sensitizing dyestuff (Rose Bengal, Acridine Orange and Fluorescein)	0.5
Toluene	600
Methanol	10

First, the aforesaid solution A was applied onto the reverse surface of a support paper sheet and the same

was dried at 120° C. for 2 to 5 minutes. Then, the solution B was applied onto the resulting surface of the support sheet, and the same was dried briefly at about 100° C. for a period of time of the order of 2 minutes. During this process, most of the methylol radicals contained in the resin of the intermediate layer remained undecomposed. Thereafter, the solution C was applied onto the briefly dried intermediate layer. After the layer on the reverse surface of the support, the intermediate layer and the photoconductive layer have thus been formed, they are subjected to a heat treatment at 100° C. for about 30 minutes to have these resins cured and firmly adhered to each other. In this way, an electrophotographic recording plate for lithography was obtained.

A copied image was formed on the face of this electrophotographic recording plate according to a known electrophotographic copying procedure, and the formed image was heat-fixed. Thereafter, an oil-repellent solution consisting of potassium ferrocyanide, sodium phosphate, an inorganic acid and a polyhydric alcohol was applied onto the image-bearing face of the printing plate to make the non-image areas of the recording plate oil-repellent. Thereafter, 1 part of this oil-repellent solution was diluted into 10 parts, so as to serve as the fountain solution. By using this fountain solution, experimental printing was conducted on a small-sized planographic press. At the end of 10,000 runs, there was noted no deterioration of the photoconductive layer. With a conventional electrophotographic recording plate for lithography, in contrast to the above one, there occurred cracks in the photoconductive layer at the end of the runs of the order of 500 prints. Furthermore, at the end of runs of the order of 1000 prints, there appeared stains in the form of cracks and spots on the faces of the prints.

Example 2

Solutions A, B and C having the undermentioned compositions were prepared for being used for the same purposes as described in Example 1. In the same manner as described in said example, an electrophotographic recording plate for lithography was produced. The hydroxyethyl acrylic synthetic resin and the carboxyl acrylic synthetic resin which were for use in the preparation of the solution C were obtained in the manner described below:

Hydroxyethyl acrylic synthetic resin.—In 100 gr. of the mixed solvent which was used in the preparation of the hydroxyethyl acryl resin in Example 1, there were dissolved 50 gr. of n-butyl methacrylate, 10 gr. of hydroxyethyl methacrylate, 30 gr. of styrene and 10 gr. of methyl methacrylate. They were subjected to polymerization according to the conditions used in Example 1 in the preparation of the hydroxyethyl acrylic synthetic resin.

Carboxyl acrylic synthetic resin.—50 gr. of ethyl acrylate, 2 gr. of acrylic acid, 28 gr. of butyl acrylate and 20 gr. of styrene were dissolved in 120 gr. of the aforesaid mixed solvent, and they were polymerized in the presence of 2.2 gr. of azobis-isobutyronitrile. The rest of the conditions were pursuant to those employed in the preparation of the carboxyl acrylic synthetic resin in Example 1.

Composition of Solution A:

	Gr.
Urea resin (using Uramin 1800, a product of Toyo	
Koatsu Industries, Inc. of Japan) -----	20
Ammonium chloride -----	1
Water -----	180

Composition of Solution B:

	Gr.
Melamine formaldehyde resin (Sumirez Resin 613, a product of Sumitomo Chemical Co., Ltd of Japan) -----	25
Polyvinyl alcohol -----	5
Hardening catalyst -----	0.5
Water -----	270

Composition of Solution C:

	Gr.
Hydroxyethyl acryl resin -----	60
Carboxyl acrylic synthetic resin -----	30
Silicone resin (KR 211, a product of The Shin-Etsu Chemical Industry Co., Ltd. of Japan) -----	10
Zinc oxide -----	500
Sensitizing dyestuff (see Example 1) -----	0.6
Toluene -----	700
Methanol -----	12

The thicknesses of the respective layers were: 2μ for the layer formed on the reverse side of the support sheet, 5μ for the intermediate layer and 10 to 15μ for the photoconductive layer. An electrophotographic recording plate for lithography prepared in this manner was regulated as regards its moisture content in an atmosphere having a humidity of 65% and for 12 hours. The resulting recording plate was determined as regards its electrostatic characteristics. It was found that the saturated potential was in the range of from 500 to 600 (—v.) and the recording plate exhibited a very little amount of dark decay, and it displayed an excellent sensitivity to light. It was also found that the recording plate showed an extremely small amount of light-fatigue on a pre-exposure (500 Lux for 60 seconds), and there was noted no harm in practical use. This plate was subjected to an electrophotographic copying process in a known manner. After the copied image was heat-fixed, the copy was given an oil-repelling treatment in a manner similar to Example 1. Thereafter, this printing plate was subjected to a planographic printing process. The printing plate of the instant example was noted to be free of deterioration of the photoconductive layer at the end of runs of the order of 10,000 prints and thus showed an excellent durability in printing.

