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[72] Inventors **Warren G. Van Dorn**
Columbus;
John F. Byrne, Worthington; Thomas
Greeno, Columbus, Ohio

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[73] Assignee **Xerox Corporation**
Rochester, N.Y.
a corporation of New York

[54] METHOD OF MAKING A LITHOGRAPHIC MASTER AND METHOD OF PRINTING THEREWITH

27 Claims, 6 Drawing Figs.

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[51] **Int. Cl.** **B41m 1/06,** B01k 5/00
[50] **Field of Search** .... 101/450—463, 464—473, 128.2, 128.3; 96/1, 1.5, 1.8; 204/180, 181; 96/1.3, 1.4

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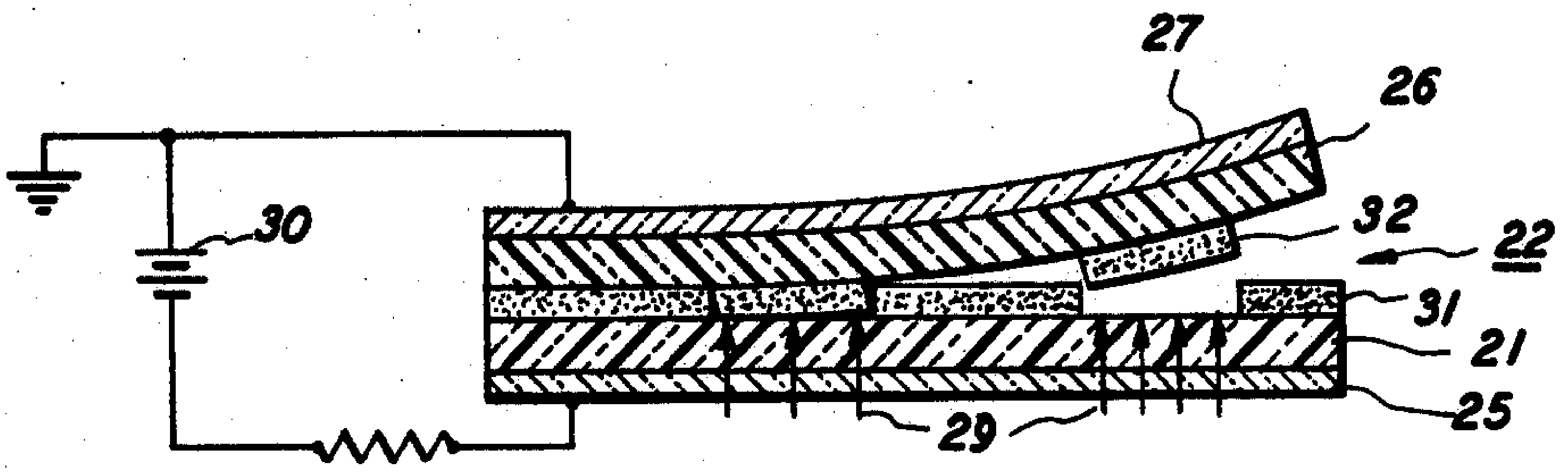
Primary Examiner—Robert E. Pulfrey
Assistant Examiner—Clifford D. Crowder
Attorney—James J. Ralabate

ABSTRACT: The subject matter of this patent application pertains to a method of preparing a lithographic printing master wherein a photoresponsive imaging composition is interpositioned between two hydrophilic substrates to form a dual electrode imaging configuration. Upon selective exposure to electromagnetic radiation and separation of each electrode complementary images are formed on the respective surfaces. The resulting imaged substrates are then utilized as lithographic masters.



