United States Patent

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[54] **ELECTROSTATICALLY IMAGED LITHOGRAPHIC PLATE**
4 Claims, No Drawings

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ABSTRACT: The disclosed electrostatically imaged lithographic plate employs a conductive paper substrate to which is applied a top coat consisting of photoconductive zinc oxide particles dispersed in a resin binder system comprising a synergistic mixture of a styrenated alkyd resin, a polyvinyl methyl ether homopolymer resin, and either a low molecular weight polystyrene resin or a low molecular weight petroleum hydrocarbon resin. The plate is imaged electrostatically, developed and then subjected to an improved conversion etch solution designed to render the nonimage areas of the plate hydrophilic; the image areas remaining hydrophobic and oleophilic.

ELECTROSTATICALLY IMAGED LITHOGRAPHIC PLATE

BACKGROUND OF THE INVENTION

Lithographic printing is a well known art. Basically it involves printing from a flat surface and requires that the image and nonimage areas thereof have different properties. Specifically, the image areas of the printing surface must be hydrophobic while the nonimage areas must be hydrophilic. Preparatory to printing, an aqueous gum etch and fountain solution is applied to the printing surface to wet the hydrophilic nonimage areas, but the solution can not wet the hydrophobic image areas. An oil-based lithographic printing ink is then applied to the printing surface of the plate. The ink is retained over the image areas but is repelled from the nonimage areas by the fountain solution. The ink image is then transferred to a final paper sheet or, more typically, to a rubber offset blanket and then to the final paper sheet. The plate is first wetted and then inked preparatory to each printing cycle.

There are numerous ways in which a lithographic plate is imaged preparatory to printing. For example, a hydrophobic, oleophilic image may be applied over hydrophilic printing surface using a grease pencil, a typewriter equipped with a special ribbon, etc. This procedure is time consuming and cumbersome, and is not applicable to imaging a lithographic plate directly from an original. Photographic techniques have been devised for imaging photographically sensitized lithographic plates, but such plates are expensive.

Recently, lithographic plates have been devised which can be imaged electrostatically. In the process of electrostatic imaging, a photoconductive surface is electrostatically charged and then selectively discharged by projecting thereon the image to be copied. The photoconductive surface thus retains the image to be copied as a latent electrostatic image which is then effective to attract oppositely charged electroscopic particles (toner) pursuant to visibly developing the image.

There are two basic electrostatic imaging processes presently in wide use. In one, an indirect process, the electrostatic image is formed on a photoconductive drum and then visibly developed with dry toner particles. The toner particles forming the image are then transferred from the drum to regular bond paper and fused thereto. In the other, a direct process, the image is formed electrostatically and developed directly on the surface of a paper sheet coated with a photoconductive material. Development is typically carried out in a wet developer or toner bath.

The present invention is concerned with the direct process for electrostatic imaging in which the photoconductive coating is carried on a conductive paper substrate. In forming the photoconductive coating, photoconductive particles, typically zinc oxide, are suspended in a resin binder, and applied as a top coating to the paper. In order that the photoconductive coating be capable of retaining an electrostatic charge for any length of time the resin binder must have high electrically insulative properties. To maintain the highly insulative characteristic of the resin binder, it must also be hydrophobic so as not to pick up moisture from the atmosphere.

Thus, one attempting to devise a lithographic plate which can be electrostatic imaged is faced with conflicting considerations. On the one hand, the entire surface of a successful electrostatically imaged plate must be hydrophobic and on the other hand a lithographic plate must be hydrophilic at the nonimage surface areas. To resolve this problem, it is known to use a so-called "conversion etch" for converting the nonimage areas of an electrostatically imaged plate from hydrophobic to hydrophilic. The image areas of the plate are masked by the oleophilic toner and thus are not affected by the conversion etch, thereby leaving these image areas hydrophobic, and effectively oleophilic. Once so converted, the electrostatically imaged plate may be used as a lithographic plate.