Example 3

For the same purposes as in Example 1, solutions A, B and C having the following compositions were prepared. In the same manner with Example 1, an electrophotographic recording plate for lithography was obtained. This plate permitted a clear copied image to be formed in the electrophotographic copying process, and also showed a durability in printing which was good for runs of over 12,000 prints. The hydroxyethyl acrylic synthetic resin and the carboxyl acrylic synthetic resin which were used in the preparation of the solution C were obtained in a manner as follows:

Hydroxyethyl acryl resin.—In 100 gr. of the mixed solvent used in the preparation of the hydroxyethyl acrylic synthetic resin of Example 1 were dissolved 60 gr. of ethyl acrylate, 10 gr. of hydroxyethyl methacrylate and 30 gr. of ethyl methacrylate, and they were polymerized in the presence of 2 gr. of azobis-isobutyronitrile. The polymerization and other conditions were pursuant to those for the preparation of the carboxyl acrylic synthetic resin in Example 1.

Carboxyl acryl resin.—50 gr. of ethyl acrylate, 2 gr. of methacrylic acid and 48 gr. of n-butyl methacrylate were dissolved in said mixed solvent and they were polymerized in the presence of 2.0 gr. of benzoyl peroxide. The polymerizing conditions and other conditions were pursuant to those for the preparation of the carboxyl acrylic synthetic resin in Example 1.

Composition of Solution A:

	Gr.
Acetal resin (Uramin F 550, a product of Toyo Koatsu Industries, Inc.) -----	150
Vinyl-benzyl-trimethyl ammonium chloride --	10
Hardening agent (ammonium oxalate) -----	1.5
Methanol -----	850
Water -----	1000

Composition of Solution B:

Cationized urea resin (using Uramin 1500 HV, a product of Toyo Koatsu Industries, Inc.)	40
n-Methylol acrylamide	10
Hardening agent (ammonium chloride)	1
Methanol	50
Water	100

Composition of Solution C:

Hydroxyethyl acrylic synthetic resin	100
Carboxyl acrylic synthetic resin	50
Zinc oxide	600
Sensitizing dyestuff (see Example 1)	1
Toluene	1000

In the foregoing examples, description has been directed to only the recording plates for lithography. It should be understood, however, that the electrophotographic recording plates of the present invention can be utilized also as ordinary electrophotographic copying papers. In such a case, the product of the present invention provides a great advantage in the aspect also of mechanical strength such that the respective layers of the recording plate are of greater bending strengths as compared to those of the conventional electrophotographic copying papers.

What is claimed is:

1. In an electrophotographic recording member comprising an electrically conductive support, a layer of low electrical resistance formed on one surface of said support, an intermediate layer formed on the other surface of said support and a photoconductive layer formed on the upper surface of said intermediate layer, said photoconductive layer consisting essentially of inorganic electrophotographic photoconductor particles imbedded in an insulating resin binder, the improvement wherein said intermediate layer consists essentially of a water-soluble thermosetting resin containing hydroxymethyl radicals and said resin binder of said photoconductive layer consists essentially of a mixture of a thermosetting acrylic synthetic resin containing hydroxyethyl radicals and a

thermosetting acrylic synthetic resin containing carboxyl radicals, said intermediate layer and said resin binder having been thermally set to effect bonding between said radicals, whereby to provide improved water-proofness and mechanical strength.

2. An electrophotographic recording member according to claim 1, wherein said water-soluble thermosetting resin in said intermediate layer is selected from the group consisting of urea-formaldehyde resin containing hydroxymethyl radicals, melamine-formaldehyde resin containing hydroxymethyl radicals and polymethylol acrylamide containing hydroxymethyl radicals.

3. An electrophotographic recording member according to claim 1, wherein said layer of low electrical resistance on one surface of said support consists essentially of resin selected from the group consisting of acetal resin prepared by condensing melamine, formaldehyde and glycol, and urea-formaldehyde resin, and said layer has an electric resistance of 10^{10} Ω -cm. or smaller.

4. An electrophotographic recording member according to claim 3, wherein said layer of low electrical resistance on one side of said support contains vinyl-benzyl-trimethyl ammonium chloride.

5. An electrophotographic recording member according to claim 1, in which said photoconductor particles consist of dye-sensitized zinc oxide.

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