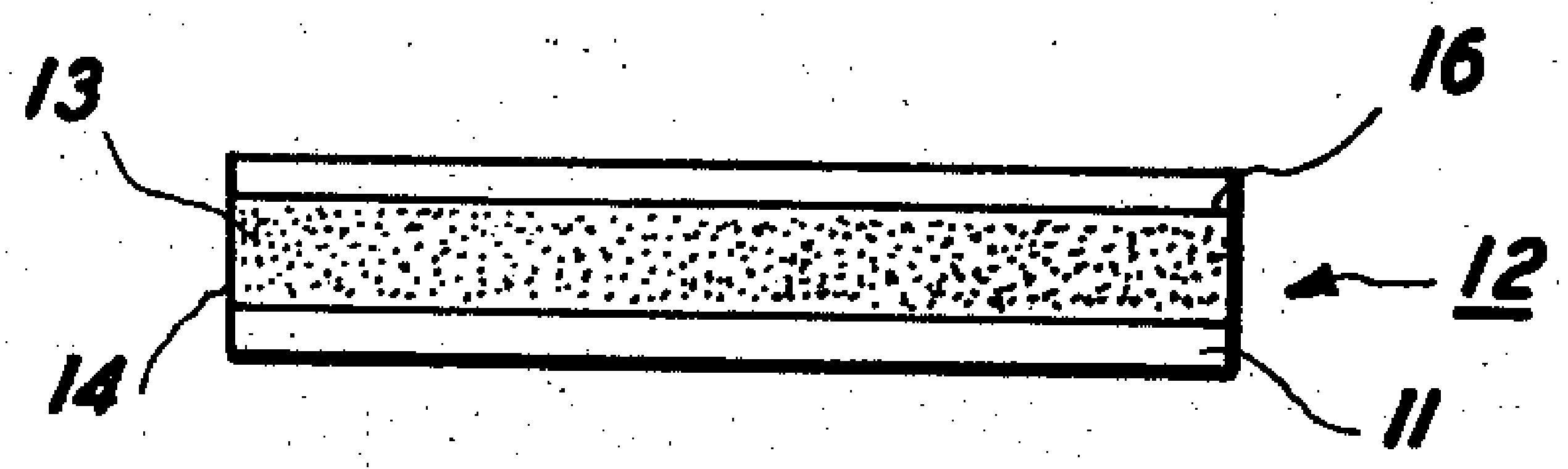


FIG. 1

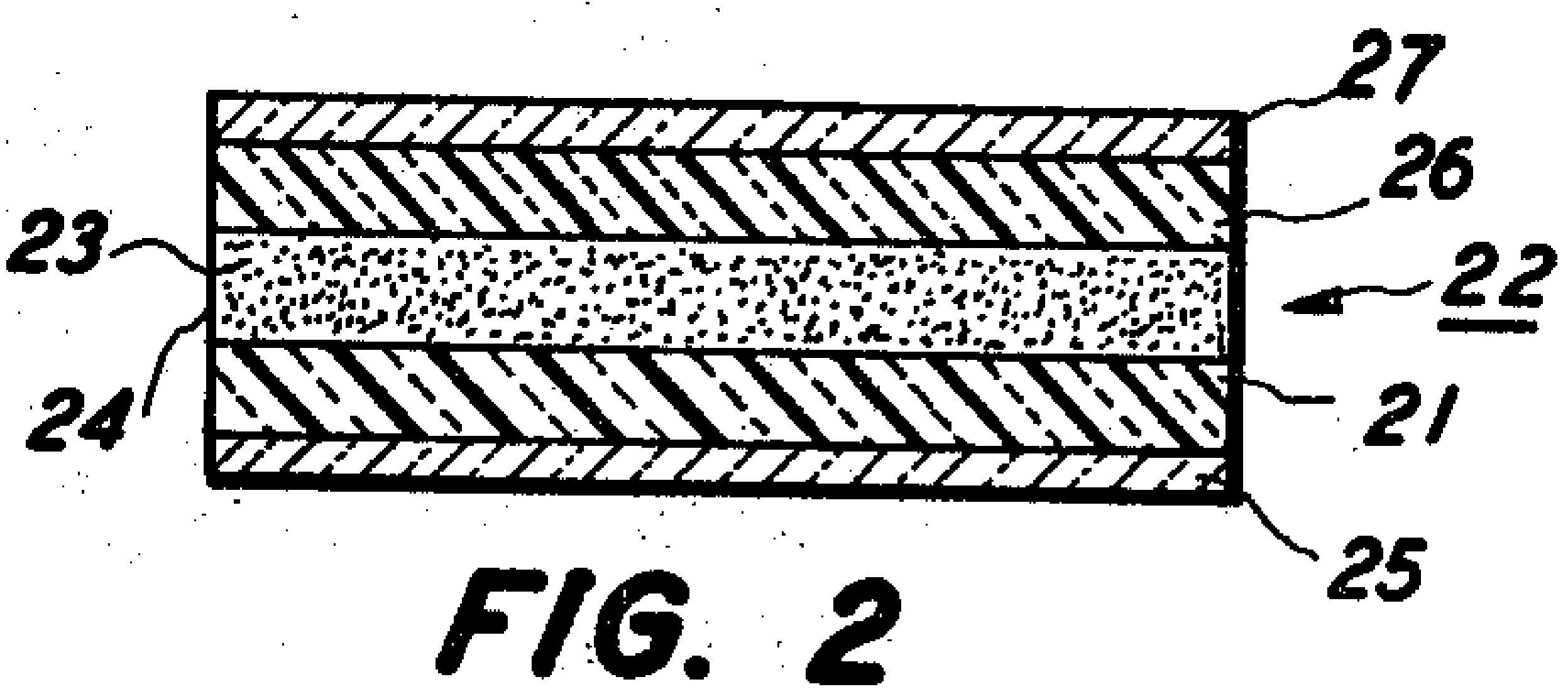


FIG. 2

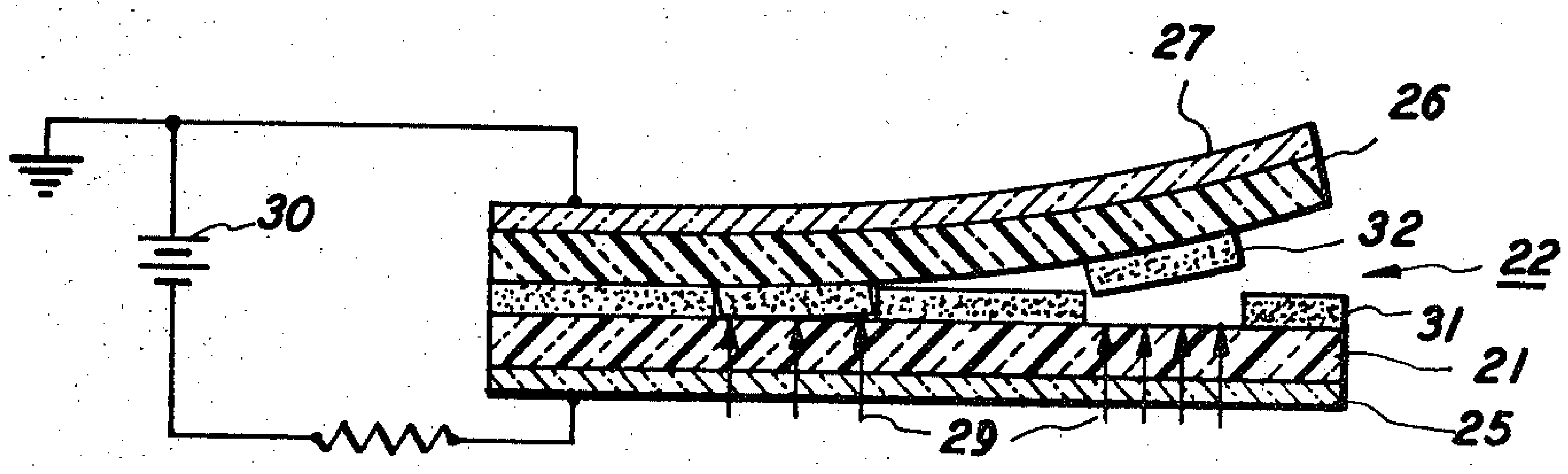


FIG. 3

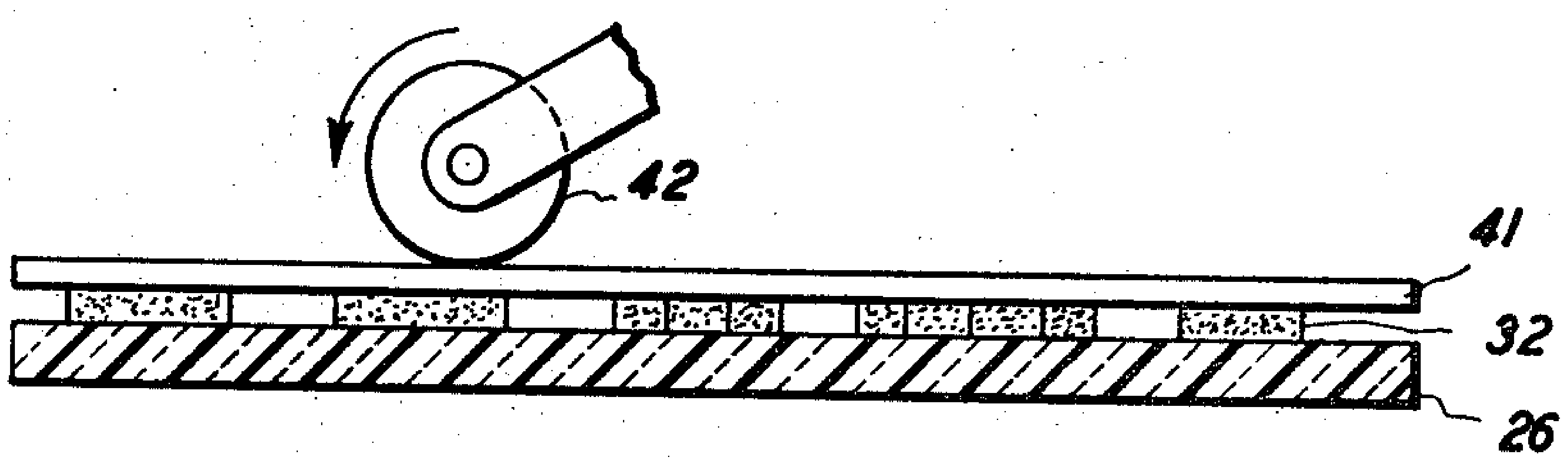


FIG. 4A

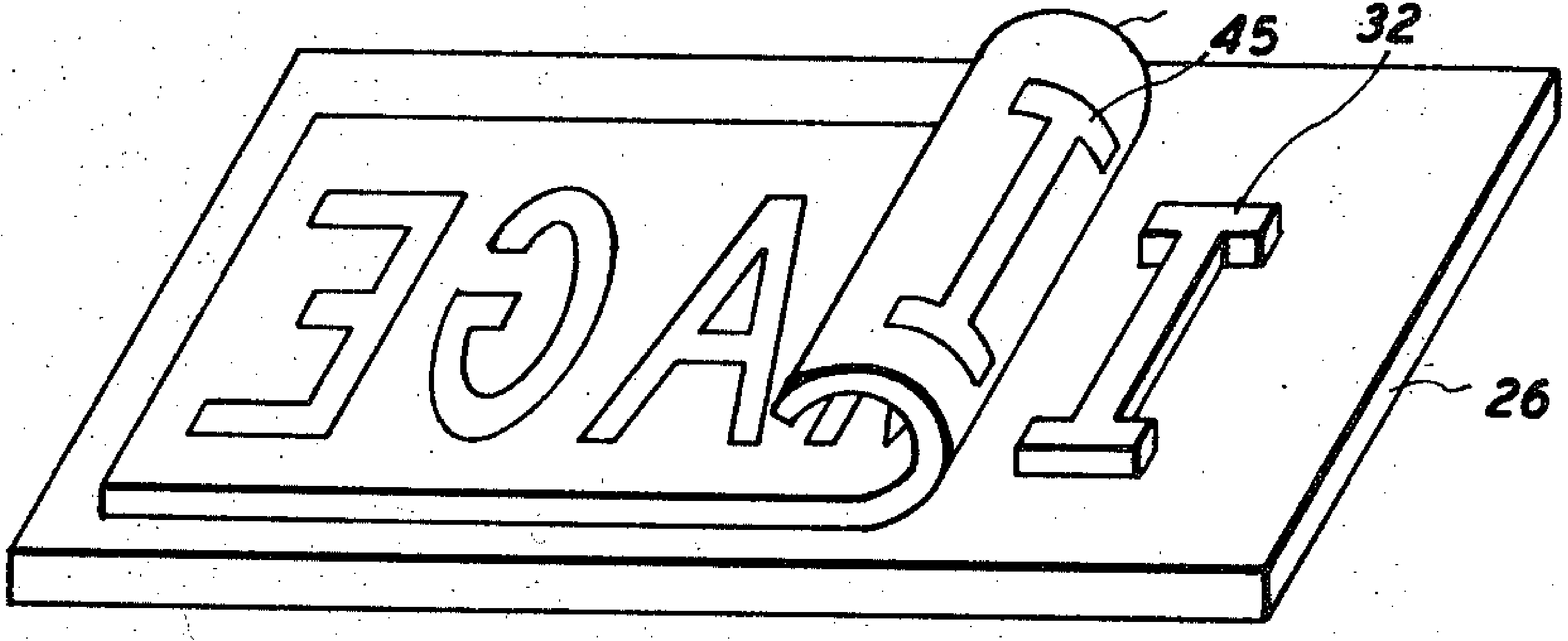


FIG. 4B

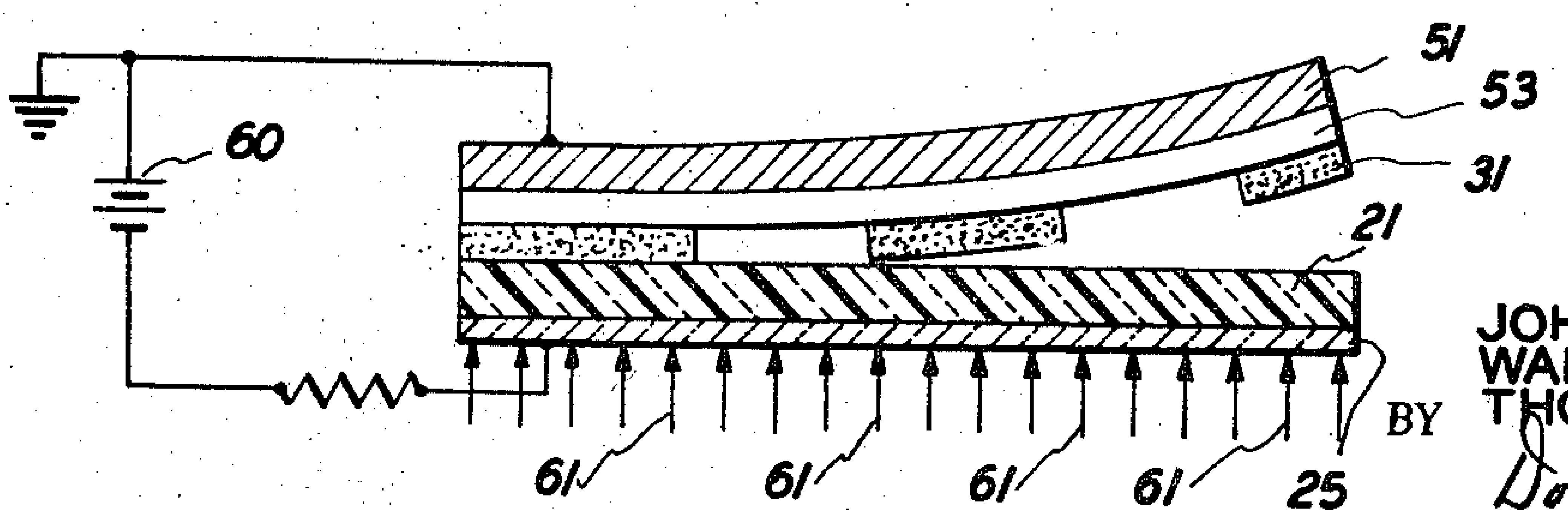


FIG. 5

INVENTORS
JOHN F. BYRNE
WARREN G. VAN DORN
THOMAS M. GREENO

BY Donald C Kolasch
James J. Palavate
ATTORNEYS

METHOD OF MAKING A LITHOGRAPHIC MASTER AND METHOD OF PRINTING THEREWITH

BACKGROUND OF THE INVENTION

This invention relates to a duplicating system and, more specifically, to lithography.

