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LITHOGRAPHIC IMAGING SYSTEM USING PHOTOCHROMIC
AND THERMOCHROMIC MATERIALS
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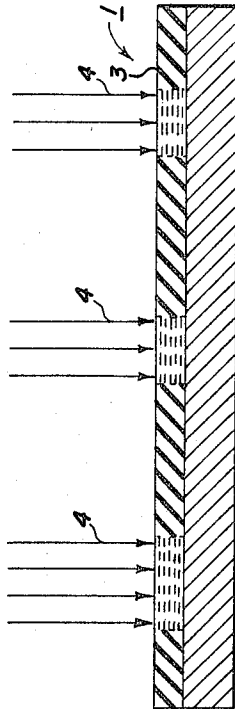


FIG. 1

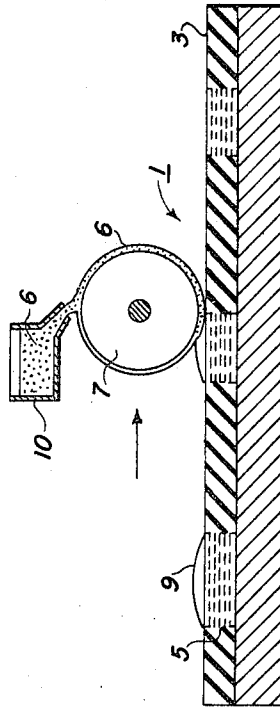


FIG. 2

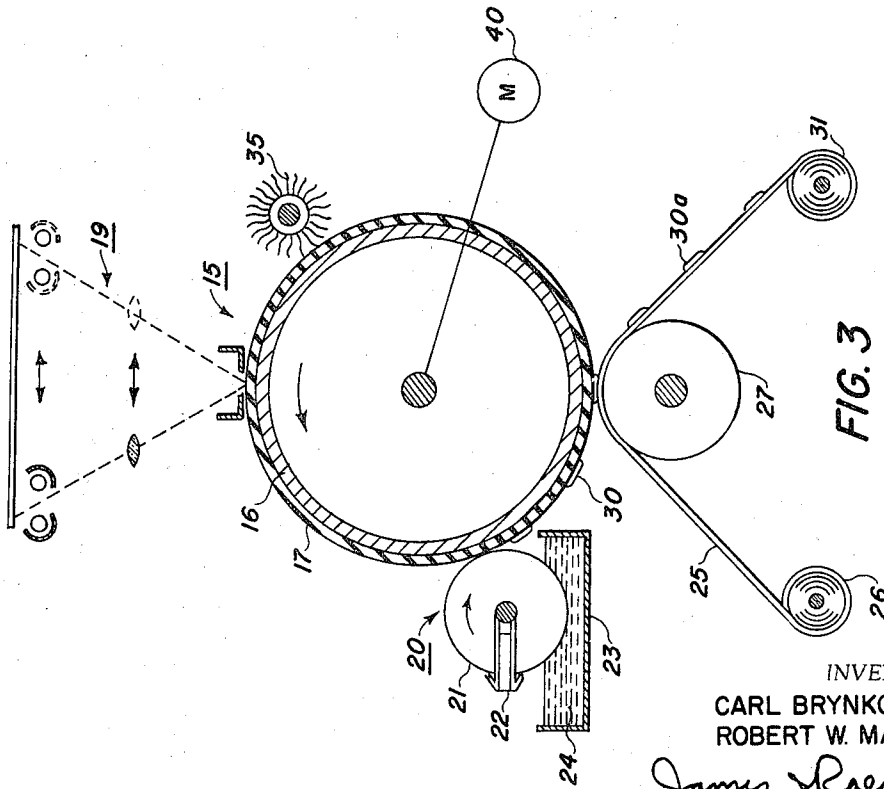


FIG. 3

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LITHOGRAPHIC IMAGING SYSTEM USING PHOTOCHROMIC AND THERMOCHROMIC MATERIALS

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17 Claims

ABSTRACT OF THE DISCLOSURE

The subject matter of this invention relates to an imaging system utilizing a lithographic master which has been prepared using photochromic and thermochromic materials.

This invention relates to an imaging 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 non-image areas for printability. In conventional lithography, the non-image area is hydrophilic while the image area is hydrophobic. In the lithographic printing process, a fountain solution is applied to the plate surface which wets all portions of the surface not covered by the hydrophobic image. This solution keeps the plate moist and prevents it from scumming up. An oil based printing ink is applied to the image surface depositing the lithographic ink only on the image area, the hydrophilic non-image area repelling the ink. The ink image may then be transferred directly to a paper sheet or other receptive surface, but generally it is transferred to a rubber 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 and finally printed.

A number of techniques are known for preparing lithographic printing plates. For example, according to one method of preparing a lithographic printing plate by an electrostatic printing process, the development powder is selected to be a material which is wetted by lithographic ink. After the powder image is formed upon the photoconductive coating, it is transferred to a lithographic sheet such as a specially treated aluminum plate. Heat is then applied in order to fix the transferred image to the lithographic sheet, thereby producing a finished printing plate. Another electrostatic method of producing a lithographic printing plate consists of coating a photoconductive material that is volatile at relatively low temperatures, such as anthracene or sulfur, on the surface of a sheet of metal especially prepared for lithography. An electrostatic latent image is produced and developed on the photoconductive coating. The development powder is hydrophobic in nature and has a relatively low melting point. The metal sheet is heated to a temperature such that the photoconductive coating evaporates in the non-image areas leaving the hydrophobic powder image on the plate. The heating is continued until the developed image is fixed to the surface of the plate. A third electrostatic printing process useful in preparing lithographic printing plates entails the development of an electrostatic latent image on a conventional xerographic binder plate with a toner material which is generally hydrophobic in nature, as is usually the binder plate. In order to prepare the plate to be used as a lithographic master, a differential must be established between the toner image and the background of the plate, inasmuch as both have hydrophobic properties. This is accomplished by treating the surface of the plate with a conversion solution which renders the background, non-image areas hydrophilic.

