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(54) **INKJET-IMAGEABLE LITHOGRAPHIC PRINTING MEMBERS AND METHODS OF PREPARING AND IMAGING THEM**

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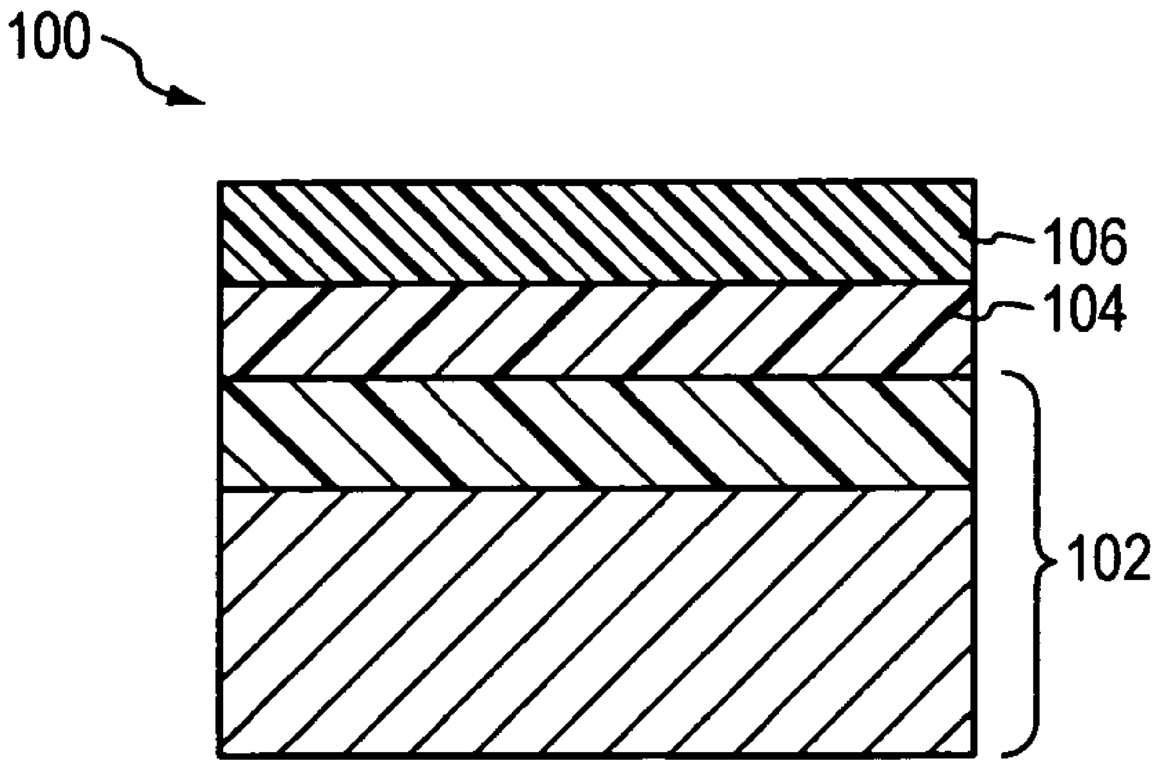
(57) **ABSTRACT**

Lithographic printing plates are imaged using an inkjet printer to imagewise apply a chemical agent onto the plate surface. The chemical causes a change that facilitates lithographic printing.