Lithographic printing is a well known and established art. In general, the process involves printing from a flat plate, relying upon the existence of different properties in the image and nonimage areas for printability. In conventional lithography, the nonimage area is hydrophilic while the image area is hydrophobic. In the lithographic printing process an aqueous fountain solution is applied to the plate surface wetting the nonimage areas of the plate. This solution keeps the plate moist and prevents it from scumming up. An oil based printing ink is applied to the image surface depositing ink only in the image areas, the hydrophilic nonimage area repelling the oil based ink. The ink image may then be transferred directly to a copy sheet or other receptive surface, but generally it is transferred to an offset blanket which in turn transfers the print to the final copy sheet. Hence, for each print made during a run, a lithographic plate is first dampened with an aqueous fountain solution, inked with a lithographic ink, transferred to an offset surface and finally printed.

A number of techniques are known for preparing lithographic printing plates. For example, it has been known that a lithographic plate can be made by electrostatic imaging systems utilizing conventionally developed xerographic plates as the lithographic master. In one such system, the resinous powder used to develop the electrostatic charge pattern is hydrophobic in nature thereby capable of being wetted by a lithographic ink. After the powder image is formed on the surface of the photoresponsive coating it is transferred to a lithographic substrate such as a treated aluminum plate. Heat is then applied to fix the image to the substrate thereby producing the finished printing master. Another such electrostatic technique of producing a lithographic printing plate consists of coating a photoconductive material such that it is volatile at relatively low temperatures, for example, anthracene or sulfur, on the surface of a metal sheet, especially adapted for lithographic use. An electrostatic latent image is produced and developed on the photoconductive coating. The development powder selected to be hydrophobic in nature also is chosen so as to have a relatively low melting point. The metal sheet is heated to a temperature such that the photoconductive coating evaporates in the nonimage areas leaving the hydrophobic powder image on the plate. Heating is continued until the developed image is fixed to the surface of the plate thereby producing the final lithographic printing plate. A third electrostatic approach entails the development of an electrostatic latent image on a conventional xerographic binder plate with resinous powder material, generally hydrophobic in nature, as is the binder plate itself. In order to prepare the plate to be used as a lithographic master, a differential is established between the developed image and the background of the plate by treating the surface of the plate with a conversion solution thereby rendering the background or nonimage areas hydrophilic.

Other nonelectrostatic methods have also been devised to prepare lithographic printing plates. In one instance, a support base having hydrophobic properties is coated with a hydrophilic metal film and the metal surface subsequently coated with a light sensitive composition. The light sensitive plate is then selectively exposed and developed. The developed surface is etched thereby removing the metallic hydrophilic film in those areas unexposed to light thus producing a pattern of the underlying resinous hydrophobic material. The remaining light sensitive coating is then removed producing a finished plate having image areas which are hydrophobic and nonimage areas which are hydrophilic. A second, nonelectrostatic process of preparing a lithographic master involves coating a substrate with a hydrophilic, water receptive, ink repellent composition containing a component which becomes hydrophobic upon exposure to heat. The coated substrate is positioned in a juxtaposed position to the original to be copied. Infrared radiation is directed onto the original to generate a heat pattern corresponding to that of the original which in turn is transferred to the sensitive hydrophilic coating adjacent thereto. The areas affected by the heat are thus converted thereby producing a hydrophobic image in a hydrophilic surface.

While basically these and other systems have been found useful for lithographic purposes, there are inherent disadvantages to their use. In the several instances wherein electrostatic techniques are employed in the preparation of lithographic printing masters as described above, several disadvantages are to be noted. For example, several of the above disclosed procedures require the use of secondary solutions to establish the necessary surface property differential. Other processes require additional mechanical or chemical treatments which lead to a degradation of the quality of the images which are subsequently reproduced from the resulting plates. In the specific process wherein the nonimage hydrophobic areas are removed as a result of the volatile nature of the photoconductive composition utilized, the noxious fumes which evolve upon evaporation of this photoconductive material makes the procedure further undesirable. In addition, the process is further limited in that the choice of the photoconductive material must be limited such as to have the required relative low boiling point and melting point. The primary disadvantage encountered in the process disclosed wherein the lithographic plates are prepared by the transferring of a resinous oleophilic image directly to a lithographic substrate is that image detail and definition is lost during the powder transfer step.

The processes not concerned with electrostatic imaging are also limited as to the extent of their usefulness. In either of the systems disclosed above, as well as other similar techniques, there are inherent basic disadvantages. Generally, the most prominent disadvantage is that elaborate preparations are necessary in order to produce the final printing plate. Furthermore, these procedures generally require chemical treatment, long exposures and very strong light sources to initiate the chemical changes required, and use of the photosensitive plate relatively soon after preparation.

It is, therefore, an object of this invention to provide a novel lithographic imaging system which will overcome the above noted disadvantages.

It is a further object of this invention to provide a novel method of preparing a lithographic printing master.

Another object of this invention is to provide an imaging system utilizing a novel lithographic printing plate.

Still a further object of this invention is to provide a duplicating system utilizing a master prepared by a noncomplex, simplified imaging process.

Yet, still a further object of this invention is to provide a time saving process of preparing a lithographic printing master.

Yet, still another object of this invention is to provide a highly flexible lithographic master making system.

SUMMARY OF THE INVENTION

The foregoing objects and others are accomplished in accordance with the present invention, generally speaking, by preparing what is generally referred to as a manifold set. A photoresponsive imaging composition is coated on the surface of a donor substrate and, in one embodiment of the invention, a lithographic or otherwise hydrophilic receiver sheet laid down over the surface of the resulting imaging layer to form the manifold configuration. An electrical field is applied across the manifold set while it is undergoing exposure to a pattern of light and shadow. Upon separation of the donor substrate and the receiver sheet, the imaging or photoresponsive layer fractures along the lines defined by the light pattern to which it has been exposed with part of the imaging layer being transferred to the receiver sheet while the remainder is retained on the donor substrate so that a positive image is produced on one surface and a negative image on the other. At least one of the donor substrate and the receiver sheet is transparent so that exposure may take place through the respective support. Either one or both may be made of a conductive material. Furthermore, the manifold set may include separate electrodes on opposite sides of an insulating donor substrate and insulating receiver sheet. Here again, either or both of the combinations of electrode and support layer may be transparent so as to permit exposure of the imaging layer from either side of the manifold set. The resulting waxy manifold image, positive or negative, formed on the surface of the lithographic receiver substrate was found to be oleophilic in nature and receptive to oil base inks. The imaged hydrophilic substrate is then fastened to a press cylinder of a conventional lithographic printing press and used in a lithographic printing mode. The printing operation is carried out utilizing commercially available fountain solutions and lithographic inks. The waxy image being hydrophobic in nature will readily accept the oleophilic ink.

Several alternate techniques have been devised whereby a lithographic plate may be prepared according to the process of the present invention when the lithographic substrate is not made a part of the initial manifold set. In one such approach, the resulting manifold image, positive or negative, on the surface of the donor substrate or receiver sheet, is brought into surface contact with a conventional lithographic substrate such as a lithographic paper plate and the manifold image transferred to the paper support by the application of external pressure. In a second similar approach the manifold image to be printed is brought into contact pressure with the respective lithographic substrate and the image made tacky by some external source such as heat. The tackified image is thereby transferred to the lithographic support. In still a third alternate embodiment to preparing the lithographic printing plate of the present invention the manifold image formed on either the receiver sheet or the donor substrate is brought into surface contact with a conventional lithographic substrate to form a second manifold set with the lithographic substrate now acting as the receiver sheet. By properly regulating the applied potential the manifold image is transferred to the surface of the lithographic support while in a field of light. Separation is then performed by peeling the lithographic sheet from the original manifold image bearing substrate. There results a waxy oleophilic image on the surface of the hydrophilic substrate which is receptive to oil base inks.

It has been determined that a waxy manifold image generally prepared according to the process of the present invention is hydrophobic in nature and thus capable of receiving oil based inks. It has further been determined that when the waxy images are ultimately formed on the surface of a hydrophiliclike substrate that the resulting configuration may be used in a lithographic printing mode. By making the proper image selection it is possible to prepare a lithographic printing master capable of producing either a negative or positive print regardless of the sense of the input information. Furthermore, the high degree of sensitivity of the photoresponsive materials of the present invention allows for the use of various exposure mechanisms such as a projection system in addition to the use of transparent originals.

DETAILED DESCRIPTION

In accordance with the present invention, a donor sheet is prepared by applying to the surface of a donor support substrate a cohesively weak photoresponsive imaging composition. Although the photoresponsive imaging composition may consist of a homogeneous layer made up of a single component or a solid solution of two or more components where the latter exhibits the desired photoresponsive and physical properties, it has generally been determined that the standard and generally preferred photoresponsive imaging coating be composed of a dispersion of a photosensitive pigment in a cohesively weak insulating binder matrix. Optimum results are obtained when a metal-free phthalocyanine pigment is dispersed in a wax binder material in the present of a petroleumlike solvent such as petroleum ether. The imaging composition may be applied to the support substrate by any suitable means such as by flow coating or by a wire-wound coating rod, and the resulting layer dried in any suitable manner such as by the application of heat or in air at room temperature. The final thickness of the donor coating or imaging layer generally will be in the range of from about 0.5 to about 45 microns with a thickness of from about 2 to about 35 microns generally preferred to produce the most desirable resulting lithographic printing master, allowing for multiple transfers and multiple plate preparation. The basic physical property desired in the imaging layer is that it be frangible, having a relatively low level of cohesive strength either in the as coated condition or after it has been suitably activated by the introduction of a liquid activator. The ratio of photoconductive pigment to the binder by volume in the dispersion or heterogeneous system may range from about 10 to 1 to about 1 to 10, but it has generally been found that proportions in the range from about 1 to 2 to about 2 to 1 produce optimum results, and accordingly, constitute the preferred range.

Following the formation of the donor sheet combination a receiver sheet is placed over the surface of the imaging layer. Each member of the donor support and receiver sheet assembly may be a conductive component, such as conductive cellophane, but more commonly they will consist in each instance of an insulating material mounted on a conductive electrode. In an electrodeless system at least one of the donor substrate and receiver sheet is transparent and, if desirable, both may be transparent so that exposure may take place from either side of the configuration. In a system where an electrode is employed, either or both of the combinations of electrode and support layer may be transparent so as to permit exposure of the imaging layer, as in the case when no electrode is used, from either side of the manifold set. In the preferred embodiment of the present invention, Mylar, polyethylene terephthalate, is used as the donor substrate backed up by a conductive electrode. Such an electrode may consist of optically transparent glass overcoated with a thin optically transparent layer of conductive material such as tin oxide. A NESA glass transparent electrode has generally been found suitable. The receiver sheet in this embodiment is a lithographic substrate such as a hydrophilic paper plate which is generally backed up by a receiver electrode which is usually an opaque electrode such as conductive black paper.