SUMMARY OF THE INVENTION

According to the invention, there is provided an improved and exceptionally durable electrostatically imaged lithographic plate utilizing a synergistic combination of a plurality of resins forming a binder system for the photoconductive pigment. The improved pigment-binder system when applied as a top coating to a conductive paper substrate adheres tenaciously thereto, is water and acid resistant, and does not separate or "pick" even after long run duplication. Moreover, the binder system of the present invention provides an exceptionally smooth, continuous photoconductive top coat surface, thus enhancing the quality and resolution of the developed electrostatic image as well as improving press performance. The resin binder system is highly electrically insulative and hydrophobic. The lithographic plate of the invention functions effectively with an exceptionally low pigment to binder ratio. Thus, the plate is more insensitive to humidity and the top coating is more highly insulative.

The photoconductive top coating is exceptionally water resistant as well as acid resistant, and does not deteriorate under repeated wettings during prolonged press runs. An offset master plate constructed according to the present invention is not subject to a critical ink-water balance settings during a press run, and even if the plate becomes "inked up" in the nonimage areas it is readily cleaned up by subsequent wettings.

The binder system of the present invention is found to, in effect, hold the zinc oxide pigment more accessible to the conversion etch solution designed to convert the nonimage areas from hydrophobic to hydrophilic. It is thus found that a weaker acid etch solution may be used. Electrostatic imaging speed is found to be quite high, and the quality of reproduction of solid black and halftone images is exceptionally good. Because of the plate's high imaging speed, background noise, e.g., toner deposition in nonimage areas, is significantly reduced.

In accordance with the invention, the binder system is composed of a mixture of three compatible resins which act synergistically to provide an electrostatically imaged lithographic plate of materially improved performance both in terms of imaging and in terms of press performance. The resin binder system is composed of appropriate amounts of a styrenated alkyd resin, a polyvinyl methyl ether homopolymer resin, and either a low molecular weight petroleum polystyrene resin or a low molecular weight hydrocarbon resin.

The polyvinyl methyl ether homopolymer resin serves as a tackifying agent to promote exceptionally strong adhesion of the top coat to the paper substrate, thereby preventing picking. In fact, attempts to separate the top coat from the paper have universally resulted in splitting of the paper instead. This resin also functions as a plasticizing agent.

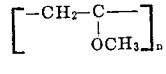
The styrenated alkyd resin is believed to principally serve as a dispersing and binding agent for the photoconductive zinc oxide and contributes to the surface smoothness, continuity and homogeneity of the top coat.

The polystyrene resin or the petroleum hydrocarbon resin gives the plate exceptional water and acid resistance while at the same time serving to hold the photoconductive zinc oxide in a manner as to be accessible to the conversion etch solution. All three resins combine to provide a highly electrically insulative and hydrophobic coating. The polyvinyl methyl ether homopolymer resin, however, is slightly water soluble and thus, it is believed, enhances the acceptance and retention of water by the nonimage areas once made hydrophilic. This would seem to explain the fact that the nonimage areas readily clean up if inadvertently inked, typically arising when the plate is not adequately wetted prior to a press printing cycle. The ink remains on the surface of the top coat and can be readily removed from nonimage areas with several applications of the aqueous fountain solution. Moreover, the copies produced are exceptionally clean and high quality.

The plate, once electrostatically imaged and developed, is subjected to a weak conversion etch employing from one-half to 4 percent ethyl acid phosphate, potassium phosphate monobasic, ammonium phosphate monobasic, or potassium biphthalate in order to provide a pH of approximately 4.5 to 5.5. The use of a weak conversion etch is instrumental in obtaining improved copy quality, particularly in terms of solid and halftone reproduction. Stronger etch solutions, while eliminating background toner on the plate also tend to blind and/or remove toner from the image areas.