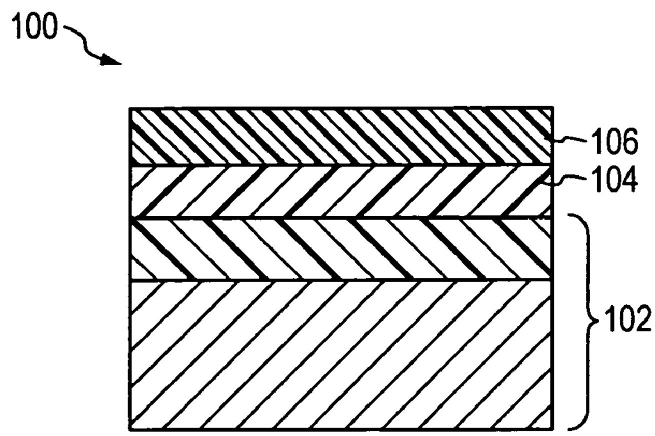



FIG. 1A

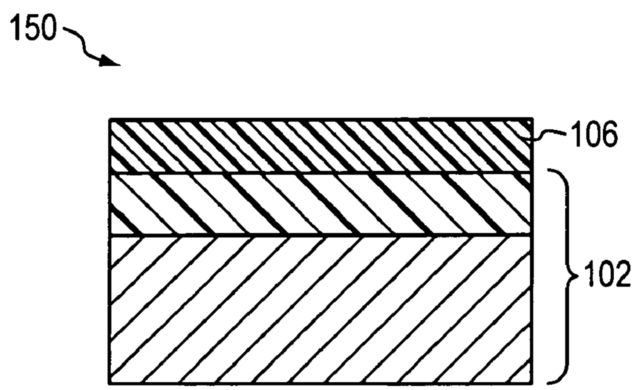



FIG. 1B

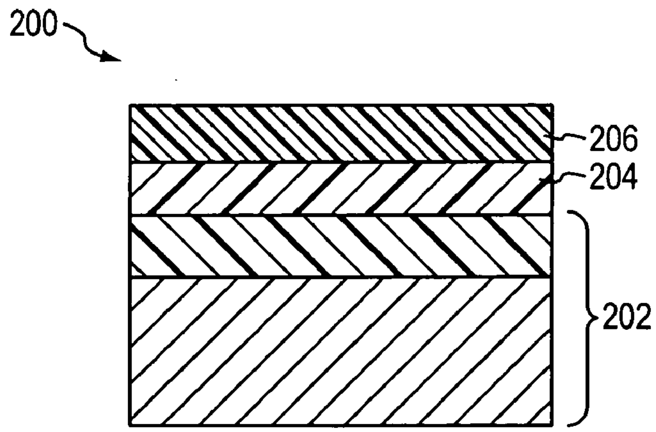



FIG. 2

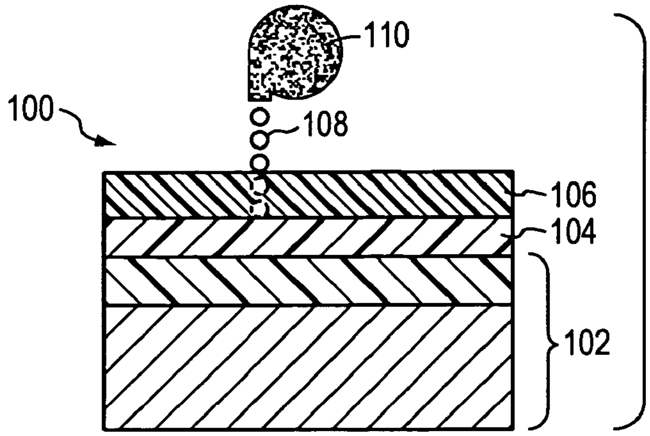



FIG. 3A

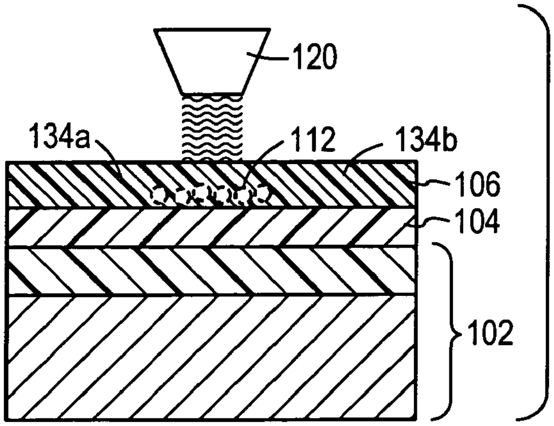



FIG. 3B

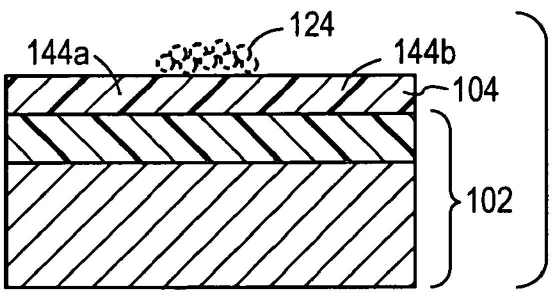



FIG. 3C

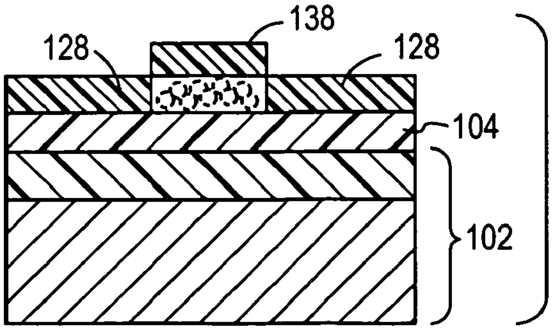



FIG. 3D

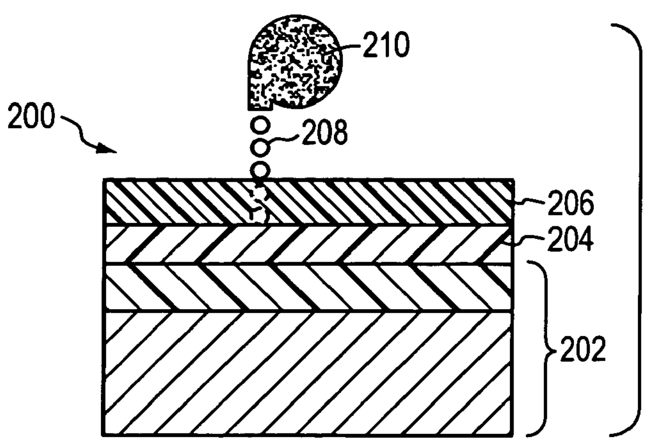



FIG. 4A

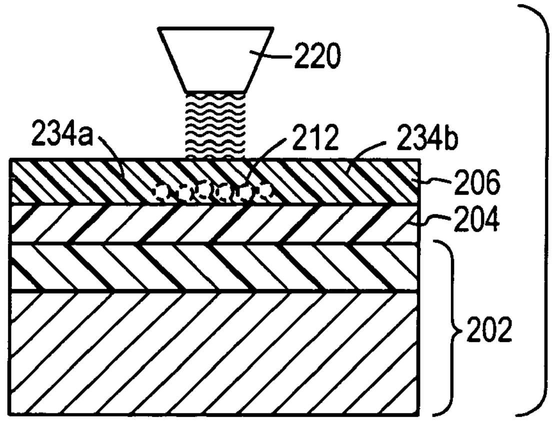



FIG. 4B

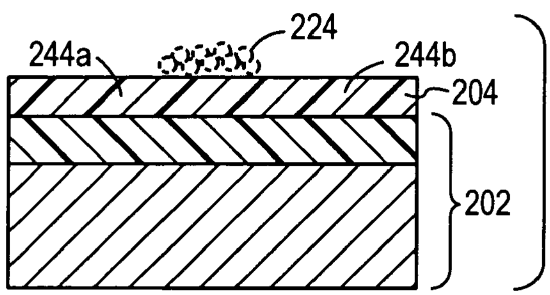



FIG. 4C

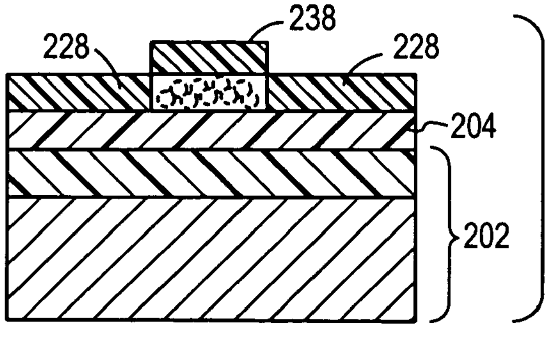



FIG. 4D

# INKJET-IMAGEABLE LITHOGRAPHIC PRINTING MEMBERS AND METHODS OF PREPARING AND IMAGING THEM

## CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefits of U.S. Provisional Application Ser. No. 60/617,695, filed on Oct. 12, 2004, the entire disclosure of which is hereby incorporated by reference.