Following the formation of the above described configuration, generally the receiver sheet is lifted or the manifold set opened and an activator applied to the imaging or photosensitive composition following which the layers are again closed together. The activator may be applied before introducing the receiver sheet into the assembly, either sequence of operation being suitable for the present system. The activator material when necessary is usually applied in the form of a solvent type liquid such as petroleum ether. However, the activation step may be eliminated if the photoresponsive layer is prepared initially so as to retain a sufficient amount of solvent following the coating step or if the imaging layer is initially fabricated so as to have a low enough cohesive strength. It is generally preferred, however, to include the activation step in the imaging process in order to produce a stronger and more permanent imaging layer which can withstand storage thereby increasing shelf life.

Although when utilized the activator may be applied by any suitable technique such as with a brush, with a smooth or rough surface roller, by flow coating, by vapor condensation or other similar methods, a very expedient approach is to spray the activator onto the surface of the imaging layer of the manifold set. Following the application of the activator fluid, the manifold set is closed as stated above with pressure applied to spread the activator and to insure the necessary surface contact between the various layers while removing any excess activator fluid which may have been deposited. The activator serves to create an adhesive bond between the imaging layer and the receiver sheet as well as to swell or otherwise weaken and thereby lower the cohesive strength of the imaging composition. It is desirable that the activator also have a high level of resistivity so that it will not provide an electrically conductive passage through the imaging layer and thus will support the electrical field which is applied during the exposure phase of the process. Accordingly, it will generally be found to be desirable to purify commercial grades of activators so as to remove impurities which might impart a higher level of conductivity, than is desired, to the activating fluid and thus the system. This may be accomplished by running the fluid through a clay column or by any other suitable purification technique.

Following the preparation of the manifold set, an electric field is applied across the imaging layer as it is exposed by means of electromagnetic radiation to an image pattern. Upon separation of the donor substrate from the hydrophilic receiver sheet the photoresponsive layer will fracture along the lines defined by the light pattern to which it has been exposed and at the surface where it is adhered to either the donor substrate or the receiver sheet. It is generally preferred although not mandatory that the separation be performed while the potential is still applied. Accordingly, once separation is complete, the exposed portions of the composition are retained on one of the surfaces, be it the donor substrate or the receiver sheet, while the unexposed portions are retained on the other of the two surfaces, thereby resulting in the simultaneous formation of a positive image on the one hand and a negative image on the other. Whether the exposed portions are retained on the donor substrate or transferred to the receiver sheet, will of course, depend upon the particular photoresponsive material employed in the imaging system as well as the polarity of the applied field. The final image produced on the respective surfaces may then be fixed either automatically by air evaporation of the volatile components contained in the imaging composition or by fixing the binder matrix by an external application of heat. The separated hydrophilic receiver sheet with the waxy manifold image is then used in a lithographic printing mode.

Alternatively, when the lithographic master or hydrophilic substrate is not made a part of the manifold set, several techniques may be utilized to prepare the lithographic master of the present invention. In one such approach either of the formed waxy manifold images, whether the image be on the donor substrate or the receiver sheet, may be pressure transferred from the particular support member to the surface of a lithographic substrate. The respective manifold image is placed in contact with the surface of a conventional lithographic substrate, such as a lithographic paper plate or a grained aluminum support and pressure applied by any suitable means such as by passing the resulting sandwich configuration between a pair of steel rolls. The amount of force applied during the transfer phase of the process will generally be limited and determined by the particular lithographic support selected. For example, if a lithographic paper master is used pressure up to about 800 lbs. per linear inch may be applied before a detrimental effect on the master plate itself is realized. The image is generally effectively transferred within this range. In another similar but different approach to the image transfer methods of preparing the lithographic master of the present invention, the manifold image is surface contacted with a lithographic substrate. By tackifying the image upon application of some external mechanism such as by exposure to heat or a solvent vapor environment the hydrophobic image is selectively transferred to a hydrophilic substrate. The requirement and limitations of this approach are determined by the specific materials making up the configuration.

In a third alternate approach to preparing the lithographic master of the present invention the resulting image formed on the surface of the donor substrate or the receiver sheet whether it be positive or negative, is reactivated by the application of an activator fluid in a manner similar to that described above. A lithographic substrate is placed over the image to form a second manifold set with the lithographic substrate serving as the receiver sheet. An electric field is applied across the resulting sandwich configuration. During the application of the electric field the image bearing surface is uniformly exposed to electromagnetic radiation. If the image bearing receiver sheet is used as one component of the second manifold set then the polarity used in the initial imaging process will be reversed. If the image bearing donor substrate is used then the polarity of the system will be similar to that of the original imaging process. While maintaining the applied potential the lithographic master substrate is peeled or otherwise removed from the respective substrate, the image now adhering to the surface of the lithographic plate. The activator fluid is allowed to evaporate and the resulting image fixed thereto by any suitable means such as by heating. An image of the original subject is thereby produced by a light-activated transfer means on the lithographic substrate which is capable of producing multiple prints.

DESCRIPTION OF THE DRAWINGS

The invention is further illustrated in the following drawings wherein:

FIG. 1 is a side sectional view of a photosensitive imaging member of the present invention;

FIG. 2 is a side sectional view of an alternate and preferred embodiment of the imaging member configuration of the present invention;

FIG. 3 is a side sectional view illustrating exposure and the resulting effect upon the photoresponsive layer of the imaging member of FIG. 2;

FIGS. 4*a* and *b* represent one method transferring the manifold image of FIG. 3 to the surface of a lithographic substrate; and

FIG. 5 represents an alternate means of transferring the manifold image of the present invention to the surface of a lithographic substrate.

Referring now to FIG. 1 there is seen a supporting donor substrate layer **11** and an imaging photoresponsive layer generally designated **12**. In this particular illustration, layer **12** comprises a photoresponsive pigment **13** dispersed in a binder matrix **14**. Above the imaging layer **12** is placed a third or receiving layer **16**. The entire combination will be termed the manifold set. In this particular embodiment of the manifold set, both the donor substrate **11** and the receiver sheet **16** are made of an electrically conductive material such as conductive cellophane, with at least one of the supports being optically transparent to provide an exposure of layer **12**.

Although the structure of FIG. 1 represents one of the simplest forms which the manifold set of the present invention may take, an alternate and preferred embodiment is illustrated in FIG. 2. In this illustration there is represented an insulating donor substrate **21** having coated on its surface a donor, imaging layer generally designated **22**. As in FIG. 1 the imaging layer may take any one of several forms as described in the discussion supra. However, for purposes of illustration it is shown as consisting of photoresponsive particles **23** dispersed in a binder matrix **24**. Superimposed upon the imaging layer is the receiver sheet **26**. The insulating donor substrate **21** is backed with a conductive electrode **25** while the image receiving sheet **26** of the manifold set is also backed with a conductive electrode **27**.

FIG. 3 illustrates the effect obtained when the manifold set of FIG. 2 is selectively exposed to radiant energy represented by lines **29** while under the influence of an electrical field resulting from the potential source **30**. As a result of the particular properties of the donor composition or matrix **22** the layer fractures along lines subjected to the electromagnetic radiation thereby producing upon separation a manifold image **32** on the receiver sheet **26** while the complimentary or background areas are retained in image form **31** on the donor substrate **21**. When the receiver sheet is a lithographic substrate such as a paper lithographic plate, then the master is formed directly as in the preferred embodiment of the present invention.

FIGS. **4***a* and *b* represent one alternate embodiment of the present invention.

In FIG. **4***a* a lithographic substrate, herein represented as a paper sheet **41**, is superimposed upon the manifold image **32** produced on the surface of the receiver substrate **26** as a result of the exposure system illustrated in FIG. **3**. Pressure is applied in a manner demonstrated by pressure roller **42**. FIG. **4***b* represents the separation phase of the transfer process whereby the lithographic substrate **41** is separated from the manifold image **32** and the support substrate **26** resulting in a waxy oleophilic image **45** on the surface of the lithographic substrate **41** to produce the resulting printing master of the present invention.

FIG. **5** represents the light-activated transfer process of preparing a positive-to-positive lithomaster of the present invention. Following the formation of manifold image **31** on the surface of the donor substrate **21** as illustrated in FIG. **3** the receiving electrode and substrate complex is removed from the system and a second combination consisting of a transfer electrode **51** and a lithographic support substrate **53** substituted therefor to produce the configuration of FIG. **5**. While applying a potential from source **60** across the resulting manifold configuration the surface of the electrode-donor complex, **25** and **21**, is simultaneously flooded with electromagnetic radiation represented by lines **61**. Upon separation, as shown, the image on the surface of substrate **21** is transferred to the surface of substrate **53**. The resulting lithographic printing master consists of a waxy hydrophobic image **31** on the surface of a lithographic substrate **53**, represented herein as paper for illustrative purposes.

Any suitable material may be used as the substrate for the lithographic master of the present invention. The surface of the substrate is hydrophilic in nature and is such that it will readily accept a water repellent image which adheres tenaciously thereto and shall neither be pulled away by printing inks nor washed away by the fountain solutions used during the printing process. Furthermore, the nonimage area of the substrate will readily be wetted by the fountain solution and hold a film of aqueous film on the surface thereof and does not permit the film to be displaced therefrom by the lithographic printing ink. The base sheet may comprise any of the materials known for this purpose such as a flexible, waterproof paper, plastic or thin sheets of metal or laminates thereof. Typical metals would include aluminum, steel, zinc, magnesium, chromium and copper.

