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(71) Applicants
Minnesota Mining and Manufacturing Company,
3M Center,
P.O. Box 33427,
Saint Paul,
Minnesota 55133,
United States of America.
(72) Inventors
Dallas Keith Pierson
(74) Agents
Lloyd Wise, Tregear & Co.

(54) **Long run electrophotographic-imaged lithographic printing plate**

(57) An electrophotographically imageable article capable of providing a lithographic printing plate comprising an electrically conductive support, a resinous coating overlying said support, the major component of which is a resin selected from the group consisting of polyurethanes, acrylics, acrylate copolymers, polysulfones and polyvinyl acetates, and a photoconductor layer overlying said resinous coating.

SPECIFICATION

Long run electrophotographic-imaged lithographic printing plate

5 This invention relates to an electrophotographic article for offset printing. More specifically, the invention relates to an article capable of being imaged electrophotographically which contains a hereinafter defined interlayer between the support and the photoconductive overlayer.

10 An electrophotographic article typically comprises a support, e.g., plastic, paper, glass, metal, which itself is electrically conductive or which is treated to render same conductive. The conductive support is then coated with a photoconductive layer, typically comprising photoconductive materials such as zinc oxide, selenium, cadmium sulfide, and the like, mixed with an insulating resin binder, if necessary, to afford adhesion of the photoconductive layer to the support.

15 To obtain a planographic master suitable for lithographic printing purposes, typically an electrostatic charge is deposited on the surface of the photoconductive layer via a corona discharge device in the absence of impinging external light, after which the charged layer is illuminated with the image of an original copy to be produced. Where light strikes the photoconductor, the surface charge is dissipated; non-illuminated areas remain charged, thereby defining a latent image of the original copy. The latent image is then developed by conventional wet or dry development techniques utilizing resinous powders which can then be heat or pressure fused to affix the powders to the photoconductor surface. The background or non-image areas can then be chemically converted, such as described in U.S. Patent No. 3,001,872, to render same hydrophilic and ink repellent. The image areas where the resinous powder has been fused are ink receptive, and the conversion process does not effect this characteristic.

20 Following imaging, development, fixing and conversion of background areas, the sheet structure can be simply utilized in conjunction with an offset printing press whereupon conventional lithography can be undertaken.

25 Such lithographic plates typically utilize paper as a support and are generally of short-run capability, for various reasons, such as the lack of adhesion of the image areas, the penetration of the paper support by the moisture contained in conventional dampening fluids which tends to cause the plate to wrinkle and stretch, etc.

30 In order to overcome such difficulties, many prior patents have been issued which disclose the use of an interlayer between the photoconductive overlayer and the support. Such interlayers have typically been of complex combinations of polymer systems. For example, U.S. Patent No. 3,778,264 discloses the use of the reaction product of an epoxy-containing polymer and other specifically defined compounds; 3,778,263 discloses a starch and vinyl polymer mixture; 3,672,888 discloses the reaction product of a hydroxyl-containing com-

35 pound and a chromium compound; 3,761,259 discloses the reaction product of a high molecular weight water soluble material, an ethylene-type vinyl resin and an acrylamide; and 3,775,108 discloses the reaction product of a vinyl polymer, a polymer having urethane bonds, and a water-soluble amino resin.

40 It has now been ascertained that a simple solution to the aforementioned problems can be obtained through the utilization of an interlayer comprised of a simple resinous coating material. No complicated reaction mixture of polymers need be manufactured prior to application of the interlayer, and use of these resinous materials provides adequate adhesion of the interlayer to the support, e.g., paper, and of the photoconductive coating to said interlayer. Furthermore, the interlayer has been found sufficient to provide a moisture barrier to prevent the foregoing problems relative to moisture in conjunction with a paper support, and the electrical characteristics necessary for electrostatic imaging are not reduced by the use of such an interlayer.

45 Through the use of such materials a better image quality is available, because typically support materials such as paper are non-uniform in terms of both electrical characteristics and physical uniformity which tend to provide insufficient pressure fusing of the imaging media.

50 Additionally, a wider variety in paper selection can be utilized with the interlayer construction of my invention. The elimination of wrinkling of the plate when functioning on the press is achieved by the elimination of the moisture problem relative to the support.

55 Furthermore, less plate stretch on the press is noted utilizing the interlayer of my invention. The plate of my invention can in fact be run with the paper grain cross-web on a press, as opposed to the machine direction thereof. Typically, in paper manufacture, the paper grain direction is the same as the paper machine direction and has the greatest amount of strength and, therefore, less susceptibility to stretching. In the cross-web direction, i.e., perpendicular to the paper machine direction in the plane of the paper, the strength is correspondingly less and the susceptibility to stretching correspondingly greater. By use of the interlayer of my invention, a plate can actually be run cross-web on a printing press without the attendant problems which have been prevalent with prior constructions.

60 In accordance with the invention there is provided an electrophotographically imageable article comprising an electrically conductive support having a resinous coating on one surface thereof, the major component of said resinous coating being a resin selected from the group consisting of polyurethanes, acrylics, acrylate copolymers, polysulfones and polyvinyl acetates, and a photoconductor coating overlying said resinous coating.