Other non-electrostatic methods have also been used to prepare lithographic printing plates. In one instance, a supporting base having hydrophobic properties is coated with a hydrophilic metal film and the metal surface coated with a light sensitive coating. The light sensitive plate is selectively exposed and developed. The developed surface is etched thereby removing the metallic hydrophilic surface in the light protected areas, exposing the resinous hydrophobic material in an imagewise configuration. The plate now presents a surface in which background areas are covered by a light hardened coating and the image areas present a hydrophobic resinous surface, the metal film having been etched therefrom. The remaining light-sensitive coating is then removed producing a finished plate having image areas with hydrophobic properties and non-image areas with hydrophilic properties. A second, non-electrostatic 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 the original which is, in turn, transferred to the sensitive hydrophilic coating adjacent thereto. The areas affected by the heat are converted thereby producing a hydrophobic image on 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 cases employing electrostatic techniques of preparing lithographic printing plates, cited above, several disadvantages are encountered. For example, certain of the above disclosed approaches require the use of secondary solutions so as to alter the properties of a non-image area and make them hydrophilic. Other processes which require the removal of the non-image, hydrophobic photoconductive areas by either mechanical or chemical means, not only make it necessary to add additional steps to the processes, but treatments of this nature lead to a degradation of the quality of the images subsequently reproduced from the fabricated plates. In the specific process where the non-image, hydrophobic areas are removed as a result of the volatile nature of the photoconductive material, the noxious fumes which evolve upon evaporation of the photoconductive material, make this approach further undesirable. In addition to this disadvantage, the process is further limited in that the choice of the photoconductive material must be restricted to those materials having a relatively low boiling point and low melting point. The primary disadvantage encountered in the process disclosed above wherein the lithographic plates are prepared by transferring a powder, oleophilic image directly to a lithographic sheet is that image detail and definition is lost during the powder image transfer.

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 disadvantages. Generally, the most prominent disadvantage to these systems is that elaborate preparations are necessary in order to produce the final printing plate.

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

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

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

Still a further object of this invention is to provide an imaging system wherein a novel lithographic plate can be prepared without resorting to image degrading treatments.

An additional object of this invention is to provide an imaging system utilizing a master prepared by a non-complex, single step process.

Yet, still a further object of this invention is to provide a process of using a novel lithographic printing plate.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing a lithographic master prepared by coating on the surface of a receiving substrate a layer of a photochromic composition from about 0.5 to 50 microns thick. It is preferred in order to provide for maximum utility of this light sensitive material that the thickness of the photochromic layer be from about 2 to 30 microns. The layer of the photochromic composition is selectively exposed to a source of actinic electromagnetic radiation. The photochromic materials are basically spectral, light sensitive dyes which exhibit reversible spectral changes upon exposure to radiant energy in specific portions of the electromagnetic spectrum. The particular source of radiant energy may constitute a source of infrared light, visible light, ultraviolet light, X-ray or any suitable radiation which is capable of initiating the required spectral change in the particular photochromic material. Maximum contrast between the exposed and unexposed areas is obtained when the photochromic material is exposed to radiant energy in the visible portions or near visible portions of the electromagnetic spectrum. Imagewise conversion of at least a portion of the photochromic layer in those areas exposed to the actinic radiation by an alteration of the surface properties in the exposed areas forms a latent image on the surface of the exposed material. As a result of the changed surface properties the exposed photochromic plate may then serve as a printing master. Following the formation of the latent image, an aqueous based developer is applied to the surface of the substrate retaining the latent image. In view of the induced change in the exposed areas of the photochromic composition, the exposed areas are more readily wetted by the water base developer than the unexposed areas. This difference in wettability of the image and background areas is dependent upon a variation in the contact angle which the two areas of the photochromic material make with the aqueous developer. It is to be noted that the exposure need only convert an adequate number of photochromic molecules so as to produce a significant difference between the contact angle of the exposed and unexposed areas. As a result of the contact angle differential which exists, the developer is held in an imagewise configuration to the exposed portion of the photochromic plate. The exposed photochromic master can then be used to continuously make prints whereby an aqueous based ink is applied to master, the ink adhering to the exposed areas of the photochromic surface and the master subsequently contacted with a copy sheet to transfer the image. Alternatively, it has been ascertained that a thermochromic compound, that is, one which exhibits reversible spectral changes upon exposure to radiant energy in the form of heat, may be substituted for the photochromic materials in the above procedure with a similar result being obtained. The exposed areas of the thermochromic materials undergo a similar surface alteration wherein the contact angle differential again is realized thereby producing a difference in wettability between the exposed and unexposed areas.

Materials which exhibit reversible spectral changes upon exposure to electromagnetic radiation of less than 7000 A. wavelength are referred to as photochromic. Materials which undergo similar reversible changes upon exposure to radiant energy in the form of heat are referred to as thermochromic. In the absence of actinic radiation or heat respectively, these materials have relatively

stable configurations with characteristic absorption properties. However, when exposed to a source of energy, such as actinic radiation in the case of the photochromic materials, e.g., ultraviolet light, and energy in the form of heat in the case of the thermochromic materials, such as is derived from infrared radiation, the properties of the exposed areas of the materials are substantially altered thereby affecting their wettability characteristics. The effect of the change in the surface characteristics is such that when contacted with any aqueous solution or developer, there is detected a difference in wettability properties between the exposed and unexposed areas. This difference in wettability is due to the nature of the contact angle which exists between both the exposed and unexposed areas and the developer.