Any suitable wet-out or fountain solution may be used in the course of the present invention. Typical such fountain solutions are 1 percent solutions by volume of gum cellulose and water, gum arabic and water, glycerol and water and isopropyl alcohol and water. Distilled water may also be used as the wet-out solution. Other typical fountain solutions are disclosed in U.S. Pat. No. 3,107,169. The fountain solutions may contain other constituents such as, for example, formaldehyde, and if glycerine is not present it may be added primarily to take advantage of its hygroscopic nature, and hence, by absorption of water prolong the period during which the surface of the lithographic plate retains its hydrophilic properties. The formaldehyde additive will also achieve this effect. Therefore, the fountain solutions containing the glycerine or formaldehyde additives or mixtures thereof are preferred inasmuch as the resultant lithographic plate may be stored before use for relatively long periods of time as compared to those plates treated with a fountain solution not containing the respective additive. Solutions containing gum arabic are also found to be very effective inasmuch as a lithographic plate treated with such a solution is found to retain its hydrophilic properties for relatively long periods of time after removal from the press so that the resultant printing plate may be reused without subjecting them to additional treatment with a fountain solution.

Any suitable lithographic printing ink may be used in the course of this invention. Typical lithographic inks and their properties are disclosed in "Ink Technology for Printers and Students" by E. A. Apps, 1963, Part II, Chapter 11. The inks are of the same fundamental style as good quality letterpress inks, and the simplest type consist of a pigment mixture dispersed in a lithographic varnish, such as heat-bodied linseed oil. The lithographic or oil based ink being oleophilic in nature adheres to the hydrophobic waxy image and is repelled by the hydrophilic nonimage areas.

It is to be understood that any suitable photoresponsive material may be employed in the course of the present invention with the choice depending largely upon the photosensitivity and spectral sensitivity desired, the degree of contrast desired in the final image, whether a heterogeneous or a homogeneous system will be used and similar considerations. Typical photoresponsive materials include: substituted and unsubstituted phthalocyanine, quinacridones, zinc oxide, mercuric sulfide, Algol yellow (C.I. No. 67,300), cadmium sulfide, cadmium selenide, Indofast brilliant scarlet toner (C.I. No. 71,140), zinc sulfide, selenium, antimony sulfide, mercuric oxide, indium trisulfide, titanium dioxide, arsenic sulfide, Pb_3O_4, gallium triselenide, zinc cadmium sulfide, lead iodide, lead selenide, lead sulfide, lead telluride, lead chromate, gallium telluride, mercuric selenide, and the iodides, sulfides, selenides and tellurides of bismuth aluminum and molybdenum. Others include the more soluble organic photoresponsive materials (which facilitate the fabrication of homogeneous systems) especially when these are complexed with small amounts (up to about 5 percent) of suitable Lewis acids. Typical of these organic photoresponsive pigments are 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinethione; 4,5-bis-(4'-amino-phenyl)-imidazolidinone; 1,5-dicyanonaphthalene; 1,4-dicyanonaphthalene; aminophthalodinitrile; nitrophthalidinitrile; 1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 3,4-di-(4-methoxy-phenyl)-7,8-diphenyl-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 3,4-di-(4'-phenoxy-phenyl-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 3,4,7,8-tetramethoxy-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 2-mercapto-benzthiazole; 2-phenyl-4-diphenyl-idene-oxazolone; 2-phenyl-4-p-methoxy-benzlidene-oxazolone; 6-hydroxy-2-phenyl-3-(p-dimethyl-amino-phenyl)-benzofurane; 6-hydroxy-2,3-di-(p-methoxy-phenyl)-benzofurane; 2,3,5,6-tetra-(p-methoxyphenyl)-furo-(3,2f)-benzofurane; 4-dimethylamino-benzylidene-benzhydrazide; 4-dimethylaminobenzylideneisonicotinic acid hydrazide; furfurylidene-(2)-4'-dimethylaminobenzhydrazide; 5-benzilidene-amino-acenaphthene; 3-benzylidene-amino-carbazole; (4-N,N-dimethylamino-benzylidene)-p-N,N-dimethylaminoaniline; (2-nitro-benzylidene)-p-bromoaniline; N,N-dimethyl-N'-(2-nitro-4-cyano-benzylidene)-p-phenylene-diamine; 2,4-diphenyl-quinazoline; 2-(4'-amino-phenyl)-4-phenyl-quinazoline; 2-phenyl-4-(4'-di-methyl-amino-phenyl)-7-methoxy-quinazoline; 1,3-diphenyl-tetrahydroimidazole; 1,3-di(4'-chlorophenyl)-tetrahydroimidazole; 1,3-diphenyl-2-4'-dimethyl-amino-phenyl)-tetrahydroimidazole; 1,3-di-(p-tolyl)-2-[quinolyl-(2'-)]-tetra-hydroimidazole; 3-(4'-dimethylamino-phenyl)-5-(4"-methoxy-phenyl-6-phenyl-1,2,4-triazine; 3-pyridil-(4')-5-(4"-dimethyl-amino-phenyl)-6-phenyl-1,2,4-triazine; 3,(4'-amino-phenyl)-5,6-di-phenyl-1,2,4-triazine; 2,5-bis[4'-amino-phenyl-(1')]-1,3,4-triazole; 2,5-bis[4'-(N-ethyl-N-acetyl-amino)-amino)-phenyl-(1')]-1,3,4-triazole; 1,5-diphenyl-3-methyl-pyrazoline; 1,3,4,5-tetraphenyl-pyrazoline; 1-methyl-2-(3'4'-dihydroxy-methylene-phenyl)-benzimidazole; 2-(4'-dimethylamino phenyl)-benzoxazole; 2-(4'-methoxyphenyl)-benzthiazole; 2,5-bis-[p-aminophenyl-(1)]-1,3,4-oxidiazole; 4,5-diphenyl-imidazolone; 3-aminocarbazole; copolymers and mixtures thereof. Any suitable Lewis acid (electron acceptor) may be employed under complexing conditions with many of the aforementioned more soluble organic materials and also with many of the more insoluble organics to impart very important increases in photosensitivity to those materials. Typical Lewis acids are 2,4,7-trinitro-9-fluorenone; 2,4,5,7-

tetranitro-9-fluorenone; picric acid; 1,3,5-trinitro-benzene chloranil; benzo9quinone; 2,5-dichlorobenzoquinone; 2-6-dichlorobenzo-quinone; chloranil; naphthoquinone-(1,4); 2,3-dichloronaphthoquinone'(1,4); anthraquinone; 2-methyl-anthraquinone; 1,4-dimethyl-anthra-quinone; 1-chloroanthraquinone; anthraquinone-2-carboxylic acid; 1,5-dichloroanthraquinone; 1-chloro-4-nitroanthraquinone; phenanthrene-quinone; acenaphthene-quinone; phranthrenequinone; chrysene-quinone; thio-naphthene-quinone; anthraquinone-1,8-disulfonic acid and anthraquinone-2-aldehyde; triphthaloyl-benzene-aldehydes such as bromal,4-nitrobenzaldehyde; 2,6-di-chlorobenzaldehyde-2, ethoxy-1-naphthaldehyde; anthracene-9-aldehyde; pyrene-3-aldehyde; oxindole-3-aldehyde; pyridine-2,6-dialdehyde, biphenyl-4-aldehyde; organic phosphonic acids such as 4-chloro-3-nitro-benzene-phosphonic acid; nitrophenols, such as 4-nitrophenol and picric acid; acid anhydrides, for example, acetic-anhydride, succinic anhydride, maleic anhydride, phthalic anhydride, tetrachloro-phthalic anhydride, perylene 3,4,9,10-tetracarboxylic acid and chrysene-2,3,8,9-tetracarboxylic acid anhydride, di-bromo maleic acid anhydride; metal-halides of the metals and metalloids of the groups IB, VII B, II A-VA and group VIII of the periodical system, for example: aluminum chloride, zinc chloride, ferric chloride, tin tetrachloride (stannic chloride), arsenic trichloride, stannous chloride, antimony pentachloride, magnesium chloride, magnesium bromide, calcium bromide, calcium iodide, strontium bromide, chromic bromide, manganous chloride, cobaltous chloride, cobaltic chloride, cupric bromide, ceric chloride, thorium chloride, arsenic tri-iodide; boron halide compounds, for example: boron trifluoride and boron trichloride; and ketones, such as acetophenone, benzophenone, 2-acetyl-naphthalene, benzil, benzoin, 5-benzoyl acenaphthene, biacene-dione, 9-acetyl-anthracene, 9-benzoyl-anthracene, 4-(4-dimethylamino-cinnamoyl)-1-acetylbenzene, acetoacetic acid anilide, indandione-(1,3),-(1-3-diketo-hydrindene),acenaphthene quinone-dichloride, anisil 2,2-pyridil, furil; mineral acids such as the hydrogen halides, sulfuric acid and phosphoric acid; organic carboxylic acids, such as acetic acid and the substitution products thereof such as monochloro-acetic acid, dichloro-acetic acid, trichloro-acetic acid, phenylacetic acid, and 6-methyl-coumarinylacetic acid (4), maleic acid, cinnamic acid, benzoic acid, 1-(4'diethyl-amino-benzoyl)-benzene-2-carboxylic acid, phthalic acid, and tetrachlorophthalic acid, alpha-beta-di-bromo-beta-formyl-acrylic acid (mucobromic acid), dibromo-maleic acid, 2-bromo-benzoic acid, gallic acid, 3-nitro-2-hydroxyl-1-benzoic acid, 2-nitro phenoxy-acetic acid, 2-nitro-benzoic acid, 3-nitro benzoic acid, 4-nitro-benzoic acid, 3-nitro-4-ethoxy-benzoic acid, 2-chloro-4-nitro-1-benzoic acid, 2-chloro-4-nitro-1-benzoic acid, 3-nitro-4-methoxy-benzoic acid, 4-nitro-1-methyl-benzoic acid, 2-chloro-5-nitro-1-benzoic acid, 3-chloro-6-nitro-1-benzoic acid, 4-chloro-3-nitro-1-benzoic acid, 5-chloro-3-nitro-2-hydroxy-benzoic acid, 4-chloro-2-hydroxy-benzoic acid, 2,4-dinitro-1-benzoic acid, 2-bromo-5-nitro-benzoic acid, 4-chloro-phenyl acetic acid, 2-chloro-cinnamic acid, 2-cyano-cinnamic acid, 2,4-dichlorobenzoic acid, 3,5-dinitro-benzoic acid, 3,5-dinitro-salycylic acid, malonic acid, mucic acid, acetosalycylic acid, benzilic acid, butane-tetra-carboxylic acid, citric acid, cyano-acetic acid, cyclo-hexane-dicarboxylic acid, cyclo-hexane-carboxylic acid, 9,10-dichloro-stearic acid, fumaric acid, itaconic acid, levulinic acid (levulic acid); malic acid, succinic acid, alpha-bromo-stearic acid, citraconic acid, dibromo-succinic acid, pyrene-2,3,7,8-tetra-carboxylic acid, tartaric acid; organic sulfonic acid, such as 4-toluene sulfonic acid, and benzene sulfonic acid, 2,4-dinitro-1-methyl-benzene-6-sulfonic acid, 2,6-dinitro-1-hydroxy-benzene-4-sulfonic acid and mixtures thereof.