## FIELD OF THE INVENTION

[0002] The present invention relates in general to lithography, and more particularly to lithographic printing members suitable for inkjet imaging.

## BACKGROUND OF THE INVENTION

[0003] In offset lithography, a printable image is present on a printing member as a pattern of ink-accepting (oleophilic) and ink-rejecting (oleophobic) surface areas. Once applied to these areas, ink can be efficiently transferred to a recording medium in the imagewise pattern with substantial fidelity. Dry printing systems utilize printing members whose ink-repellent portions are sufficiently phobic to ink as to permit its direct application. In a wet lithographic system, the non-image areas are hydrophilic, and the necessary ink-repellency is provided by an initial application of a dampening fluid to the plate prior to inking. The dampening fluid prevents ink from adhering to the non-image areas, but does not affect the oleophilic character of the image areas. Ink applied uniformly to the printing member is transferred to the recording medium only in the imagewise pattern. Typically, the printing member first makes contact with a compliant intermediate surface called a blanket cylinder which, in turn, applies the image to the paper or other recording medium. In typical sheet-fed press systems, the recording medium is pinned to an impression cylinder, which brings it into contact with the blanket cylinder.

[0004] Lithographic plates can be fabricated in various ways, ranging from traditional manual techniques involving photoexposure and chemical development to automated procedures involving computer control. Computer-to-plate systems can utilize pulses of electromagnetic radiation, produced by one or more laser or non-laser sources, to create physical or chemical changes at selected points of sensitized plate blanks (which, depending on the system, may be used immediately or following conventional photodevelopment); ink-jet equipment used to selectively deposit ink-repellent or ink-accepting spots on plate blanks; or spark-discharge equipment, in which an electrode in contact with or spaced close to a plate blank produces electrical sparks to alter the characteristics of certain areas on a printing surface, thereby creating "dots" which collectively form a desired image. To circumvent the cumbersome photographic development, plate-mounting, and plate-registration operations that typify traditional printing technologies, practitioners have developed electronic alternatives that store the imagewise pattern in digital form and impress the pattern directly onto the plate.

[0005] Digital imaging of printing plates by inkjet printing is currently widely investigated; see, e.g., U.S. Pat. Nos. 6,526,886 and 6,691,618. The '618 patent, for example, discloses a method of imaging a lithographic printing plate having an alkaline-soluble polymeric coating with a pH-elevating agent. The need to use alkaline solutions to develop these plates, however, poses environmental and safety problems. It would be desirable to have inkjet-imageable lithographic printing plates that can be solely developed by water, or which do not require a development step.

## SUMMARY OF THE INVENTION

[0006] In general, a printing member in accordance with the invention includes a substrate, an optional intermediate layer, and a reactive top layer thereover. The top layer is capable of absorbing an inkjet imaging fluid that reacts with the top layer to alter at least one property thereof, e.g., lithographic affinity and/or solubility. The optional intermediate layer can be hydrophilic or oleophilic, and may be crosslinked to improve wear resistance. An advantage of this approach is structural and process simplicity, since imaging is accomplished by chemical modification of an existing layer. There is no need for exposure to an energy source.

[0007] Accordingly, in a first aspect, the invention provides a lithographic printing member having a water-soluble top layer having a first lithographic affinity, an optional crosslinked intermediate layer preferably having a similar affinity, and a substrate thereunder, as well as methods of imaging such a printing member. The top layer is chemically reactive with an imaging fluid. When the imaging fluid is applied to the top layer, at least a portion of the top layer undergoes a phase change, transforming it from a water-soluble state to a water-insoluble state having an opposite lithographic affinity. For example, in one embodiment, the lithographic printing member has a water-soluble and hydrophilic top layer, an optional crosslinked hydrophilic intermediate layer, and a substrate thereunder. When the imaging fluid is applied to the top layer, at least a portion of the top layer is transformed from a water-soluble and hydrophilic state to a water-insoluble and oleophilic state.

[0008] To provide a lithographic image, an imaging fluid is dispensed onto the top layer of the printing member in an imagewise pattern. The imaging fluid chemically reacts with the top layer and transforms it from a water-soluble to a water-insoluble state having an opposite lithographic affinity. The imaged printing member is then subjected to a solvent, such as an aqueous fluid, to dissolve non-image, i.e., water-soluble, portions of the top layer. Finally, the soluble portions of the top layer are removed, leaving an imagewise lithographic pattern on the printing member ready for inking.

[0009] In one embodiment, the top layer contains a water-soluble polymer. Suitable water-soluble polymers include, but are not limited to, polyvinyl phosphonic acid, polyvinyl alcohol comprising amine moieties, and other polymers comprising at least one of an amine moiety, a carboxylic acid moiety, a sulfonic acid moiety, and a phosphonic acid moiety.

[0010] An imaging fluid containing an esterifying agent can insolubilize and oleophilize the water-soluble polymeric top layer. Alternatively, the top layer can be insolubilize and oleophilize by an imaging fluid containing an alkylating agent. Suitable compositions for the imaging fluid include, but are not limited to, tetramethylammonium hydroxide, phenyltrimethylammonium hydroxide, trimethylsulfonium hydroxide, trimethylsulfoxonium hydroxide, 1,3-(bistripropylammonium)xylene hydroxide, and polymers comprising quaternary ammonium salts.

[0011] In a second aspect, the invention provides a lithographic printing member having a water-dispersible top layer, a crosslinked intermediate layer having a lithographic affinity opposite that of the top layer, and a substrate thereunder, as well as methods of imaging such a printing member. The top layer becomes crosslinked and water-insoluble when reacted with a suitable imaging fluid. For example, in one embodiment, the top layer is water-dispersible and oleophilic and the crosslinked intermediate layer is hydrophilic.