65 After imaging, development, image fixing and conversion of the non-image areas to a hydrophilic state, the article can be used as a lithographic plate in conventional offset lithography.

The plate of my invention includes a support sheet, typically paper, which can be impregnated

with an electrically conductive material, or alternatively can be purchased commercially already having appropriate electrical characteristics. An exemplary paper is Electrophotographic Offset Master Base, commercially available from the Allied Paper Corporation. Other supports are equally commercially available, such as, for example, metal vapor-coated plastics.

The resinous interlayer of my invention can then simply be applied over this support by conventional coating techniques, such as knife, blade, roll coating, etc. The resins having utility in the interlayer of my invention include conventional polyurethanes, acrylics, acrylate copolymers, polysulfones, and polyvinyl acetates which are insensitive to the coating solvent of the photoconductor overlayer. Surprisingly, complex combinations of materials are not necessary for functionality in my invention, and conventional urethane resin varnishes, such as the commercially available REZ 77-5, tradename for a urethane resin varnish commercially available from the PPG Chemicals, Inc., will yield excellent results.

Other components can be added to the interlayer to achieve or optimize various characteristics desired. For example, surfactants may be included to allow better wetting of the support material, curing agents may be included if the resin is capable of being cured, etc., as long as the particular resin chosen constitutes the majority of constituent weight of the interlayer.

Carbon black may be included in the interlayer composition if it is desired to change the resistivity characteristics of the coating. Resistivity is known to relate to the development mode utilized. For example, liquid development techniques require more resistivity than dry techniques.

The coating weight of the interlayer can vary over a rather broad range, from about 1.0 to about 10.0 grams per square meter. Reduced coating weights may eliminate the functionality of the interlayer, while increasing coating weights may cause an undesirable reduction in the electrical properties of the plate and weakness of the interlayer.

Following application of the resinous coating, which can be dried by simple air drying, a conventional photoconductive coating can be applied over the interlayer. Exemplary photoconductive materials include commercially available zinc oxide dispersion resins.

In this manner, a photoconductive structure can be prepared which is capable of functioning as a lithographic plate following imaging, development, image fixing, i.e., pressure or heat fusing, and conversion of the background areas to provide hydrophilicity thereto.

Subsequent to such activity, the plate can be effectively mounted on conventional offset lithographic presses, thereby to effectively produce up to 5,000 copies.

My invention will now be further exemplified by the use of the following non-limiting examples, wherein all parts are by weight unless otherwise specified.

In the examples, moisture absorption values were obtained by the conventional Cobb techniques de-

lined in ASTM T 441 os-69. Furthermore, imaging and development were undertaken with either the Model 1135 ESP Platemaker or the MR 417 Dual Platemaker, both available from Minnesota Mining and Manufacturing Company. To convert background areas, 3M's ESP Etch Solution was utilized.

In Examples 1 and 2, 3M's VQC II Imaging Powder was utilized, which is a true pressure fusing toner powder. The balance of the examples utilize 3M's ESP Toner Powder which is not a true pressure fusing toner, but which provides excellent image resolution and cleanliness of background on non-image areas.

An exemplary photoconductive zinc oxide coating material for use as the imaging layer in the examples can be prepared by dispersing, until a Hegman grind of 5-6 (NS scale) is achieved, 79.2 parts toluene, 35.2 parts of a 50 percent solids 690 x 300 acrylic resin from DeSoto, Inc., 105.6 parts of Zinc Oxide 345-PC from St. Joe Minerals Corp., and 5.3 parts of a 6 percent by weight solution of Rhodamine B dye in methonal.

Example 1

A commercially available paper base suitable for lithographic purposes, commonly referred to as "electrostatic offset master base," was obtained from Allied Paper Corporation. Onto one side of this base, at a dry coating weight of approximately 5g/m², was coated a urethane polymer interlayer composition comprising 175 parts of the reaction product of polycaprolactone diol, neopentyl glycol, and 4,4'-diphenylmethane diisocyanate, 6 parts carbon black, and 145 parts methyl ethyl ketone. The resistivity of the dry surface of the interlayer was found to be 5.1×10^7 ohm. Over this interlayer was coated a zinc oxide/resin binder/dye sensitizer photoconductive layer similar to that disclosed above at a dry weight of approximately 32g/m².

After electrophotographic imaging, pressure fixing of the image, and chemical conversion to render the background areas hydrophilic, this master was run on a Multi 1250 offset lithographic press. After 5000 sheets of paper had been printed, the quality of the copy thus obtained was still excellent and the master did not show significant signs of deterioration. A similarly prepared master, but which contained no interlayer, could only produce 667 good quality copies before the image areas began to deteriorate.

Example 2

The construction in Example 1 was prepared, except that the interlayer coating solution contained, in addition to the components stated in Example 1, 28 parts of Union Carbide PKHH phenoxy resin as a crosslinking agent. The master thus prepared yielded more than 5000 good quality impressions.

Example 3

An interlayer solution similar to that in Example 2, but containing no carbon black, was coated as described. The resistivity of the dry interlayer surface was found to be 2×10^{12} ohm at 100 volts. The Cobb moisture absorption was 0 g/m² at 120

seconds. The master imaged well and produced more than 1300 excellent quality impressions.