The contact angle is a measure of the wettability of a particular liquid on a solid surface. As herein used it is defined as being the angle through the liquid which is measured between the horizontal solid surface and the tangent to the drop of developer at the point at which the surface of the drop intersects the horizontal surface. The tangent will be in a plane perpendicular to the horizontal surface which also passes through the center of the drop. In the case of the present invention, those areas under exposure are effected in such a manner so as to become water receptive as a result of a reduction in contact angle between the exposed surface and the water droplets. This difference in wettability of the image and background areas forms the basis for the development and imaging techniques of the present invention.

The photochromic or thermochromic layer may be composed solely of one or more of the respective compounds providing that it has sufficient strength. Generally, the particular energy sensitive compound may range from about 100% to about 1% by weight of the photochromic or thermochromic material with the remainder when necessary being a resinous binder composition. For convenience, the particular energy sensitive material will generally be dissolved in solid solution form or dispersed in the natural or synthetic resinous binder additive. This resin may be thought of, as mentioned above, as a binder or matrix for the respective material. The use of such resins allows for the photochromic or thermochromic compound to be chosen from an even larger class of materials including those which generally will not form a good phase separation image alone. Since many photochromic compounds are relatively expensive, the use of the resin also serves to decrease the overall costs of the imaging layer.

Any suitable photochromic compound may be used in the course of the present invention. Typical organic photochromic compounds include spiropyrans such as

- 1,3,3-trimethyl-6'-nitro-8'-allyl-spiro [(2''H-1'-benzopyran-2,2'-indoline)];
- 1,3,3-trimethyl-5,6'-dinitro-spiro (2'H-1'-benzopyran 2,2'-indoline);
- 1,3,3-trimethyl-7'-nitro-spiro (2'H-1'-benzopyran 2,2'-indoline);
- 3-methyl-6-nitro-spiro-[2H-1-benzopyran-2,2'-(2'H-1'-beta-naphthopyran)];
- 1,3,3-trimethyl-8'-nitro-spiro (2'H-1'-benzopyran-2,2'-indoline);
- 1,3,3-trimethyl-6'-methoxy-8'-nitro-spiro (2'H-1'-benzopyran-2,2'-indoline);
- 1,3,3-trimethyl-7-methoxy-7'-chloro-spiro (2'H-1'-benzopyran-2,2'-indoline);
- 1,3,3-trimethyl-5-chloro-5'-nitro-8' methoxy-spiro [(2'H-1'-benzopyran 2,2'-indoline)];
- 1,3-dimethyl-3-isopropyl-6'-nitro-spiro (2'H-1-benzopyran-2,2'-indoline);
- 1-phenyl-3,3-dimethyl-6'-nitro-8'-methoxy-spiro (2'H-1'-benzopyran-2,2'-indoline);
- 7'-nitro-spiro-xantho-10,2' (2'H-1'-benzobetanaphthopyran)];

3,3'-dimethyl-6'-nitro-spiro (2'H-1'-benzopyran-2,2'-benzothiazole);
 3,3'-dimethyl-6'-nitro-spiro (2'H-1'-benzopyran 2,2'-benzo-oxazole);
 1,3,3-trimethyl-6-nitro-spiro (2'H-1'-benzopyran-2,2'-indoline);
 6'-nitro-8'-methoxy-1,3,3-trimethyl-indolinobenzopyrylospiran;
 6'-nitro-1,3,3-trimethyl-indolinobenzopyrylospiran;
 8'-allyl-1,3,3-trimethylindolinobenzopyrylospiran;
 8'-carbomethoxy-1,3,3-trimethylindolinobenzopyrylospiran;
 8-methoxy-1,3,3-trimethylindolinobenzopyrylospiran;
 6',8'-dinitro-1,3,3-trimethylindolinobenzopyrylospiran;
 7'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;
 8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;
 6',8'-dibromo-1,3,3-trimethylindolinobenzopyrylospiran;
 6'-chloro-8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;
 5-nitro-6'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;
 6'-nitro-8'-fluoro-1,3,3-trimethylindolinobenzopyrylospiran;
 6'-methoxy-8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;
 5'-nitro-8'-methoxy-1,3,3-trimethylindolinobenzopyrylospiran;
 6'-bromo-8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;

Anthrones such as 4,4'-methylanthrone; 4,4'-methoxybi-anthrone; 3-chloro-10-(9'-xanthylidene)-anthrone; 3-methyl - 10 - (9' - xanthylidene - anthrone; 4' - chloro-10-(9'-xanthylidene)-anthrone; and 10'-9'-2'-methyl xanthylidene)-anthrone; sydnone such as N-(3-pyridyl)-sydnone; N-benzylsydnone; N-p-methylbenzyl-sydnone; N-3,4-dimethylbenzyl-sydnone; N-p-chlorobenzylsydnone, N,N'-ethylene-bissydnone; and N,N'-tetramethylenebis-sydnone; anils such as salicylidene aniline; 5-bromo salicylidene - alpha - naphthylamine; salicylidene - m - phenylenediamine; salicylidene-m-phenylenediamine; salicylidene-m-toluidine; salicylidene 3,4-xylylidene; salicylidene-p-anisidine; o-nitrobenzidine-p-aminobiphenyl; o-nitrobenzidine-m-nitroaniline; o-nitrobenzidine-p-phenetidine; salicylidene - p - aminobenzoic acid; p - hydroxy benzidine - p - bromoaniline; p - hydroxy - benzidine 2,4 - xylylidene - 2 - hydroxy - 3 - methoxybenzidine 2,5 - xylylidene; and salicylidene - o - chloroaniline; hydrazones such as the 2,4 - dinitro - phenylhydrazone of 5 - nitrosalicylaldehyde; benzaldehyde beta-naphthyl-hydrazone; benzaldehyde anisylhydrazone; benzaldehyde - m - chloro - phenylhydrazone; benzaldehyde - p - bromophenylhydrazone; cinnamaldehyde phenylhydrazone; cinnamaldehyde beta-naphthylhydrazone; cinnamaldehyde - m - tolylhydrazone; cinnamaldehyde - p - tolylhydrazone; cinnamaldehyde 3,4 - xylylhydrazone; p-dimethylamino benzaldehyde beta-naphthylhydrazone; 2-furaldehyde beta - naphthyl - hydrazone; 1 - phenol - 1-hexen - 3 - one - phenylhydrazone; piperonal anisylhydrazone; piperonal - m - chlorophenylhydrazone; piperonal beta - naphthylhydrazone; piperonal - m - tolylhydrazone; p-tolualdehyde phenylhydrazone; vanillin beta naphthylhydrazone; osazones such as benzil beta-naphthyl-osazone; benzil m - tolylosazone; benzil 2,4 - xylylosazone; 4,4' - dimethoxy benzil beta - naphthyllosazone; 4,4' - dimethoxy benzil phenylosazone; 4,4'-dimethoxy benzil-2,4 - xylylosazone; 3,4,3',4' - bis (methylenedioxy) benzil alpha - naphthyllosazone; 3,4,3',4' - bis (methylenedioxy) benzil 2,4-xylylosazone; semicarbazones such as chalcone semicarbazone; chalcone phenyl semicarbazone; 2-nitro-chalcone semicarbazone; 3-nitrochalcone semicarbazone; cinnamaldehyde semicarbazone; cinnamaldehyde thiosemicarbazone; o-methoxy cinnamaldehyde semicarbazone; o-methoxy cinnamaldehyde thiosemicarbazone; o-methoxy cinnamaldehyde phenylsemicarbazone; 1 - (4 - methoxyphenyl) - 5 - methyl - 1 - hexen - 3 - one - semicarbazone;