[0012] To provide a lithographic image, the imaging fluid is dispensed onto the top layer of the printing member in an imagewise pattern. The imaging fluid chemically reacts with the top layer, thereby crosslinking and insolubilizing this layer. The imaged printing member is then subjected to an aqueous fluid to dissolve non-image, i.e., water-dispersible, portions of the top layer. Finally, the water-dispersible portions of the top layer are removed, leaving an imagewise lithographic pattern on the printing member ready for inking.

[0013] In one embodiment, the water-dispersible top layer can be, for example, an epoxy-resin dispersion coating. Suitable compositions for the imaging fluid include various crosslinking agents that are chemically reactive with epoxide functionalities. Preferred crosslinking agents include, but are not limited to, multifunctional amines and tetra-carboxylic acids.

[0014] In some embodiments, the top layer is hydrophilic and the intermediate layer and/or substrate is oleophilic. For example, the top layer may be or comprise a dispersion of a surface-grafted, hydrophilic polyurethane that reacts with an oxazoline; a dispersion of a polyacrylic acid copolymer that has reacted with a polyfunctional amine; or a core/shell latex with a hydrophilic shell crosslinked with gluteraldehyde. Any of these systems may be coated onto typical oleophilic polymers such as an oleophilic polyurethane, acrylic, styrene-acrylic, phenoxy resin or the like. In some versions, it may be advantageous to employ an intermediate adhesion layer between the hydrophilic top coat and the oleophilic undercoat.

[0015] It should be stressed that, as used herein, the term "plate" or "member" refers to any type of printing member or surface capable of recording an image defined by regions exhibiting differential affinities for ink and/or fountain solution. Suitable configurations include the traditional planar or curved lithographic plates that are mounted on the plate cylinder of a printing press, but can also include seamless cylinders (e.g., the roll surface of a plate cylinder), an endless belt, or other arrangement.

[0016] Furthermore, the term "hydrophilic" is used in the printing sense to connote a surface affinity for a fluid which prevents ink from adhering thereto. Such fluids include water for conventional ink systems, aqueous and non-aqueous dampening liquids, and the non-ink phase of single-fluid ink systems. Thus a hydrophilic surface in accordance herewith exhibits preferential affinity for any of these materials relative to oil-based materials.

[0017] The term "fountain solution," as used herein, pertains to a solution used to clean or remove the water-soluble portions of the imaged printing members of the methods of this invention and may be water, combinations of at least 90% water and 10% or less organic solvents and additives such as alcohols, surfactants, and glycols, and buffered or salt-containing neutral or nearly neutral water solutions. The term "fountain solution," as used herein, does not include alkaline aqueous solutions with a pH of greater than about 10, acidic aqueous solutions with a pH of less than about 3.5, or organic solvents without at least 90% by weight of water present.

[0018] Also, as used herein, the term "water-soluble" refers to a material that can form a greater than 1% solution in water or a mixture of a water-miscible solvent such as alcohol and water wherein the mixture is more than 50% water.

[0019] As one of skill in the art will appreciate, features of one embodiment and aspect of the invention are applicable to other embodiments and aspects of the invention. The above-discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description and drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The foregoing discussion will be understood more readily from the following detailed description of the invention when taken in conjunction with the accompanying drawings.

[0021] **FIG. 1A** is an enlarged sectional view of an embodiment of a negative-working printing member according to the invention that contains a substrate, a crosslinked hydrophilic intermediate layer, and a water-soluble hydrophilic top layer.

[0022] **FIG. 1B** is an enlarged sectional view of an embodiment of a negative-working printing member according to the invention that contains a substrate and a water-soluble hydrophilic top layer.

[0023] **FIG. 2** is an enlarged sectional view of an embodiment of a negative-working printing member according to the invention that contains substrate, a crosslinked hydrophilic intermediate layer, and a water-dispersible oleophilic top layer.

[0024] **FIGS. 3A-3D** are enlarged sectional views of the negative-working printing member of **FIG. 1** illustrating an imaging mechanism according to the invention.

[0025] **FIGS. 4A-4D** are enlarged sectional views of the negative-working printing member of **FIG. 2** illustrating an imaging mechanism according to the invention.

[0026] The drawings and elements thereof may not be drawn to scale.

## DETAILED DESCRIPTION OF THE INVENTION

1. Imaging Apparatus

[0027] An imaging apparatus suitable for use in conjunction with the present printing members includes at least an inkjet printer. To facilitate accurate imaging of the printing members according to the invention, the paper-handling or substrate-handling subsystem of the inkjet printer should have a short, straight paper path. A printing plate is generally stiffer and heavier than the paper or media typically used in commercially available inkjet printers. If the construction of the printer requires the printing plate to be bent before or after it is presented to the imaging print head, then the movement of the printing plate through the printer may not be as accurate as the media for which the printer was designed. Printers such as the EPSON STYLUS COLOR 3000 (available from Epson America, Inc., Long Beach, Calif.) have a suitably short, straight paper path. A platen is preferably placed at the entrance to the paper feed mechanism. The platen may have a registration guide rail to support the plate as it is pulled into the printer by the feed mechanism, facilitating the accurate transport of the plate under the imaging print head.

**[0028]** The imaging apparatus may further include a developing processor for embodiments where off-press development of the imaged plate is envisioned. U.S. Pat. No. 6,691,618, for example, describes a suitable developing processor. The development process may involve conveying the imaged plate through a series of stations, which may include a hot air dryer, a pre-heat oven, a development station, a rinse station, and a post-bake oven. The plate is ready to be used on press after this off-press developing step.

**[0029]** In other embodiments, the imaged plate can be developed on-press. In these embodiments, after imaging of the printing member, no conventional development of the latent image is required. Instead, the plate is first heated in an oven to dry the image and, typically, to complete the reaction with the imaging fluid. Second, the plate is mounted on the plate cylinder of a conventional offset lithographic press. Third, the latent image is developed by operating the press such that the plate cylinder is rotated and the working fluids of the press, i.e., the press ink and fountain solution, are applied to the plate. The plate is then ready to be used to print images on paper or other media by the normal operation of the press.