Example 4

5 An interlayer solution similar to that in Example 2, but containing 3 percent carbon black, based on nonvolatile components, was coated as described. The resistivity of the dry surface was found to be 4.4×10^{10} ohm. The master imaged well and produced
10 more than 1500 impressions of excellent quality.

Example 5

Masters similar in construction to those described in Example 2 were run on a Rotaprint R30SK printing
15 press in both a normal and a crossweb mode. In the normal mode, the lead edge of the master on the press is the same as the lead edge of the master as it exits from the electrophotographic imaging device. In the crossweb mode, the lead edge of the master
20 on the press is the same as a side edge of the master as it exists from a roll-fed electrophotographic imaging device. Fifteen masters were tested on this press: nine were run crossweb, six were run in a normal mode, eight contained an interlayer as
25 described above, and seven were of similar construction but contained no interlayer. In general, the constructions containing the interlayer described herein proved to be more durable on the press than constructions containing no interlayer. Specifically,
30 in the crossweb mode, masters containing no interlayer suffered such a large tendency to stretch that the non-image areas began to crack and accept ink, presumably by physical entrapment in the cracks. This cracking phenomenon occurred generally with-
35 in the first 100 impressions on the masters run; the resulting copies were unacceptable due to an extremely dirty background. By contrast, masters prepared with an interlayer could be run in the crossweb mode to 1700 impressions, yielding copies
40 of excellent quality containing clean background areas and dense, sharply defined image areas.

Example 6

A lithographic master was prepared as described
45 in Example except that the interlayer coating composition comprised a solution of 90 parts Neocryl A-622 acrylic latex from Polyvinyl Chemical Co. and 10 parts water coated at a dry coating weight of 7.9 g/m^2 . More than 1800 excellent quality impressions
50 were printed from this master.

Example 7

A lithographic master was prepared as described in Example 1 except that the interlayer coating
55 composition comprised a solution of 35 parts VAGH (vinylchloride vinyl acetate copolymer from Union Carbide) dissolved in 315 parts methyl ethyl ketone. The interlayer dry coating weight was 2.6 g/m^2 . This construction yielded greater than 2000 excellent
60 quality impressions.

Example 8

A lithographic master was prepared as described in Example 1 except that the interlayer coating
65 composition comprised a solution of 33 parts VINAC

ASB 516 (a carboxy polyvinyl acetate from Air Products Co.) dissolved in 50 parts ethanol, 250 parts methyl ethyl ketone, and 15 parts water coated at a dry weight of 2.7 g/m^2 . Greater than 1800 excellent
70 quality impressions were obtained.

Example 9

A lithographic master was prepared as described in Example 1 except that the interlayer coating
75 composition comprised a solution of 32 parts Car-boset 525 (carboxylated acrylic resin from B.F. Goodrich Co.) in 297 parts methyl cellosolve coated at a dry weight of 2.5 g/m^2 . The master thus prepared produced 1800 excellent quality copies.

Example 10

A lithographic master was prepared as described in Example 1 except that the interlayer coating
85 composition comprised a solution of 55 parts Union Carbide P 1710NT 15 polysulfone resin dissolved in 400 parts ethylene dichloride coated at a dry weight of 5.8 g/m^2 . The master thus prepared yielded in excess of 1300 excellent quality impressions.

Example 11

A lithographic master was prepared as described in Example 1 except that the interlayer coating
95 composition comprised a solution of REZ Interior-Exterior 77-5 Polyurethane Gloss Clear Plastic Coat-ing (a commercial urethane alkyd varnish from Pittsburgh Paint, PPG Industries Inc.) diluted with VM&P naphtha to a solids content of 15 percent and coated at a dry weight of 2.8 g/m^2 . This construction yielded at least 1000 excellent quality impressions.

CLAIMS

1. An electrophotographic sheet structure comprising an electrically conductive support, and overlying said support a resinous layer, the major component of said resinous layer being a resin selected from the group consisting of polyurethanes, acrylics, acrylate copolymers, polysulfones, and polyvinyl acetates, and a photoconductive layer overlying said resinous layer.
2. The structure of claim 1 wherein said photoconductive layer comprises zinc oxide dispersed in an insulating binder.
3. The structure of claim 1 wherein said support
115 is paper.
4. An electrophotographically imaged lithographic plate comprising an electrically conductive support, and overlying said support a resinous layer, the major component of which is a resin selected
120 from the group consisting of polyurethanes, acrylics, acrylate copolymers, polysulfones and polyvinyl acetates, and a photoconductive layer overlying said resinous layer, said photoconductive layer containing fused oleophilic ink receptive toner powder
125 image areas thereon, the background areas thereof being hydrophilic and ink repellent.
5. The plate of claim 4 wherein said support is paper.
6. The plate of claim 4 wherein said photoconductive layer comprises zinc oxide dispersed in an
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insulating binder.

7. An electrophotographic sheet structure according to Claim 1 and substantially as herein described.

5 8. An electrophotographically imaged lithographic plate substantially as described in any of the examples herein.

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