1 - (1 - naphthyl) - 1 - hexen - 3 - one - semicarbazone; 1 - phenyl - 1 - penten - 3 - one - semicarbazone; stilbene derivatives such as 4,4'-diformamido-2,2'-stilbene disulfonic acid; 4,4'-diacetamido-2,2'-stilbene disulfonic acid and its sodium, potassium, barium, strontium, calcium, magnesium and lead salts; 4,4'-bis (4-acetamidobenzoyl-eneamido)-2,2'-stilbene disulfonic acid; 4,4'-bis (p-(p-acetamido - benzamido) benzamido) - 2,2' - stilbene disulfonic acid; fulgides (substituted succinic anhydrides) such as alpha - anisyl - gamma - phenyl fulgide; alpha, gamma-dianisyl fulgide; alpha, gamma-dicumyliso fulgide; alpha, gamma-diphenyl fulgide; alpha, gamma-distyryl fulgide; alpha - piperonyl - gamma - phenyl fulgide; tetraphenyl fulgide; amino-camphor compounds such as 3 - (p - dimethyl aminophenylamino) - camphor and 3 - (p - diethylaminophenylamino) - camphor; thio indigo dyes: o-nitrobenzyl derivatives such as 2-(2',4'-dinitrobenzyl) pyridine; 2,4,2' - trinitrodiphenylmethane; 2,4,2', 4',2'',4'' - hexanitro - triphenylmethane; ethyl bis (2,4-dinitrophenyl) acetate; 2 - (2' - nitro - 4' - carboxybenzyl pyridine); 3,3' - dinitro - 4,4' - bis (2 - pyridylmethyl) azoxybenzene; and 4 - (2' - nitro - 4' - cyanobenzyl) pyridine. Typical inorganic photochromic systems are photochromic glasses doped alkaline earth sulfides, such as magnesium sulfide, calcium sulfide, and barium sulfide, doped with manganese; copper halides, such as cuprous chloride; mercuric halides, mercuric cyanates, mercuric thiocyanates and mercuric selenides; the selenocyanides, such as chloro-mercuric selenocyanide; bromo-mercuric selenocyanide, hydrosulpho-mercuric selenocyanide, hydroseleno-mercuric selenocyanide; activated titanium dioxide, bismuth oxalate, lithium amide; and mixtures thereof. The spiropyrans are, however, a preferred class of photochromic materials due to their superior and more sensitive imaging capabilities.

Any suitable thermochromic material may be used in the course of the present invention. Generally, most of the above mentioned photochromic materials will also satisfy the requirements of thermochromism and therefore may be considered both thermochromic and photochromic. In addition to the above listed materials which will satisfy the requirements of both photochromism and thermochromism, any other suitable thermochromic compound may be used. Other thermochromic compounds are diphenylmethylenanthrone; diphenylmethylenexanthene; diphenyl disulfide; p,p'-dibromodiphenyl disulfide; dinaphthyl disulfide (both alpha and beta forms); 4,4'-dicarboxy - 1,1' - dinaphthyl disulfide; 8,8' - dihydroxy-1,1' - dinaphthyl disulfide; 5,5' - dimethyl - 8,8' - dihydroxy - 1,1' - dinaphthyl disulfide; dibenzoyl - 8,8' - dihydroxy - 1,1' - dinaphthyl disulfide; bis (thio - alpha - naphthoyl) - disulfide; 9,9' - dianthryl-disulfide; dibenzthiazolyl-2-disulfide; tetramethylthiuram disulfide; 1-naphthyl phenyl thio-ketone; diphenyl thiocarbonate; methyl 1-dithionaphthoate; 9,10 - di - p - anisylantracene; dimethylfulvene; 3,5-dinitrosalicylic acid; tetracyclone; 4 - triphenyl - 1,2 - quinone; 1,3 - diketo - 2 - phenyl - 5 - bromoindan; o - hydroxy - p,p',p'',o''' - tetramethoxytetraphenylsuccinic acid bis - lactone; 2,2' - diketo - 3,3' diphenyl - 3,3' dicoumaranyl; N,N' - dicyclohexyl - p - xylo - p - quinonediimine; 9 - diazothioxanthene; 1,1' methylenedi - (2 - hydroxy - 5 - phenylacridine); 1 - (4,4 - dimethyl 2,6-dioxocyclohexylmethylene) - 2 - hydroxy - 3,4 - dimethylacridine; 1,1' methylenedi - (2 - hydroxy - 3,4 - dimethylphenazine); triphenylchloromethane ditolyl - alpha - naphthylchloromethane; monocyclopentadienyltitanium dichloride; salicylidene - m - toluidine; salicylidene - o - 4 xylylidene; salicylidene - o - chloroaniline; salicylidene m - chloroaniline; salicylidene - p - chloroaniline; salicylidene - m-aminophenol; salicylidene - p - aminobenzoic acid; salicylidene - alpha - naphthylamine; salicylidene - alpha - naphthylamine; 5 - bromosalicylidene - m - toluidine; 5 - 5' di-