2. Inkjet Printing Process

**[0030]** Inkjet printing involves projecting tiny drops of ink fluid directly onto the plate surface without physical contact between the inkjet printer and the plate. The inkjet printer stores electrical data corresponding to the image to be printed (specifically, the image or background area, depending on whether the plate is positive-working or negative-working), and controls a mechanism for ejecting ink droplets imagewise onto the plate. Printing is performed by moving the print head across the plate or vice versa.

**[0031]** There are generally two mechanisms that commercially available inkjet printers utilize to control how ink droplets are jetted. In continuous inkjet printing, the print head propels a continuous stream of ink through a nozzle. This stream is broken down into identical droplets, which are then selectively charged. Depending on the construction of the printer, either the charged or the uncharged droplets are deflected and guided towards the receiving medium. The undeflected droplets are collected and recycled. Continuous inkjet printers require complex hardware, but they offer high speed printing as an advantage.

**[0032]** In drop-on-demand inkjet printers, ink droplets are generated and ejected through the orifices of the print head only as needed. Some drop-on-demand systems use a thermal process to create the pressure required to eject ink droplets. These thermal jet (or bubble jet) printers use heat to generate vapor bubbles in a volatile component of the ink fluid. As these bubbles build up pressure and vaporize, ink droplets are jetted out of the print head one at a time. Other drop-on-demand systems utilize a piezoelectric actuator to eject ink droplets. In these printers, a computer signal imposes an electrical potential across a piezoelectric material which causes it to deform. Ink droplets are ejected as the piezoelectric material deforms and returns to its normal dimensions. Although drop-on-demand inkjet printers have relatively slow printing speed, they offer small drop size and highly controlled ink droplet placement.

**[0033]** The imaging step according to the invention can be performed by any suitable inkjet printers and techniques described above. Commercially available drop-on-demand models are preferred, however, because of their durability and high resolution.

3. Lithographic Printing Members

**[0034]** A representative printing member according to the invention includes a substrate, an optional intermediate layer, and a top layer. **FIG. 1A** illustrates an embodiment of a negative-working printing member **100** according to the invention that includes a substrate **102**, a crosslinked hydrophilic intermediate layer **104**, and a water-soluble hydrophilic top layer **106** that is chemically reactive with an inkjet imaging fluid **108** (see **FIGS. 3A-3D**). **FIG. 1B** illustrates a variation **150** of the printing member **100** without the intermediate layer **104**. **FIG. 2** illustrates another embodiment of a negative-working printing member **200** according to the invention that includes a substrate **202**, a crosslinked hydrophilic intermediate layer **204**, and a water-dispersible oleophilic top layer **206** that is chemically reactive with an inkjet imaging fluid **208** (see **FIGS. 4A-4D**). Each of these layers and their functions will be described in detail below.

**[0035]** 3.1. Substrate **102**, **202**

**[0036]** The substrate provides dimensionally stable mechanical support to the printing member. The substrate should be strong, stable and, preferably, thin and flexible. One or more surfaces of the substrate can be either hydrophilic or oleophilic. Suitable substrate materials include, but are not limited to, metals, polymers, and paper.

**[0037]** Metals suitable for use in substrates according to the invention include, but are not limited to, aluminum, zinc, steel, chromium, and alloys thereof, which may have another metal (e.g., copper) plated over one surface. Metal substrates can have thicknesses ranging from about 50 μm to about 500 μm or more, with thicknesses in the range of about 100 μm to about 300 μm being preferred.

**[0038]** One or more surfaces of a metal substrate may be anodized. Anodizing increases the hardness and abrasion resistance of the metal surface, which improves the mechanical strength of the substrate. The anodic layer can also control dissipation of heat into the substrate, thus increasing the imaging efficiency of the printing member. An anodized aluminum substrate consists of an unmodified base layer and a porous, anodic aluminum oxide coating thereover. The anodized aluminum surface is hydrophilic; however, without further treatment, the oxide coating would lose wettability due to further chemical reaction. Anodized substrates are, therefore, typically exposed to a silicate solution or other suitable reagent (e.g., a phosphate reagent) that stabilizes the hydrophilic character of the plate surface. In the case of silicate treatment, the surface may assume the properties of a molecular sieve with a high affinity for molecules of a definite size and shape-including, most importantly, water molecules.

[0039] A preferred substrate is an anodized aluminum plate with a low degree of graining and an anodic layer having a thickness between about 0.5 μm and about 3 μm (available, for example, from Precision Lithograining Corp., South Hadley, Mass.). Graining can be achieved by methods known in the art such as by means of a wire brush, a slurry of particulates or by chemical or electrolytic means.

[0040] Polymers suitable for use in substrates according to the invention include, but are not limited to, polyesters (e.g., polyethylene terephthalate and polyethylene naphthalate), polycarbonates, polyurethane, acrylic polymers, polyamide polymers, phenolic polymers, polysulfones, polystyrene, and cellulose acetate. A preferred polymeric substrate is a polyethylene terephthalate film such as MYLAR and MELINEX (available from E. I. duPont de Nemours Co., Wilmington, Del.).

[0041] Polymeric substrates can be coated with a transition layer to improve the mechanical strength and durability of the substrate and/or to alter the hydrophilicity or oleophilicity of the surface of the substrate. A hydrophilic transition layer may include porous materials with oxygen functional groups at the surface. The addition of hydrophilic fillers such as, for example, silica particles also enhances the hydrophilicity of the transition layer. Examples of suitable materials for hydrophilic transition layers according to the invention include proprietary hard coat materials supplied by Bekaert Specialty Films, LLC (San Diego, Calif.). Other suitable formulations and application techniques for transition layers are disclosed, for example, in U.S. Pat. No. 5,339,737, the entire disclosure of which is hereby incorporated by reference.

[0042] Polymeric substrates can have thicknesses ranging from about 50 μm to about 500 μm or more, depending on the specific printing member application. For printing members in the form of rolls, thicknesses of about 200 μm are preferred. For printing members that include transition layers, polymer substrates having thicknesses of about 50 μm to about 100 μm are preferred.