DETAILED DESCRIPTION

In accordance with the present invention, the binder system is composed of styrenated alkyd resin, a polyvinyl methyl ether homopolymer resin and either a low molecular weight polystyrene resin or a low molecular weight petroleum hydrocarbon resin. Suitable styrenated alkyd resins are Desoto E-130-09 and Desoto E-13A, supplied by the Desota Chemical Company. Alternatively, Arotap 3204-X-60, a resin manufactured by Archer Daniels, may be used as the styrenated alkyd resin component of the binder system. Polyvinyl methyl ether homopolymer resins suitable for use in the invention are Gantrez M-574, M-555, M-556 and M-094, supplied by General Aniline & Film. The Gantrez M resins are a series of linear polymers, consisting of methyl vinyl ether units



as is described in the Handbook of Material Trade Names, by Zimmerman and Lavine, Supplement IV (1965) published by Industrial Research Service, Inc., Dover, N. H. The low molecular weight polystyrene resin or the low molecular weight petroleum hydrocarbon resin should preferably have a molecular weight in the range of 800 to 5,000. Suitable polystyrene resins are Piccolastic D-100, E-75 and E-100, all manufactured by The Pennsylvania Industrial Chemical Corporation. A suitable petroleum hydrocarbon resin is Piccopale H-2, also manufactured by The Pennsylvania Industrial Chemical Corporation.

Suitable photoconductive zinc oxides are Photox 8, 80, 85, and 801, and mixtures thereof, all supplied by the New Jersey Zinc Company. American Zinc and St. Joseph Lead also supply satisfactory photoconductive pigments. A photoconductive pigment to binder ratio of from 3-5 to 1 is made possible by the binder system of the invention. This has an exceptionally low pigment to binder ratio, not found in prior plates. A low pigment to binder ratio is desirable as it renders the plate less sensitive to humidity and reduces charge leakage from the image areas.

In addition to the above components of the top coat, it is preferred to also incorporate a dye system to enhance the spectral response of the photoconductive pigment. The dye system may consist of small discreet amounts of various dyes such as Fluoroscein, Martius Yellow, Pontamine Blue, Anthraquinone Green, Eosin, Naphthol Green, Rose Bengal, and others.

In the preparation of the top coat, the various resins and dyes, together with the zinc oxide, are added to a ball mill. A suitable solvent such as toluene is added to the mill, and the resulting mixture is milled for a suitable length of time, such as 8 to 24 hours. Protracted milling is desirable since this contributes to the ultimate surface smoothness, homogeneity, and continuity of the top coat. After milling the top coat preferably should have a grind smoothness of from 4 to 7 on the Hegeman Scale and a viscosity of from 100 to 400 centipoise. Grinds over 7 should be avoided to prevent destruction of the photoconductive properties of the zinc oxide.

The paper substrate suitable for use in the lithographic plate of the present invention may be a high wet strength, relatively heavy stock paper which has been treated so as to be electrically conductive. Paper of this type is commercially available from numerous manufacturers, such as The Riegel Paper Co. Lighter stock paper may be used for short run duplication. Alternatively, a high wet strength paper may be prime coated, preferably on both sides, with a coating comprised of a butadiene-styrene resin, such as Butaprene PL-96 supplied by Firestone Plastics, a quaternary ammonium chloride, such as Dow QX-2611.7, supplied by Dow Chemical, and distilled water; the percentages of these compliments by weight being approximately 60 percent, 30 percent and 10 percent, respectively. Alternatively, polyvinyl alcohol may be substituted for the Butaprene PL-96 and Calgon 261 for the Dow QX-2611.7.

Once the electrically conductive paper substrate is at hand, the top coat is applied thereto by conventional coating means, such as a reverse roll coater or a wire wound rod. Coverage is preferably on the order of 25 to 30 pounds of top coat per 3,000 square feet of paper. After controlled drying, the lithographic plate of the present invention is ready for electrostatic imaging.

Electrostatic imaging is performed in conventional fashion directly on the lithographic plate of the present invention. A high negative charge is placed on the top coat surface by a corona discharge unit. This charging process takes place in the dark. The charged lithographic plate is then exposed to the image to be copied by projecting the image onto the top coat surface. The uniform surface charge is selectively conducted away through the photoconductive top coat and the conductive paper substrate to produce a latent electrostatic image conforming to the original image. The length of time required to completely dissipate the surface charge over the nonimage areas of the plate determines the speed of the plate. Thus, the faster the plate, the less time the plate need be exposed to the original image. Ideally, the plate should be as fast as possible. Not only does this speed up the overall imaging process but it also reduces the chance of surface charge leakage from the image areas.