bromodisalicylidene - p - phenylenediamine; 3 - nitrosalicylidene - m - toluidine; o - methoxybenzylidene - p - aminobenzoic acid; p - hydroxybenzylidene - m - toluidine; 2 - hydroxy - 5 - methyl - benzylidene - m - toluidine; 2 - hydroxy - α - naphthylidene - m - toluidine; derivatives of 2 - hydroxy - α - naphthylidene compounds, such as 2 - hydroxy - α - naphthylidene - chloroaniline; 2 - hydroxy - α - naphthylidene bromoaniline, 2 - hydroxy - α - naphthylidene anisidine, 2 - hydroxy - α - naphthylidene amino benzoic acid, 2 - hydroxy - α - naphthylidene aminophenol, 2 - hydroxy - α - naphthylidene - 4 - xylidine and mixtures thereof. When selecting a thermochromic compound it is preferred that one which satisfies the requirement of both photochromism and thermochromism be chosen in order to lend flexibility to the present imaging system.

As mentioned above, since many of the photochromic and thermochromic compounds are relatively expensive as compared with suitable resin binders which may be used in combination therewith, the energy sensitive materials usually will be dissolved in or dispersed in at least one of such resinous compositions. Typical resins include Staybelite Ester 10 and Pentalyn H, glycerol and pentaerythritol esters, respectively, of partially (50%) hydrogenated rosin commercially available from Hercules Powder Company; Velsicol EL-11, a terpolymer of styrene, indene and isoprene commercially available from Velsicol Chemical Company; polyalpha-methyl styrene; Piccolyte S-70 and S-100, polyterpene resins made predominantly from beta pinene, commercially available from Pennsylvania Industrial Chemical Company and having ring and ball melting points of 70° C. and 190° C. respectively; Piccopale 70 SF and 85, nonreactive olefin diene resins, commercially available from Pennsylvania Industrial Chemical Company, having melting points of 70° C. and 85° C. and molecular weights of about 800 and about 100 respectively; Piccodiene 2212, a styrene-butadiene resin commercially available from Pennsylvania Industrial Chemical Company; Piccolastic A-75, D-100 and E-100, polystyrene resins having melting points of about 75° C., 100° C., and 100° C. respectively, commercially available from Pennsylvania Industrial Chemical Company; Neville R-21 and R-9 and Nevillac Hard coumarone-indene resins commercially available from the Neville Chemical Company; Amberol ST 137X, an unreactive and unmodified phenol formaldehyde resin commercially available from Rohm & Haas; ethyl cellulose; ethyl hydroxy cellulose; nitrocellulose; ethyl acrylate polymers; methyl acrylate polymers; methyl methacrylate polymers; Carboset XH-1, an acrylic acid polymer commercially available from B. F. Goodrich Company; Pliolite AC, a styrene-acrylate copolymer and Pliolite VTAC, a vinyl toluene-acrylate copolymer, commercially available from Goodyear Tire and Rubber Company; Neolyn 23, alkyd resin available from Hercules Powder Company; chlorinated rubber; paraffin wax; polycarbonates, polyurethanes; epoxy compounds; polyvinylchloride; polyvinylidene chloride; polyvinylbutyral; shellac; amine-formaldehydes; polyvinylacetals; silicones; phenoxy resins; polyvinyl fluorides and mixtures and copolymers thereof.

Any suitable material may be used as the support base for the plate of the present invention. Typical such bases are zinc, aluminum, glass, brass, polyethylene, polypropylene, Mylar, the latter being a polyethylene terephthalate resin available from E. I. du Pont de Nemours & Company, thermosetting resins, such as urea-formaldehyde and epoxy resins, and ordinary bond paper. The selection of the supporting substrate is based upon the desired use of the resulting lithographic plates, such as to give the plate additional strength or to provide added flexibility in situations requiring it. For purposes of this invention, polyethylene, polypropylene, Mylar, and ordinary bond paper are generally preferred as the support base, due to their inherent flexibility properties which

make their use particularly adaptable to a continuous, reusable cylindrical imaging system.

Any suitable aqueous based developer which will distinguish the areas of the respective materials which have been exposed and altered by radiant energy from those which have not been so exposed may be used in the process of this invention, said developers having viscosities ranging from one to one-hundred thousand centipoises, preferably, five thousand to twenty-thousand centipoises, inasmuch as optimum results are obtained within this preferred range. When colorless it is expedient to include therewith a suitable aqueous based ink. By the expression aqueous based developer is meant a developer comprising a major proportion of water and a minor proportion of another solvent, such as alcohol. Included within the scope of this expression are those materials which also contain a colorant for recognition purposes such as an aqueous based ink. Typical developer components are vinyl resins such as carboxy vinyl polymers, polyvinylpyrrolidones, methylvinylether-maleic anhydride interpolymers, polyvinyl alcohols, cellulose, such as sodium carboxymethyl cellulose, hydroxypropylmethyl cellulose, hydroxyethyl cellulose, methyl cellulose, cellulose derivatives such as esters and ethers thereof water, starch, alkali soluble proteins, casein, gelatin, acrylate salts such as ammonium polyacrylate and sodium polyacrylate, polyacrylate acid, polymethylacrylic acid and copolymers thereof and the alkali and ammonia salts of alginic acid and mixtures thereof. For purposes of this invention, optimum results were obtained with the vinyl resins inasmuch as the preferred viscosity levels could be readily reached at low concentrations and these resins do not dissolve the photochromic materials.