[0043] A wide variety of papers may be utilized as a substrate. Typically, papers are saturated with a polymeric treatment to improve dimensional stability, water resistance, and strength during wet lithographic printing.

[0044] In embodiments of the invention that do not include an intermediate layer between the top layer and the substrate (e.g., **FIG. 1B**), the substrate and the top layer (subsequent to reaction with the imaging fluid) generally have opposite affinities for ink and/or a liquid to which ink will not adhere. In embodiments that do contain an intermediate layer (e.g., **FIGS. 1A and 2**), on the other hand, the substrate and the top layer (subsequent to reaction with the imaging fluid) need not have opposite lithographic affinities. Instead, the intermediate layer is designed to have a lithographic affinity opposite to that of the reacted top layer, as described below. However, it is generally preferable to provide a substrate and an intermediate layer of like affinities to promote adhesion and to accommodate damage to the intermediate layer without loss of performance. Specifically, even though the intermediate layer is typically not soluble in aqueous solutions and is not removed during the imaging process, it can still be scratched or damaged during the printmaking process. A substrate of like affinity will accept or reject ink in the same manner as the overlying intermediate layer in those areas where the intermediate layer is damaged, thus maintaining print quality and prolonging the press life of the printing member.

[0045] 3.2 Intermediate Layer **104**, **204**

[0046] The intermediate layer is coated on the substrate. In embodiments employing a polymeric substrate, the intermediate layer can be the transition layer described above. The intermediate layer can be either hydrophilic or oleophilic, provided that it has an affinity opposite to that of the top layer after the top layer has reacted with the imaging fluid for ink and/or a liquid to which ink will not adhere. It should generally adhere well to the substrate and to the top layer and should withstand repeated application of fountain solution or ink during printing without substantial degradation or solubilization. The intermediate layer is optional in some embodiments.

[0047] Suitable materials for fabricating a hydrophilic intermediate layer include, but are not limited to, polyvinyl alcohol, polyacrylamide, polyvinyl pyrrolidone, and cellulosics. Polyvinyl alcohol is preferred. Homopolymers and copolymers with amine, carboxylic acid, sulfonic acid, and/or phosphonic acid moieties can also be used. Specific examples include homopolymers and copolymers of vinyl alcohol with amino-functional groups, vinyl phosphonic acid, acrylamide, methylol acrylamide, methylol methacrylamide, acrylate acid, methacrylate acid, hydroxyethyl acrylate, hydroxyethyl methacrylate, and maleic anhydride/vinylmethylether copolymers. A polyceramic layer containing PVOH—ZrOH (see, e.g., U.S. Pat. Nos. 6,182,569, 6,182,570, and 6,186,067) can also be used.

[0048] To increase toughness and wear resistance, the hydrophilic polymer coating is preferably crosslinked. Crosslinking agents such as formaldehyde, glyoxal, polyisocynate, melamine-type crosslinkers, ammonium zirconyl carbonate, titanate crosslinkers, hydrolyzed tetraalkylorthosilicate, and diepoxide crosslinkers can be added to crosslink specific functional groups in the polymer. For example, diepoxide crosslinkers can effectively crosslink amino groups and carboxylic acid groups. Polyvinyl alcohol can be crosslinked by hydrolyzed tetraethoxysilane according to procedures described in U.S. Pat. No. 3,971,660, by ammonium zirconium carbonate as described in U.S. Pat. No. 6,490,975, and by melamine with a catalyst such as an organic sulfonic acid.

[0049] The mechanism of the crosslinking reaction is not critical. For example, either radical-initiated crosslinking or oxidative crosslinking may be used.

[0050] In embodiments of the invention that include an oleophilic intermediate layer, the materials used in the oleophilic coating should demonstrate good adhesion to the substrate below it and to the hydrophilic coating that is to be applied on top of it. Their oleophilic properties should be such that, when placed on a press, the imaged areas accept ink immediately. Run lengths in the order of thousands of impressions are preferred. The oleophilic materials should therefore have suitable toughness, wear resistance, and be non-reactive with the ink.

[0051] Many homopolymers and copolymers can be used as the oleophilic intermediate layer according to the invention. They include polyurethanes, epoxy resins, polystyrene, copolymers of styrene, acrylics, copolymers of acetate and ethylene, polyacrylics, copolmyers of acrylics, polyvinyl acetate, phenol and cresol formaldehyde resins, cellulose ethers and esters, polyvinyl acetals, diazo resins, and synthetic rubbers. They can be applied from a solvent solution, or can be used in the form of an aqueous resin dispersion and be applied from water. Intermediate layers made from aqueous resin dispersions can be heat-treated to cause the dispersed resin particles to coalesce, which increases their toughness. In addition, commercially available subtractive coatings (e.g., subtractive plate NSSH manufactured by Precision Lithograining, South Hadley, Mass.) with or without blanket light exposure can be used as the oleophilic coating.

[0052] Other components that can be included in the intermediate layer are colorants, plasticizers, surfactants, crosslinking agents and monomers including initiators. The latter two are added to increase toughness and can be activated by either heat or light.

[0053] 3.3 Top Layer **106**, **206**

[0054] The top layer receives the imaging fluid and comprise a material, or a mixture of materials, that are permeable to and chemically reactive with a suitable inkjet imaging fluid. The top layer captures the image on the printing member by undergoing a property change, including but not limited to solubility and/or oleophilicity, in response to the imaging fluid.

[0055] Materials forming the top layer can be applied to the intermediate layer (or, in embodiments where the intermediate layer is optional, to the substrate) in any suitable manner using conventional coating equipment and procedures. Upon drying, the top layer is generally at least 0.1 μm in thickness and can be as thick as 10 μm. Thus, in negative-working embodiments of the present invention, the top layer should be thick and substantially continuous enough to provide the desired image upon fluid application, but not so thick that the non-image areas are difficult to remove after imaging. Similarly, in positive-working embodiments of the present invention, the top layer should not be so thick that the imaged areas are difficult to remove after imaging.