In addition, other photoresponsive compositions may be formed by complexing one or more suitable Lewis acids with polymers which are ordinarily not thought of as photoresponsive. Typical polymers which may be complexed in this manner include the following illustrative materials: polyethylene terephthalate, polyamides, polyimides, polycarbonates, polyacrylates, polymethymethacrylates, polyvinyl fluorides, polyvinyl chlorides, polyvinyl acetates, polystyrene, styrene-butadiene copolymers, polymethacrylates, silicone resins, chlorinated rubber, and mixtures and copolymers thereof where applicable; thermosetting resins such as epoxy resins, phenoxy resins, phenolics, epoxy-phenolic copolymers, epoxy urea formaldehyde copolymers, epoxy melamine-formaldehyde copolymers and mixtures thereof, where applicable. Other typical resins are epoxy esters, vinyl epoxy resins, tall-oil modified epoxies, and mixtures thereof where applicable.

It is also to be understood in connection with the heterogeneous system that the photoresponsive particles themselves may consist of any suitable one or more of the aforementioned photoresponsive pigments, either organic or inorganic, dispersed in, in solid solution in, or copolymerized with any suitable insulating resin whether or not the resin itself is photoresponsive. This particular type of resin may be particularly desirable to facilitate dispersion of the particle, to prevent undesirable reactions between the binder and the photoresponsive pigment or between the photoresponsive pigment and the activator, and for other similar purposes. Typical resins of this nature include polyethylene, polypropylene, polyamides, polymethacrylates, polyacrylates, polyvinyl chlorides, polyvinyl acetates, polystyrene, polysiloxanes, chlorinated rubbers, polyacrylonitrile, epoxies, phenolics, hydrocarbon resins and other natural resins such as rosin derivatives as well as mixtures and copolymers thereof.

As stated above, the photoresponsive or imaging layer generally should have a relatively low cohesive strength either in the as coated condition or following activation. This, of course, is true for both the homogeneous systems and the heterogeneous systems. One technique for achieving low cohesive strength in the imaging layer is to employ relatively weak, low molecular weight materials therein. Thus, for example, in a single component, homogeneous layer, a monomeric compound or a low molecular weight polymer complexed with a Lewis acid to impart a high level of photosensitivity to the layer may be employed. Similarly, when a homogeneous layer utilizing two or more components in solid solution is selected to make up the donor layer either one or both of the components of the solid solution may be a low molecular weight material such that the layer has the desired low level of cohesive strength. This approach may also be taken in connection with the preparation of a heterogeneous imaging layer. Although the binder material in the heterogeneous system may in itself be photosensitive, it is not necessary that it have this property so that materials such as microcrystalline wax, paraffin wax, low molecular weight polyethylene and other low molecular weight polymers may be selected for use as the binder material solely on the basis of physical properties and the fact they are insulating materials, without regard to their photoresponsiveness. This is also true of the two component homogeneous system where nonphotoresponsive materials with the desired physical properties may be used in solid solution with photoresponsive material. Any other suitable technique for achieving low cohesive strength in the imaging layer of the present system may also be employed. For example, suitable blends of incompatible materials such as a blend of a polysiloxane resin with a polyacrylic ester resin may be used either as a binder layer in a heterogeneous system or in conjunction with a homogeneous system in which the photoresponsive material may be either one of the incompatible components complexed with a Lewis acid or a separate and additional component of the layer.

While as stated above either one or both of the donor support substrate and receiving sheet or substrate may be conductive in nature such as conductive cellophane the use of such flexible, transparent conductive materials for the most part will furnish a relatively weak support. Therefore, the use of an insulating donor substrate and receiver sheet backed up in each instance by a working electrode allows for the use of high strength insulating polymers such as polyethylene, polypropylene, polyethylene terephthalate (Mylar), cellulose acetate, Saran, a vinyl chloride-vinylidene chloride copolymer and similar materials. Not only does the use of this type of high strength polymer provide a strong substrate for the manifold images formed on the donor substrate and receiver sheet but in addition it provides an electrical barrier between the electrodes and the imaging layer which tends to inhibit electrical breakdown of the system. When the lithographic master is prepared directly the receiver sheet will take the form of a hydrophilic support suitable for forming a lithographic master such as a lithographic paper, grained aluminum, etc. as set out above Further, structural combinations of the manifold set are more fully described in copending U.S. Pat. application Ser. No. 452,641, filed May 3, 1965 now abandoned in favor of copending application Ser. No. 708,380 filed Feb. 26, 1968, having a common assignee.

Any suitable activator agent may be employed during the course of the present invention. Generally speaking, the activator may consist of any suitable solvent having properties as set out above and which has the above described effect on the imaging or donor layer. For purposes of this invention the term "solvent" shall be understood to include not only materials which are conventionally thought of as solvents but also those which are thought of as partial solvents, swelling agents or softening agents for the imaging layer. It is generally preferred that the activator solvents have a relatively low boiling point so that fixing of the resulting duplicating image may be accomplished by solvent evaporation, with a very mild application of heat, if necessary. It is to be understood, however, that the invention is not limited to the use of these relatively volatile activators. In fact, very high boiling point, nonvolatile activators, including silicone oils such as dimethyl polysiloxanes and very high boiling point long chain aliphatic hydrocarbon oils ordinarily used as transformer oils such as Wemco-C transformer oil, available from Westinghouse Electric Co., have also been successfully utilized in the imaging process. Generally speaking, therefore, any suitable volatile or nonvolatile solvent activator may be employed. Typical solvents include Sohio Odorless Solvent 3440, an aliphatic (kerosene) hydrocarbon fraction commercially available from Standard Oil Co. of Ohio, carbon tetrachloride, petroleum ether, Freon 214 (tetrafluorotetrachloropropane), other halogenated hydrocarbons such as chloroform, methylene chloride, trichloroethylene, perchloroethylene, chlorobenzene, trichloromonofluoro methane, tetrachloro difluoroethane, trichlorotrifluoroethane, amides such as formamide, dimethyl formamide, esters such as ethyl acetate, isopropyl acetate, butyl acetate, amyl acetate, cyclohexyl acetate, isobutyl propyanate and butyl lactate, ethers such as diethyl ether, diisopropyl ether, dioxane, tetrahydrofuran, ethylene glycol monoethyl ether, aromatic and aliphatic hydrocarbons such as benzene, toluene, xylene, hexane, cyclohexane, gasoline, mineral spirits and white mineral oil, ketones such as acetone, methylethyl ketone, methyl isobutyl ketone, and cyclohexanone and vegetable oils such as coconut oil, bamboo bassu oil, palm oil, olive oil, castor oil, peanut oil, neats foot oil, and mixtures thereof.

With respect to the exposure phase of the process of the present invention an electrical field is applied across the manifold set as it is exposed to the image to be reproduced. By preparing the imaging configuration in such a manner that the initial degree of adherence of the donor layer to the donor support is only slightly higher than that of the donor layer to the receiving substrate, the imaging layer will remain on the donor support substrate unless the combined effect of exposure and applied field are added to the bond strength of the receiving sheet and the donor layer thereby exceeding the strength of the bond between the donor layer and the donor support substrate. In this way an amplification effect is achieved and transfer may be effected with relatively low levels of light exposure. The application of the required electrical field is relatively straightforward, generally falling within a range of from about 1,000 to about 25,000 volts per mil, with a preferred field strength in the range of from about 1500—2000 volts per mil; however, with some materials there is a preferred polarity orientation. Thus, for example, with an imaging layer made up of finely divided metal-free phthalocyanine particles dispersed in a microcrystalline wax, it has been determined that the best images generally are formed when the illuminated electrode backing of the donor support substrate is made positive and the nonilluminated receiving sheet backing electrode negative.

A visible light source, an ultraviolet light source or any other suitable source of actinic electromagnetic radiation may be used to expose the manifold set of the present invention. Higher quality images are obtained by exposing from the donor side of the imaging layer, and accordingly, the receiver sheet is usually separated from the remaining layers of the manifold set just after image exposure and generally with the power still being supplied to both electrodes. However, short delays in separation after the exposure step do not appear to have deleterious effects on the images produced. Essentially the same results are obtained when separation is made after the power to the system is turned off, but, generally, the images are somewhat poorer in quality. Exposure parameters such as the magnitude of the applied potential and the like may be found in the above mentioned copending U.S. Pat. application Ser. No. 452,641.

If a relatively volatile activator is employed, such as petroleum ether, carbon tetrachloride or Freon 214, fixing of the duplicating image occurs almost instantaneously inasmuch as a relatively small amount of the activator is present. With somewhat less volatile activators, such as the Sohio Odorless Solvent 3440 or Freon 214, described above, fixing may be accelerated by blowing air over the images or warming them to a temperature of about 150° F., whereas with the even less volatile activators, such as transformer oil, fixing is accomplished by a blotting effect which may be supplied by an accessory substrate. In addition to the above disclosed fixing techniques any other suitable method may be employed which will occur to those skilled in the art.

PREFERRED EMBODIMENTS

To further define the specifics of the present invention, the following examples are intended to illustrate and not limit the particulars of the present system. Parts and percentages are by weight unless otherwise indicated. The examples are also intended to illustrate various preferred embodiments of the present invention.