Any conventional and/or suitable aqueous based ink may be used in the process of the present invention, either alone or in conjunction with the above developer components. This includes both the inks containing a water soluble dye substances and the pigmented inks. Typical dye substances are Methylene Blue, available from Eastman Kodak Company, Brilliant Yellow, commercially available from Harlaco Chemical Company, potassium permanganate, ferric chloride, cobaltous chloride, commercially available from Dayco Laboratories and Methylene Violet, Rose Bengal, and Quinoline Yellow, the latter three commercially available from Allied Chemical Company. Typical pigments are carbon black, titanium dioxide, white lead, zinc oxide, zinc sulfide, iron oxide, chromium oxide, lead chromate, zinc chromate, cadmium yellow, cadmium red, red lead, antimony dioxide, magnesium silicate, calcium carbonate, calcium silicate, phthalocyanines, benzidines, dinitranilines, naphthols, and toluidines. The pigmented inks are preferred inasmuch as the final reproduced prints are longer lasting and possess optimum optical density characteristics. Specifically preferred among the pigments is carbon black because it is more suitable for most printing operations.

It is also possible to use simple compounds or colored water soluble complexes, such as those which are formed by a certain number of transition elements. Typical examples are the known cuprous tetramine complex, the chromium salts such as chromium sulfate, chrome and potassium alum, potassium chromate, the aquo- and acido-complexes of trivalent chromium, certain ferric compounds such as ferric thiocyanate, and the thiocyanato-ferrates, the prussic compounds of iron, the acetato-ferric salts, iron-ammonium citrate, the thiocyanate and the thiocyanato-cobaltates of bivalent cobalt, cobalt sulfate and chloride, the chlorides and sulfates of bivalent nickel, the copper tartrates complex, copper-glycine, the insoluble compounds formed between iron and gallic acid, the complexes of ferrous salts with α -picolinic acid and analogous compounds which contain one atom of nitrogen cyclically combined in the alpha position in relation to a carboxyl group, iron or bivalent cobalt complexes with the α -dioximes such as dimethyl-glyoxime, the ferric

complexes with salicylic acid, compounds formed between titanium and iron salts and chromotropic acid.

As mentioned above, the photochromic materials are basically light-sensitive dyes which exhibit reversible spectral changes upon exposure to radiant energy in the visible or near visible portions of the electromagnetic spectrum. The normal state of photochromic materials is the transparent or colorless state. If exposed to near ultraviolet radiation, i.e., from about 3,000 to 4,000 angstrom units, the colorless state of the photochromic material will assume the colored or opaque state in the exposed areas. If the original colorless state is again desired, the opaque state may be reversed by exposure to visible light of the proper wavelength distribution, from about 5,000 to 7500 angstrom units. Thus, a high degree of system flexibility is available in that the photochromic materials can be changed in either direction from an unexcited state to an excited state, or vice versa, thereby allowing for the preparation of an imaging master either by direct positive imaging or by positive-to-negative imaging. Similarly, the thermochromic materials will undergo comparable changes as experienced by the photochromic materials when exposed to heat and revert to their original status upon cooling, thereby also exhibiting reversible properties. The thermal energy is normally provided in the form of heat generally derived from electromagnetic radiation in the infrared or near infrared portion of the electromagnetic spectrum. The exposure time to the actinic energy is determined by the particular energy sensitive composition in use and the light intensity. For the purposes of the present invention this time will generally be within the range of from 10 to about 120 seconds, however, in the case of the photochromic materials an optimum range generally will fall within a 10 to 60 second time span.

As previously stated, the particular energy sensitive composition may range from about 100% to about 1% by weight of the respective material whether it be a photochromic or a thermochromic composition. When present in an amount less than 100%, the remainder of the composition comprises a resinous binder material. The thickness of the energy sensitive coating composition may range anywhere from about 0.5 to about 50 microns. However, for maximum efficiency and expediency in handling it is desirable and preferred that the photochromic or thermochromic material be maintained at a thickness of about 2 to about 30 microns.

The invention is further illustrated in the accompanying drawings in which:

FIGURE 1 is a magnified sectional view of an imaging member of the present invention selectively exposed to electromagnetic radiation.

FIGURE 2 is a magnified sectional view of the exposed plate of FIGURE 1 illustrating image development.

FIGURE 3 illustrates a side sectional view of an exemplary continuous imaging apparatus of the present invention.

Referring now to FIG. 1, there is seen an imaging support member generally designated 1 made up of a support base 2 having coated on the surface thereof a photochromic light sensitive composition 3. The radiation sensitive coating is applied to the surface of the support substrate by either flow coating, dipping, spraying, with a doctor blade, or by any other suitable coating operation. Upon selective exposure of the photochromic composition 3 to radiant energy in the ultraviolet range of the electromagnetic spectrum, designated for illustrative purposes by lines 4, there is detected a visible change 5 in the photochromic layer 3 thereby producing a visible image on the surface of the support member.

FIG. 2 illustrates the development technique whereby an aqueous based developer 6 from source 10 is applied by means of roller 7 to the imaged surface of the photochromic plate 1. The developer 6 is thereby held in imagewise configuration 9 to the surface altered areas 5 of the plate.