[0056] Apart from the components capable of reacting with the imaging fluid, the top layer may also contain various additives as appropriate to the application. For example, in embodiments where the printing member is preferably heated to initiate or complete the chemical reaction between the top layer and the imaging fluid, an infrared absorber may be included. Suitable infrared absorbers include infrared light-absorbing dyes or pigments that can effectively absorb radiation having a wavelength of 700 to 1,500 nm. It is preferable that the dyes or pigments have an absorption maximum between the wavelengths of 750 and 1,200 nm. Various infrared light-absorbing dyes or pigments are described in U.S. Pat. Nos. 5,858,604, 5,922,502, 6,022,668, 5,705,309, 6,017,677, and 5,677,106. Examples of useful infrared light-absorbing dyes include squarylium, croconate, cyanine (including polymethine), phthalocyanine (including naphthalocyanine), merocyanine, chalcogenopyryloarylidene, oxyindolizine, quinoid, indolizine, pyrylium, and metal dithiolene dyes. Cyanine and phthalocyanine dyes are preferred infrared light-absorbing dyes. Examples of useful infrared light-absorbing pigments include black pigments, metal powder pigments, phthalocyanine pigments, and carbon black. Carbon black is a preferred infrared light-absorbing pigment. Mixtures of dyes, pigments, or both can also be used. The infrared light-absorbing dyes or pigments are added in the top layer preferably at a level of 0.01 to 30% by weight of the top layer, more preferably at a level of 0.1 to 20% by weight of the top layer, and most preferably at a level of 0.5 to 10% by weight of the top layer.

[0057] The top layer may also comprise nonionic and/or amphoteric surfactants. Specific examples of the nonionic surfactant include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearic acid monoglyceride, polyoxyethylene nonylphenyl ether, and the like. Specific examples of amphoteric surfactants include alkyldi(aminoethyl)glycine, hydrochloric acid salt of alkylpolyaminoethylglycine, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolinum betaine, N-tetradecyl-N,N-betaine, and the like.

[0058] Dyes can be added in a small amount to adjust the plate color. Specific examples of these dyes include Oil Yellow No. 101, Oil Yellow No. 103, Oil Pink No. 312, Oil Green BG, Oil Blue BOS, Oil Blue N. 603, Oil Black BY, Oil Black BS, Oil Black T-505 (all marketed by Chemical Industries, Co., Des Moine, Iowa), Victoria Pure Blue, Crystal Violet (C.I. 42555), Methyl Violet (C.I. 42535), Ethyl Violet, Rhodamine B (C.I. 145170B), Malachite Green (C.I. 42000), Methylene Blue (C.I. 52015), and the like.

[0059] Further, if necessary, a plasticizer may be added to impart flexibility to the top layer. Examples of suitable plasticizers include butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutylphthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, an oligomer or a polymer of acrylic acid or methacrylic acid, and the like.

[0060] Specific embodiments of the top layer are discussed below.

[0061] 3.4 Inkjet Imaging Fluid **108**, **208**

[0062] The inkjet imaging fluid contains at least one chemical compound in its composition capable of reacting with the top layer. The chemical compound(s) may be present in the imaging fluid in a concentration as high as 20% or even higher by weight, but preferably less than 5% by weight. It is also preferable, although not necessary, that the chemical compound(s) be in the form of a homogeneous solution or a stable colloidal dispersion, so that it can pass through the nozzles of an inkjet print head.

[0063] The main liquid carrier can be water or an organic solvent or combinations thereof. The choice of the liquid carrier depends on the specific inkjet printer. Both aqueous-based and solvent-based fluids can be used in the present invention depending on the inkjet technology that is being used (i.e., piezo, thermal, bubble jet or continuous inkjet).

[0064] While water is the preferred medium for aqueous imaging fluids, the aqueous composition may comprise one or more miscible co-solvents, e.g., a polyhydric alcohol. These co-solvents may be high-boiling humidifying solvents such as glycerin, propylene glycol, ethxylated glycerin, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, and trimethylol propane. The purpose of adding one or more high-boiling humidifying solvents is to prevent the imaging fluid from drying during idle periods which could cause the inkjet nozzles to clog. Other high-boiling solvents can be added to improve the solubility of the chemical compound tailored to react with the top layer. Such solvents may include, but are not limited to, methyl pyrrolidone, propylene glycol monoethyl ether, propylene glycol monobutyl ether, and propylene glycol ethyl ether acetate. The amount of aqueous carrier medium in the aqueous composition may be in the range from 30 to 99.995% by weight, preferably from 50 to 95% by weight.

[0065] Organic solvents that may be used as a carrier medium for the inkjet imaging fluid include, but are not limited to, alcohols, ketones or acetates.

[0066] As known in the art of the inkjet technology, the jet velocity, separation length of the droplets, drop size and stream stability is greatly affected by the surface tension and the viscosity of the aqueous composition. Inkjet imaging fluids suitable for use with inkjet printing systems may have a surface tension in the range from 20 to 60 dyne/cm, and preferably from 30 to 50 dyne/cm. Control of surface tensions in aqueous inkjet fluids may be accomplished by additions of small amnounts of surfactants. The level of surfactants to be used can be determined through simple empirical experiments. Several anionic and nonionic surfactants are known in the inkjet art. Commercial surfactants include the SURFYNOL series, e.g., SURFYNOL 104, SURFYNOL 45, SURFYNOL FS-80, SURFYNOL PSA-216 (available from Air Products, Allentown, Pa.); the DYNOL series, e.g., DYNOL 604 (available from Air Products, Allentown, Pa.); the TRITON series, e.g., TRITON X-100 (available from Rohm and Haas, Philadelphia, Pa.); the ZONYL series (available from E. I. duPont de Nemours Co., Wilmington, Del.); the FLUORAD series (available from Minnesota Mining and Manufacturing Co., St. Paul, Mn.); the AEROSOL series (available from American Cyanamid Co., Wayne, N.J.); and similar chemicals. The viscosity of the fluid is preferably not greater than 20 mPA·s, e.g., from 1 to 10 mPA·s, preferably from 1 to 5 mPA·s at room temperature.