EXAMPLES I & II

A commercial, metal-free phthalocyanine is first purified by acetone extraction to remove organic impurities. Since this extraction step yields a less sensitive beta crystalline form, the desired alpha form is obtained by dissolving 100 grams of the beta form in 600 cc.'s of sulfuric acid, precipitating it by pouring the solution into 3,000 cc.'s of ice water and washing with water to neutralize. The resulting purified alpha phthalocyanine is salt milled for 6 days and desalted by slurrying in distilled water, vacuum filtering, water washing and finally methanol washing until initial filtrate is clear to produce the x-form phthalocyanine. After vacuum drying to remove residual methanol, the x-form phthalocyanine thereby produced is used to prepare the imaging layer according to the following procedure: 2 grams of Paraflint RG wax, a microcrystalline wax available from Moore and Munger Inc. having a melting point of about 214° F., and 0.5 grams of Sunoco 5825, a microcrystalline wax with a melting point of about 150° F. is blended with a trimixture of 1.25 grams of the above purified x-form metal-free phthalocyanine, 0.8 grams Watchung Red B, 1-(4′-methyl-5′-chloroazobenzene-2′-sulfonic acid)-2-hydroxy-3-napthoic acid, C.I. No. 15865, commercially available from E. I. duPont de Nemours & Co. and 1.25 grams Algol Yellow GC, 1,2,5,6-di(C,C′-diphenyl)- thiazoleanthraquinone, C.I. No. 67300, commercially available from General Dyestuffs, in 60 cc.'s of reagent grade petroleum ether. This formulation is added in a 1 pint wide-mouth glass jar together with a ½ pint volume and ½ inch diameter porcelain balls. The jar lid is lined with a 5 mil Teflon coating to avoid contamination and the lid screwed on the jar which serves as a ball mill container. The jar is wrapped with a black vinyl electrical pressure sensitive tape, type No. 33, available from Minnesota Mining and Manufacturing Corp. to protect the mill jar from shock and to shield the mill jar contents from light. This formulation is then ball milled at a rate of about 90 r.p.m.'s for about 24 hours. Following the 24 hour milling an additional 20 cc.'s of the petroleum ether is added. The mill is then rotated another 15 minutes after the addition of the second increment of the ether. A uniform coating of the resulting paste is applied to the top side of a 2 mil thick Mylar film using a No. 10 wire-wound drawdown rod to produce a donor sheet. The coating is air dried at room temperature for about 5 minutes. The imaging coating is measured to be about 2.5 microns in thickness. The air dried donor sheet is then fastened, donor coating facing up, to the electrically conductive surface of a transparent NESA glass electrode. About 1 cc. of a 5 percent activator solution of Piccotex 100, a styrene copolymer, in Sohio Odorless Solvent 3440, a kerosene fraction commercially available from Standard Oil of Ohio is applied in a bead along one edge of the horizontal donor sheet. A second 2 mil thick Mylar sheet is placed over the donor coating bearing the bead of activator solution and the activator solution is spread uniformly over the donor coating by rolling a 1 inch diameter and 6 inches long rubber roller once across the 2 mil Mylar receiver sheet. A sheet of electrically conductive black paper, the latter serving as the opaque electrode in the system, is laid over the second Mylar receiver sheet. A potential of about 10,000 volts is applied through a 1250 megohm resistor across the transparent and opaque electrodes with the NESA glass made the positive pole and the black conductive paper the negative pole. About 5 seconds after the electric field power is turned on the manifold set is exposed to a light image by projecting a negative, continuous tone image upward through the transparent NESA electrode. The exposure is about 0.05 foot-candle illumination from an incandescent lamp about 2800K for a duration of about 4 seconds, making a total incident energy of about 0.20 foot-candle-seconds. About 3 seconds after the light exposure step, the receiver Mylar sheet and the opaque electrode are peeled off manually while the full 10,000 volt potential is still applied. Following separation a copy of the original negative is observed on the Mylar donor substrate and a reversal or positive of the original negative is observed on the Mylar receiver sheet. Both manifold images are fixed by warming to a temperature of about 160° F. on a hot plate. Each of the manifold images is placed in contact with the top of a lithographic paper plate and passed at about 1 inch per second between steel rolls about 3 inches in diameter and spring loaded with an inter-roll force of about 1600 pounds. The total force applied is about 800 pounds per linear inch. An imprint of each image is thereby pressure transferred to its respective lithographic plate. Each imaged lithographic printing plate is then attached to a conventional lithographic press and successfully printed utilizing conventional fountain solutions and lithographic printing inks.

EXAMPLES III & IV

The above procedure described in Examples I and II is repeated up to and including the separation of the image receiver sheet from the donor substrate. The resulting image bearing substrates are contacted under pressure conditions similar to those in the above Examples I and II with a lithographic aluminum grained substrate and an imprint of the respective waxy images transferred thereto. The resulting aluminum lithographic plates satisfy the requirements of lithography.

EXAMPLES V & VI

A donor paste is prepared according to the process of Examples I and II and a uniform coating of the paste applied to a 2 mil Mylar donor substrate mounted on a NESA electrode. The donor coating is activated with a 5 percent solution of the Piccotex 100 resin in a Sohio 3440 Solvent described in the above examples and a Mylar receiver sheet is placed over the activated donor layer. The receiver sheet is backed up by an opaque black conductive paper. When closure of the manifold set is complete, 7,000 volts are applied across the transparent and opaque electrode complex through a 51 meg-ohm resistor. Again, as in Examples I and II, the NESA glass serves as the positive electrode and the opaque electrode as the negative pole. About 5 seconds after the power is turned on the manifold set is exposed to a light image by projecting a negative, continuous tone image upward through the transparent NESA electrode. The exposure is about 0.05 foot-candles from an incandescent lamp for a duration of about 5 seconds, making a total incident energy of about 0.25 foot-candle-seconds. About 3 seconds after the light exposure step, the receiver Mylar sheet and opaque electrode are peeled off manually while the full potential is still applied. Following separation, a copy of the original negative is observed on the Mylar donor substrate and a reversal or positive on the Mylar receiver sheet. Both manifold images are again fixed by warming to a temperature of about 160° F. on a hot plate. Each of the manifold images is placed in contact with a lithographic paper plate and an imprint of each image pressure transferred as in Examples I and II to the surface of the respective paper plate. Each imaged lithographic paper plate is attached to a conventional lithographic press and successfully printed utilizing conventional fountain solutions and lithographic printing inks.

EXAMPLES VII & VIII

The above procedure described in Examples V and VI is repeated up to and including the separation of the image receiver sheet from the donor substrate. The resulting image bearing substrates are contacted under pressure conditions similar to those in Examples I and II with lithographic aluminum grained substrates and an imprint of the respective waxy images transferred thereto to produce the lithographic printing plates.

EXAMPLES IX & X

Manifold images are prepared on the surface of a receiver sheet and a donor substrate according to the process described in Examples I and II. Following separation and fixing, the resulting manifold images are each placed separately in immediate contact with the surface of an aluminum lithographic master. The resulting sandwich configurations are heated to about 250° F. for about 1 minute by means of a common household flat iron, the force applied being only that due to the weight of the iron. An imprint of each image is thereby transferred to its respective lithographic plate to form the master.

Example XI

A donor paste is prepared according to the process of Examples I and II. A uniform coating of the resulting paste is applied to the surface of a 2 mil thick Mylar film using a No. 8 wire-wound drawdown rod and the resulting coating air dried at room temperature for about 5 minutes. The imaging layer is measured to be about 5 microns in thickness. The air dried donor sheet is then fastened, donor coating facing up, to the electrically conductive surface of a transparent NESA glass electrode. An activator solution similar to that used in Examples I and II is applied to the donor composition and a 2 mil Mylar receiver sheet is placed over the top of the imaging layer. An opaque conductive black paper electrode is placed over the receiver Mylar sheet to complete fabrication of the manifold set. A potential of about 7,000 volts is applied through a 51 meg-ohm resistor across the electrode complex with the NESA glass made the positive pole and the opaque electrode the negative pole. About 5 seconds after the electric power is turned on, the manifold set is exposed to a light image by projecting a negative, continuous tone image upward through the transparent NESA electrode. The exposure is about 0.05 foot-candles for about 5 seconds, making a total incident energy of about 0.25 foot-candle-seconds. About 3 seconds following the light exposure step, the receiver Mylar sheet and the opaque electrode are peeled off manually with the full 7,000 volts applied. Following separation, a manifold image is observed on the surface of the receiver Mylar sheet. The manifold image on the receiver sheet is fixed thereto by heating on a hot plate which is at a temperature of about 160° F. An aluminum lithographic plate is horizontally placed and connected to the negative pole of the original power source. A thin layer of petroleum ether, that which was used to prepare the donor paste, is coated on the surface of the aluminum substrate, and the receiver image along with the Mylar substrate and opaque backing electrode is lowered onto the petroleum ether layer. The conductive opaque electrode is connected through the 51 meg-ohm resistor to the positive pole of the power source. A potential of about 7,000 volts is applied across the sandwich configuration. After 5 seconds the receiver sheet with the opaque electrode is peeled off while the 7,000 volts are still applied. A waxy image is observed on the surface of the lithographic aluminum substrate. The image is fixed thereto by heating the plate to a temperature of about 275° F. thereby producing the lithographic printing master.

EXAMPLE XII

Five grams of Sunoco 1290 microcrystalline wax having a melting point of about 160° F. is blended with a trimixture of 3 grams of x-form metal-free phthalocyanine as prepared in Example I, 2 grams of Watchung Red B and 1 gram of Benzidene Yellow type 30-0535, commercially available from Hilton Davis Corp. in 100 cc.'s of clay bed purified reagent grade petroleum ether. This formulation is ball milled at a rate of about 90 r.p.m.'s for about 20 hours. The resulting paste is heated to a temperature of about 150° F. and then cooled back to room temperature. A uniform coating of the resulting paste is then applied to the surface of a 2 mil thick Mylar film using a No. 6 wire-wound drawdown rod to produce an imaging coating about 2.5 microns thick. The coating is air dried at room temperature for about 5 minutes. The air dried donor sheet is then fastened as in the above examples to a NESA glass electrode and the surface of the donor composition activated by applying a bead of Dow Corning silicone 200, with a viscosity of about 0.65 centistokes, as the activator along one edge of the donor. The donor composition is covered with an aluminum lithographic substrate and a rubber roller, passed across the exposed surface thereby distributing the activator uniformly over the donor composition. A sheet of electrically conductive black paper is laid over the aluminum lithographic substrate to serve as the opaque electrode in the system. A potential of about 3,000 volts is applied through a 51 meg-ohm resistor across the electrode system with the NESA glass made the positive pole and the black conductive paper the negative pole. About 5 seconds after the electric field is turned on, the manifold set is exposed to a light image by projecting a negative, continuous tone image upward through the transparent NESA electrode. The exposure is about 0.10 foot-candles for about 5 seconds. About 3 seconds after the light exposure step, the aluminum receiver sheet and the opaque electrode are peeled off while the voltage potential is still applied. A manifold image is observed on the surface of the aluminum lithographic substrate. The resulting image is fixed by warming to a temperature of about 160° F. on a hot plate. This example demonstrates the direct mode of preparing a lithographic printing master with a waxy manifold image on the surface of an aluminum lithographic substrate.