In FIG. 3, there is illustrated a simple exemplary apparatus for carrying out the imaging technique of the present invention. In this apparatus, there is seen a rotary photochromic glass drum 15 made up of an aluminum cylinder 16 with a coating of photochromic glass 17 thereon. The photochromic glasses which may be used in the course of the present invention are of the nature disclosed in the publication entitled "Science," volume 144, page 150, the article "Photochromic Silicate Glasses Sensitized by Silver Halides" by W. H. Armistead and S. D. Stookey. The cylinder, when in operation, is generally rotated at a uniform velocity by drive means 40 in the direction indicated by the arrow so that the surface of the drum passes beneath a scanning imaging mechanism 19 or other means for exposing the photochromic drum to the image to be reproduced. Following exposure, the imaged surface of the drum moves past the developing unit generally designated 20 consisting of a gravure applicator 21, doctor blade 22, and trough 23 containing the aqueous ink developer 24. Upon contact with the gravure applicator, the aqueous based ink is deposited upon the surface of the exposed photochromic drum in an imagewise configuration, corresponding to the exposed areas of the light sensitive surface.

After passing the development unit 20 the photochromic cylinder or drum bearing a developed image 30 continues around so as to contact copy web 25 which is fed from supply roll 26 and passed up against the drum surface by transfer roller 27 and which travels at the same speed as the periphery of the drum. Thus, the developed image 30 is transferred upon contact to the surface of the copy web. The transferred image 30a is then rewound on take-up roller 31 while allowing adequate time for the transferred image to dry. The drum surface continues around to pass beneath brush 35 which removes any remnants of the developer from the drum.

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.

Example I

Four grams of 6'-nitro-1,3,3-trimethyl-indolinobenzopyrylospiran and 8 grams of Amberol ST-137X resin (described above) are dissolved in about 88 grams of toluene. This solution is dip coated in the dark to a thickness of about 2 microns on an aluminum plate and air dried. The dried aluminum coated plate is then exposed for 10 seconds to an image transparency with a 9-watt fluorescent light available from the Eastern Corporation under the trade name "black light" using a filter which passes about a 10 angstrom bandwidth centered on 3660 angstroms. After exposure, a maroon colored image is seen to form on the surface of the film. The image on the surface of the photochromic material is then contacted with a water base washable blue ink by means of a gravure roller and the final print made by contacting the resulting master plate with a copy sheet. Images of good density and good resolution are obtained.

Examples II and III

The procedure of Example I is repeated with the exception that in Example II 4 grams of the resin and ½ gram of the 6'-nitro-1,3,3-trimethylindolinobenzopyrylospiran are used in the coating solution while in Example III the ratio is 1 gram of resin to 2 grams of the same photochromic spiran compound. Each of these produce about equal results with those produced by Example I.

Examples IV-XV

The procedure of Example I is followed exactly with the exception that the following resins are substituted for the Amberol resin of Example I in Examples IV-XV, respectively; Piccolyte S-70, Piccolyte S-100, Piccopale

70SF, Piccopale 85, Piccodiene 2212, alphamethylstyrene polymer, Staybelite Ester 10, Piccolastic D-100, Piccolastic E-100, Neville R-9, Neville R-21, and Nevillac Hard. All produce about the same results as Example I.

Examples XVI-XIX

In Examples XVI and XVII, the procedure of Example I is repeated except that the photochromic compound employed is 3-N-pyridyl sydnone in Example XVI and phenyl sydnone in Example XVII.

In Examples XVIII and XIX, the following photochromic compounds are employed: In Example XVIII, the 2,4-dinitrophenyl-hydrazone of 5-nitro-salicylaldehyde is employed; and, in Example XIX, 3-N-pyridyl salicylidene is employed. In these two examples the procedure of Example I is followed except that the same filter is employed with a 100 watt light source for a 120 second exposure. In all instances, the images formed are about equal in quality with the one produced by the procedure of Example I.

EXAMPLE XX

The procedure of Example I is repeated exactly except that the coated film is first uniformly exposed to the 3660 angstrom light source until it achieves a deep maroon color. Following this exposure a transparency to be reproduced is overlaid on the imaging layer and exposed to a source of yellow light for one hour which serves to bleach or reconvert the excited colored form of the photochromic compound back to its unexcited, colorless form in exposed areas. The liquid development and transfer steps of Example I are then carried out resulting in a photographic reversal of the original transparency.

EXAMPLES XXI-XXVII

The procedure of Example I is followed with the exception that the following photochromic compounds are used respectively, in Examples XXI-XXVII in place of the spiropyran photochromic compound of Example I: 2,4-dinitro-phenylhydrazone; benzil betanaphthylsazone; 2-nitrochalcone semicarbazone; alpha, gamma-diphenyl fulgide; 4,4'-diformamido-2,2'-stilbene disulfonic acid; 3-(p-dimethylaminophenylamino)-camphor; and 2-(2',4'-dinitrobenzyl) pyridine. These produce essentially the same results as Example I.

EXAMPLES XXVIII-XXXIII

The procedure of Example I is repeated except that the following resins are substituted for the amberol resin in Examples XXVIII-XXXIII, respectively; ethyl hydroxy cellulose; ethyl cellulose; nitrocellulose; polyethylacrylate; polymethylacrylate and polymethylmethacrylate. All produce about the same results as Example I.

EXAMPLE XXXIV

Four grams of N-methylacriphenyl-8'-methoxy-benzospiropyran and 8 grams of Amberol ST-137X resin are dissolved in about 88 grams of toluene. This solution is dip coated in the dark to a thickness of about 2 microns on an aluminum plate and air dried. The dried thermochromic layer is then exposed to a line copy material containing a pigmented image by an infrared light source of a voltage of about 1350 volts, at a current of about 8 amps for about 120 seconds. The image areas absorb the infrared radiation and are heated to a temperature exceeding about 165° F. As a result of the heat which is transferred by both radiation and conduction in the image areas to the thermochromic sheet, the latter undergoes a color change in an imagewise manner. The resulting imagewise pattern in the thermochromic sheet is contacted with a water base ink with the ink adhering to the exposed areas of the plate. Upon contact with a copy sheet, the developed image is transferred thereto from the thermochromic master plate. Images of good quality and resolution are obtained.