As soon as the latent electrostatic image has been formed on the plate it is transferred to a liquid toner bath where the image is developed by attracting oppositely charged toner particles to the image areas. A suitable bath is composed of Hunt toner and dispersant at a concentration of approximately 3 to 5 milliliters of toner per quart of dispersant. Once the image areas of the plate are developed by the deposition of toner particles thereon, the plate is removed to a drying station where the toner bath dispersant is driven off and the toner particles are permanently adhered to the image areas.

Since the nonimage areas of the plate are hydrophobic, it is not immediately useful in a lithographic printing. Consequently, the plate must first be subjected to a conversion etch operating to convert the nonimage areas to hydrophilic. The following conversion etch formulations have been developed and found to be highly successful.

Component	Percent by weight
Potassium or sodium ferrocyanide	2-15
Ethyl acid phosphate, potassium phosphate monobasic, ammonium phosphate monobasic, or potassium biphthalate	½-4
Distilled water	78-95

The percentage of the acid component is selected to provide a pH of approximately 4.5 to 5.5 to insure a stable etch. A humectant, such as glycerine, may be substituted for a portion of the distilled water.

Conversion does not occur in the image areas since the pigment is masked by the toner. Consequently, the image areas remain hydrophobic. In addition, the toner is oleophilic thus aiding in the inking of the image areas during printing.

The conversion etch solution may simply be applied to the surface of the lithographic plate with a cotton pad. It is preferred that after a short interval the plate be cleansed with distilled water in order to remove excess conversion etch solu-

tion. This is believed desirable in order not to contaminate the ink and water systems of the lithographic press.

Immediately after the plate has been washed with distilled water, it may be mounted in an offset duplicating unit such as a Multilith 1250, or A. B. Dick 620 or 621 offset press. It has been found that a lithographic plate constructed according to the invention may be used to run off as many as 2,000 copies without noticeable deterioration. In fact, it is found that the plate may be removed from the duplicating unit, cleaned and reused at some later time without appreciable degradation of copy quality.

The following examples are presented for purposes of illustration and are not to be interpreted as limiting the invention defined in the appended claims.

EXAMPLE 1

Component	Percent by weight
Photox 8 (zinc oxide)	36.23
Photox 85 (zinc oxide)	11.59
Desoto 09 (styrenated alkyd resin)	6.52
Gantrez M-574 (polyvinyl methyl ether resin)	3.55
Piccolastic D-100 (polystyrene resin)	5.07
Toluene	37.04
Flouroscein	0.087
Martius yellow	0.043
Pontamine blue	0.043
Antraquinone green	0.043
Eosin	0.022
Naphthol	0.11
Rose bengal	0.60

The percentages of the dyes used are on the basis of a 1 percent solution in methanol. A blend of two types of pigment is used for balanced speed and image quality.

The components of the top coat were mixed together in a ball mill and milled overnight. The top coat solution was applied to an electrically conducted paper substrate and dried.

It will be observed that the pigment to binder ratio in the lithographic plate of Example 1 is approximately 3.2 to 1, which is significantly low as compared to prior art electrostatically imaged plates. The percentages of the various resins making up the binder system are Desoto 09—43 percent, Gantrez M-574—23.5 percent and Piccolastic D-100—33.5 percent.

Example 2

A lithographic plate was constructed having the same top coat composition as the plate of Example 1, except that Piccopale H-2, a hydrocarbon resin, was substituted for the polystyrene resin, Piccolastic D-100. From all observations, the resulting lithographic plate was practically identical in terms of imaging and press performance to the plate of Example 1.

EXAMPLE 3

Component:	Percent by weight
Photox 8	37.50
Photox 85	10.00
Desoto 09	5.63
Gantrez M-556	3.50
Piccolastic D-100	5.00
Toluene	38.38

The composition of the dye system is identical to that employed in the lithographic plate of Example 1. The pigment to binder ratio is approximately 3.4 to 1.0. The percentages of Desoto-09, Piccolastic D-100 and Gantrez M-556 making up the binder system are 40 percent, 35 percent and 25 percent, respectively.