EXAMPLE XIII

The process of Example XII is repeated with a lithographic paper plate being substituted for the aluminum substrate. The potential applied during the imaging step is 4,000 volts and the light exposure produces an incident energy of about 0.25 foot-candle-seconds. There is produced on the surface of the lithographic paper master a waxy manifold image with the resulting plate serving as an ideal lithographic printing master.

EXAMPLE XIV

The process of Example XII is repeated with the exception that the aluminum master receiver sheet is wrapped around a 4 inch diameter aluminum roller and the resulting configuration rolled across the activated donor layer with a 4,000 volt potential applied and exposure to an image at about one-third foot-candle. The resulting aluminum lithographic plate is removed from the aluminum roller and utilized in a lithographic mode.

EXAMPLE XV

A donor formulation is prepared according to the process of Examples I and II and coated on the surface of a 2 mil thick Mylar film using a No. 10 wire-wound drawdown rod. The coating is air dried at room temperature for about 5 minutes. The resulting donor substrate is fastened with donor coating facing upward to an electrically conductive transparent NESA glass electrode. The resulting donor coating is activated with an activator solution as in Examples I and II and a 3 mil aluminum lithographic substrate is placed over the activated donor coating. A second aluminum plate is placed over the receiver aluminum lithographic substrate to serve as the second electrode in the system. A potential of about 4,000 volts is applied through a 51 meg-ohm resistor and the donor coating exposed to a light image with exposure being at about 0.5 foot-candle-seconds. About 3 seconds after the light exposure step, the receiver aluminum lithographic substrate and the backing electrode are peeled off manually while the full potential is still applied. A waxy manifold image is observed on the surface of the receiver lithographic substrate and the resulting plate utilized as a lithographic printing master.

EXAMPLE XVI

The process of Example XV is repeated but for the substitution of a lithographic paper plate for the aluminum reciever substrate. The resulting paper master is printed in a lithographic mode.

Although the present examples are specific in terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to prepare the lithographic printing master of the present invention, other steps or modifications may be used, if desirable. For example, during the procedure wherein the donor paste is heated and cooled after milling but prior to coating, the cooling step may be executed in a manner so as to shock the donor composition. Thus, this cooling step may be carried out either gradually or instantaneously. In addition, other materials may be incorporated in the photosensitive material, binder, donor sheet, receiver sheet or lithographic substrate which will enhance, synergize, or otherwise desirably effect the properties of these materials for their present use. For example, increased image durability and hardness may be achieved by treatment with a hardening agent or with a hard polymer solution which will wet the image material but not the substrate.

Anyone skilled in the art will have other modifications occur to him based on the teachings of the present invention. These modifications are intended to be encompassed within the scope of this invention.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,554,125 Dated January 12, 1971

Inventor(s) Warren G. Van Dorn et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the grant (only) insert Columns 17, 18, 19 and 20, containing claims 1 - 27.

We claim:

1. A method of preparing a lithographic duplicating master which comprises selectively exposing at least one surface of a manifold set to actinic radiation while said set is subjected to an electric field, said surface being transparent to said radiation, said manifold set comprising a waxy hydrophobic, frangible, electrically photosensitive imaging composition interpositioned between a donor substrate and a hydrophilic receiver sheet, separating said receiver sheet from said donor substrate whereby said imaging composition fractures in imagewise configuration to provide adhering to the surface of said receiver sheet a waxy hydrophobic image of said imaging composition to produce said lithographic master.

2. The method as described in claim 1 wherein said exposing step is carried out through said donor substrate and said hydrophilic receiver sheet comprises a lithographic paper substrate.

3. A process of preparing a lithographic duplicating master which comprises selectively exposing at least one surface of a manifold set to electromagnetic radiation while said set is subjected to an electric field, said surface being transparent to said radiation, said manifold set comprising a hydrophobic frangible electrically photosensitive imaging composition interpositioned between a donor substrate and a receiver sheet, separating said receiver sheet from said donor substrate, whereby said imaging composition fractures in imagewise configuration to provide adhering to the surface of said receiver sheet an image of said imaging composition and said donor substrate having adhered to its surface an image complimentary to that on the receiver sheet and transferring at least one of said images to the surface of a hydrophilic substrate to produce said lithographic master.

10. The method as described in claim 9 wherein said i
transfer step is carried out by the external application of
sure.

11. The method as described in claim 9 wherein said ir
transfer step is light-activated.

12. The method as described in claim 9 wherein said ir
transfer step is carried out by the external application of h

13. A method of making multiple copies from a lithogra
duplicating master which comprises:

a. selectively exposing at least one surface of a manifol
to actinic radiation while said set is subjected to an
tric field, said surface being transparent to said radia
said manifold set comprising a frangible waxy hydro
bic electrically photosensitive imaging composition i
positioned between a donor substrate and a hydrop
receiver sheet;

b. separating said hydrophilic receiver sheet from
donor substrate whereby said imaging composition
tures in imagewise configuration to provide adherin
the surface of said receiver sheet a waxy hydroph
image of said imaging composition;

c. dampening said receiver sheet;

d. applying to the surface of said image bearing hydrop
receiver sheet a lithographic ink, said ink being
tributed thereon conforming to said image;

e. contacting said ink surface with a copy sheet the
transferring an imprint of said image to said sheet; and

f. repeating steps (d) and (e) until the desired number o
pies are produced.

14. The method as described in claim 13 wherein
hydrophilic receiver sheet comprises a lithographic paper
strate.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,554,125 Dated January 12, 1971

Inventor(s) Warren G. Van Dorn et al. PAGE - 2

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4. The process as described in claim 3 wherein said transfer step is light-activated.

5. The process as described in claim 3 wherein said transfer step is effected by the external application of pressure.

6. The process as described in claim 3 wherein said transfer step is effected by the external application of heat.

7. A method of preparing a lithographic printing master which comprises rendering a hydrophobic electrically photosensitive imaging composition coated on the surface of a donor support substrate, fracturable in response to actinic electromagnetic radiation and electric field by applying thereto an activator for said composition, placing a hydrophilic receiver sheet over said photoresponsive composition, exposing said imaging composition to a pattern of actinic electromagnetic radiation through the surface of at least one of said donor substrate and receiver sheet while an electric field is applied across said imaging composition, said surface being transparent to said radiation, and separating said receiver sheet from said donor substrate, said hydrophilic receiver sheet having formed on the surface thereof a hydrophobic waxy image, to produce said lithographic master.

8. The method as described in claim 7 wherein said exposing step is carried out through said donor substrate and said hydrophilic receiver sheet comprises a lithographic paper substrate.

9. A method of preparing a lithographic printing master which comprises rendering a hydrophobic electrically photosensitive imaging composition coated on the surface of a donor support substrate, fracturable in response to actinic electromagnetic radiation and an electric field, placing a receiver sheet over said imaging composition, exposing said imaging composition to a pattern of actinic radiation through the surface of at least one layer of said donor substrate and receiver sheet while an electric field is applied across said imaging composition, said surface being transparent to said radiation, separating said receiver sheet from said donor substrate with the exposed portion of said imaging composition being retained on one of said donor and receiver layers while the unexposed portion is retained on the other of said layers and transferring at least one of said formed images to the surface of a hydrophilic substrate to produce said printing master.

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15. A method of making multiple copies from a lithogra printing master which comprises:

a. selectively exposing at least one surface of a manifol to electromagnetic radiation, while said set is subject an electric field, said surface being transparent to radiation, said manifold set comprising a fran hydrophobic electrically photosensitive imaging com tion interpositioned between a donor substrate a receiver sheet;

b. separating said receiver sheet from said donor subs whereby said imaging composition fractures in image configuration to provide adhering to the surface of receiver sheet an image of said imaging compositior said donor substrate having adhered to its surfac image complimentary to that on said receiver sheet;

c. transferring at least one of said formed images to the face of a hydrophilic substrate;

d. dampening said hydrophilic substrate;

e. contacting said image successively with a lithographi and with the surface of a transfer sheet thereby trar ring an ink image to said transfer sheet;

f. contacting said transfer sheet with the surface of a sheet whereby an ink image is transferred to said sheet, and

g. repeating steps (d), (e) and (f) until the desired nu of copies are produced.

16. The process as described in claim **15** wherein said i transfer step (c) is carried by the external application of sure.

17. The process as described in claim **15** wherein said i transfer step (c) is light-activated.

18. The process as described in claim **15** wherein said i transfer step (c) is carried out by the external applicat heat.

19. The process as described in claim **15** wherei hydrophilic substrate comprises a lithographic paper bas

20. The method of claim **13** wherein the imaging cor tion comprises an organic electrically photosensitive ma dispersed in a waxy hydrophobic binder.

21. The method of claim **20** wherein the organic elect photosensitive material is phthalocyanine.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,554,125 Dated January 12, 1971

Inventor(s) Warren G. Van Dorn et al. PAGE - 3

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22. The method of claim **13** wherein said electric field is in the range of from about 1,000 volts per mil to about 25,000 volts per mil.

23. The method of claim **13** wherein said donor substrate is transparent to said actinic radiation and said set is exposed on the donor surface to said actinic radiation.

24. The method of claim **15** wherein the imaging composition comprises an organic electrically photosensitive material dispersed in a waxy hydrophobic binder.

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25. The method of claim **24** wherein the organic ele
photosensitive material is phthalocyanine.

26. The method of claim **15** wherein said electric fi
the range of from about 1,000 volts per mil to about
volts per mil.

27. The method of claim **15** wherein said donor sub
transparent to said actinic radiation and said set is exp
the donor surface to said actinic radiation.

Signed and sealed this 16th day of November 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Pat