EXAMPLES XXXV-XXXVIII

In the following examples, the procedure of Example XXXIV is repeated except that the following thermochromic compounds are employed: In Example XXXV, benzo-beta-naphthol-spiropyran is used; in Example XXXVI, 1,3,3-trimethylindolino-betanaphthospiropyran is employed; in Example XXXVII, beta naphthothioxanthospiropyran is substituted for the thermochromic compound of Example XXXIV; in Example XXXVIII, xantho-beta-naphthospiropyran is used. In all instances, the resulting developed images formed are about equal in quality with that produced by the procedure of Example XXXIV.

Although the present examples were very 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 plate of the present invention, other steps or modifications may be used, if desirable. For example, the imaging process may be carried out by a technique whereby a pattern of photochromic or thermochromic material is coated on a hydrophilic surface. The pattern of the energy sensitive material is so designed so as to act as a gate for ink flow to the hydrophilic substrate in those areas exposed to electromagnetic energy. In addition, other materials may be incorporated in the developer and the photochromic and thermochromic plates which will enhance, synergize, or otherwise desirably effect the properties of these materials for the present use. For example, in the case of the thermochromics melting point depressants may be added whereas in the case of the photochromic materials dye sensitizing agents may be incorporated therein.

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

What is claimed is:

1. A method of making multiple copies from a lithographic master which comprises:

- (a) coating on the surface of a support substrate a photosensitive composition selected from the group consisting of thermochromic and photochromic materials having a wettability property which can be altered upon exposure to radiant energy;
- (b) selectively exposing said photosensitive composition to an actinic energy source so as to alter said wettability property in the form of an image pattern on the surface of said composition;
- (c) contacting the image surface of said composition with a water base ink, said ink adhering to said image pattern;
- (d) contacting said inked surface with a copy sheet in such a manner that a print of the image is transferred to said copy sheet; and
- (e) repeating steps (c) and (d) until the desired copies are produced.

2. The process as defined in claim 1 wherein said photosensitive composition is a photochromic material comprising 6'-nitro-1,3,3-trimethyl - indolinobenzopyrilo-spiyan.

3. The process as defined in claim 1 wherein said photosensitive composition is a thermochromic material comprising diphenylmethylenanthrone.

4. A method of copying from a lithographic master which comprises bonding to the surface of a support substrate a photosensitive composition, said composition being selected from the group consisting of photochromic and thermochromic materials having a wettability property which may be altered upon exposure to radiant energy, exposing said composition to an energy source in such a manner so as to alter said wettability property in the form of an imagewise pattern, contacting the imaged surface with an aqueous based developer, said developer adhering to said image pattern and contacting said developed

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surface with a copy sheet so as to transfer an imprint of the image pattern thereto.

5. The process as defined in claim 4 wherein said photosensitive composition comprises a thermochromic material and said energy source comprises radiation in the infrared portion of the electromagnetic radiation spectrum.

6. The process as defined in claim 5 wherein said thermochromic material comprises diphenylmethylenethrone.

7. The process as disclosed in claim 4 wherein said photosensitive composition comprises a photochromic material and said energy source comprises radiation in the near visible portion of the electromagnetic radiation spectrum.

8. The process as defined in claim 7 wherein said photochromic material comprises 6'-nitro-1,3,3-trimethyl-indolino-benzopyrilo-spyran.

9. The process as disclosed in claim 4 further including repeating the development and transfer steps at least once.

10. A lithographic printing process which comprises:

(a) coating the surface of a support substrate with a photochromic composition, said composition having a wettability property which may be altered upon exposure to electromagnetic radiation,

(b) selectively exposing said photochromic composition to said electromagnetic radiation so as to alter said wettability property in an imagewise configuration,

(c) developing the imaged surface of said photochromic composition with an aqueous base developer, said developer adhering to the surface of said composition in conformity with said image,

(d) contacting the developed surface with a copy sheet in such a manner so as to transfer a print of said image to said copy sheet; and

(e) repeating steps (c) and (d) at least once.

11. The process as defined in claim 10 wherein said photochromic material is initially in a lower unexcited state and said electromagnetic radiation is of sufficient energy to convert the exposed areas of said photochromic material to a higher excited photochromic state.

12. The process as defined in claim 10 wherein said photochromic material is initially in a higher excited state and said electromagnetic radiation is of sufficient energy to convert the exposed areas of said photochromic material to a lower unexcited photochromic state.

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13. The process as defined in claim 10 wherein said photochromic material comprises 6'-nitro-1,3,3-trimethyl-indolino-benzopyrilo-spyran.

14. A lithographic printing process which comprises:

(a) coating the surface of a support substrate with a thermochromic composition, said composition having a wettability property which may be altered upon exposure to electromagnetic radiation,

(b) selectively exposing said thermochromic composition to said electromagnetic radiation so as to alter said wettability property in an imagewise configuration,

(c) developing the imaged surface of said thermochromic composition with an aqueous base developer, said developer adhering to the surface of said composition in conformity with said image,

(d) contacting the developed surface with a copy sheet so as to transfer a print of said developed image to said copy sheet; and

(e) repeating steps (c) and (d) at least once.

15. The process as defined in claim 14 wherein said thermochromic material is initially in a lower unexcited state and said thermal radiation is of sufficient energy content to convert the exposed areas of said thermochromic material to a higher excited thermochromic state.

16. The process as defined in claim 14 wherein said thermochromic material is initially in a higher excited state and said thermal radiation is of sufficient energy to convert the exposed areas of said thermochromic material to a lower unexcited thermochromic state.

17. The process as defined in claim 14 wherein said thermochromic material comprises diphenylmethylenethrone.

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