EXAMPLE 4

Component:	Percent by weight
Photox 8	43.00
Photox 85	8.60
Desoto 09	4.80
Piccolastic D-100	4.30
Gantrez M-574	3.01
Toluene	36.30

The composition of the dye system was the same as in the previous examples. The pigment to binder ratio is 4.3 to 1. The percentages of the various resins making up the resin binder system were Desoto 09—40 percent, Piccolastic D-100—5 percent, and Gantrez M-574—25 percent, as in the plate of Example 3.

It has been determined that the styrenated alkyd resin component should make up approximately 35 to 45 percent of the binder system, particularly at pigment to binder ratios of from 3 to 5:1. As the pigment to binder ratio increases the concentration of the styrenated alkyd resin should also be increased in order to achieve adequate dispersion and film binding strength. Styrenated alkyd resin concentrations exceeding 60 percent are not desirable since top coat adhesion and water and acid resistance decreases. This is believed to be due to the fact that the high concentration of styrenated alkyd resin prevents the inclusion of sufficient quantities of polyvinyl methyl ether homopolymer resin and either the low molecular weight polystyrene resin or the petroleum hydrocarbon resin. On the other hand, binder systems having less than 10 percent styrenated alkyd resin give rise to a poorly dispersed top coat having inadequate film binding strength.

Ideally, the percentage of polyvinyl methyl ether homopolymer resin used in the binder system should be in the range of from 20 to 30 percent. Percentages in excess of 50 percent cause the top coat to be excessively water sensitive, giving rise to poor adhesion at the nonimage areas of the plate. With percentages of polyvinyl methyl ether homopolymer resin less than 15 percent, it is found that adhesion of the top coat to the paper substrate, particularly at the image areas, is degraded, and picking results.

The preferred proportion of low molecular weight polystyrene resin or low molecular weight petroleum hydrocarbon resin is from 30 to 40 percent. Percentages in excess of 60 percent result in poor film binding strength and poor adhesion of the top coat to the paper substrate. Percentages less than 25 percent result in a top coat having inadequate water and acid resistance.

Lithographic plates according to the invention have been formed having pigment to binder ratios as high as 7 to 1. While such plates performed satisfactorily, the higher pigment to binder ratios, at least in excess of 7 to 1, are not desirable since the resulting plates are more sensitive to humidity and less electrically insulative. Moreover, at higher pigment to binder ratios, the concentration of styrenated alkyd resin should be increased in order to obtain adequate dispersion and film binding strength. As a consequence, lesser concentrations of a polyvinyl methyl ether homopolymer resin and either polystyrene resin or petroleum hydrocarbon resin can be employed, thus jeopardizing the desirable attributes contributed by these components.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in the above article without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention which, as a matter of language, might be said to fall therebetween.

Having described the invention, what I claim as new and desired to secure by Letters Patent is:

1. A lithographic plate suitable for electrostatic imaging comprising, in combination:

A. a conductive base

B. a film-forming binder system comprising, by weight,

1. 20 to 60 percent styrenated alkyd resin,

2. 15 to 50 percent polyvinyl methyl ether homopolymer resin, and

3. 25 to 60 percent low molecular weight polystyrene resin; and

C. a photoconductive zinc oxide pigment,

1. said pigment dispersed in said binder system and applied as a surface coating to said base.

2. The lithographic plate defined in claim 1 wherein said binder system is comprised of, by weight,

1. 35 to 45 percent styrenated alkyd resin,
2. 20 to 30 percent polyvinyl methyl ether homopolymer resin, and
3. 30 to 40 percent low molecular weight polystyrene resin petroleum.

3. The lithographic plate defined in claim 2 wherein

1. the ratio of pigment to binder is from 3 to 5:1.

4. The lithographic plate defined in claim 2 having image and nonimage areas on said surface coating, said image areas having been visibly developed with electroscopic particles, and

1. said nonimage areas having been converted from hydrophobic to hydrophilic by treating with an aqueous solution comprising
   a. a first component selected from the group consisting of potassium ferrocyanide and sodium ferrocyanide, and
   b. a second component selected from the group including ethyl acid phosphate potassium phosphate monobasic, ammonium phosphate monobasic, and potassium biphthalate.