[0067] The inkjet imaging fluid may further comprise other ingredients. A biocide may be added to prevent unwanted microbial growth which may occur in the fluid over time, and which would otherwise degrade the shelf life of the fluid. Suitable biocides include, but are not limited to, PROXEL GXL (available from Zeneca Specialties, Manchester, UK), sodium OMADINE (available from Olin Mathieson Chemical Corp., New York, N.Y.), GIVGARD DXN (available from Givaudan Corp., New York, N.Y.), solution of 1,2-benzothiazoline-3-one, sodium hydroxide and dipropylene glycol, 2-pyridinethiol-1-oxide, sodium salt, DOWICIL (available from Dow Chemical, Midland, Mich.), cis-1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride, and similar chemicals or mixtures of such chemicals. When used, the biocide will typically be 0.1 to 3% by weight of the ink.

[0068] Additional additives that may be optionally present in the ink include thickeners, pH adjusters, buffers, conductivity-enhancing agents, drying agents and defoamers.

[0069] Dyes may be added in order to enhance the image contrast after jetting the image on the top layer. Many dyes and pigments are known to be suited for inkjet technology. Suitable dyes are further selected based on their compatibility in the carrier medium (i.e., aqueous-based or solvent-based) and on their compatibility with the reactive chemical compound, e.g., they should not lead to coagulation.

[0070] Specific embodiments of the imaging fluids and the compositions of the top layers are discussed below in detail, along with the imaging techniques associated therewith.

4. Imaging Techniques

[0071] 4.1. Printing Member **100**, **150** and Imaging Fluid **108**

[0072] According to the embodiment illustrated in **FIG. 1A**, the printing member **100** includes a grained, anodized, and/or silicated aluminum substrate **102**, an optional crosslinked hydrophilic intermediate layer **104**, and a water-soluble and hydrophilic top layer **106**. In **FIG. 1B**, a variation **150** of the printing member **100** includes the substrate **102** and the water-soluble and hydrophilic top layer **106** only. The water-soluble and hydrophilic top layer **106** becomes water-insoluble and oleophilic when reacted with the inkjet imaging fluid **108**.

[0073] **FIGS. 3A-3D** illustrate the consequences of imaging an embodiment of printing member **100**. As illustrated in **FIG. 3A**, an inkjet printer **110** is used to apply droplets of the imaging fluid **108** imagewise onto the water-insoluble and hydrophilic top layer **106**. The imaging fluid **108** wets and penetrates the top layer **106**, and creates an imaged area **112**. The imaged plate **110** may then be heated, e.g., in an oven, or alternatively, by exposure to an infrared radiation source **120**, as shown in **FIG. 3B**. The heated fluid **108** reacts with the water-soluble and hydrophilic top layer **106** and forms a water-insoluble and oleophilic imaged area **124**. The imaged plate **100** may then be developed by exposure to fountain solution or water **128** that dissolves the non-image portions **134***a*, **134***b* of the water-soluble layer **106**, thereby revealing portions **144***a*, **144***b* of the underlying crosslinked hydrophilic layer **104** (or in variation **150**, not shown, the hydrophilic aluminum substrate **102**). **FIG. 3C** illustrates the imaged plate **100** after processing with fountain solution and/or water. As shown in **FIG. 3D**, the fountain solution **128** is repelled by the imaged oleophilic area **124**, which then accepts printing ink **138**.

[0074] Examples of water-soluble polymers suitable for forming the top layer **106** according to the invention include polymers comprising an amine, a carboxylic acid, a sulfonic acid, and/or a phosphonic acid moiety. Specific examples include polyvinyl phosphonic acid and polyvinyl alcohol with amine moities.

[0075] Suitable compositions for imaging fluid **108** may include various types of insolubilizing agents that can oleophilize the hydrophilic top layer **106**. For example, imaging fluid **108** may contain one or more esterifying agents, examples of which include, but are not limited to tetramethylammonium hydroxide, phenyltrimethylammonium hydroxide, trimethylsulfonium hydroxide, trimethylsulfoxonium hydroxide, 1,3-(bistripropylammonium)xylene hydroxide.

[0076] Alternatively, inkjet imaging fluid **108** may contain a component for promoting an esterification and/or alkylation reaction. Preferred examples include polymers containing quaternary ammonium salts.

[0077] In other alternative embodiments, inkjet imaging fluid **108** may contain a component for salt formation or amidization, such as, for example, tetramethylenediamine, hexamethylenediamine, m-phenylenediamine, n-propylamine, or n-butylamine.

4.2 Printing Member **200** and Imaging Fluid **208**

[0078] According to the embodiment illustrated in **FIG. 2**, the printing member **200** includes a grained, anodized, and/or silicated aluminum substrate **202**, a crosslinked hydrophilic intermediate layer **204**, and a water-dispersible and oleophilic top layer **206**. The water-dispersible top layer **206** becomes crosslinked and water-insoluble when reacted with the imaging fluid **208**.

[0079] **FIGS. 4A-4D** illustrate the consequences of imaging an embodiment of the printing member **200**. As illustrated in **FIG. 4A**, an inkjet printer **210** is used to apply droplets of the imaging fluid **208** imagewise onto the water-dispersible top layer **206**. The imaging fluid **208** wets and penetrates the top layer **206**, and creates an imaged area **212**. The imaged area **212** may then be heated, e.g., in an oven, or alternatively, by exposure to an infrared radiation source **220**, as shown in **FIG. 4B**. The heated fluid **208** reacts with the water-dispersible and oleophilic layer **206** and forms an insoluble area **224**. The imaged plate can then be developed by exposure to fountain solution or water **228** that dissolves the non-image portions **234***a*, **234***b* of the water-dispersible and oleophilic top layer **206**, thereby revealing portions **244***a*, **244***b* of the underlying crosslinked hydrophilic intermediate layer **204**. **FIG. 4C** illustrates the imaged plate **200** after processing with fountain solution and/or water. As shown in **FIG. 4D**, the fountain solution **228** is repelled by the imaged oleophilic area **224**, which then accepts printing ink **238**.

[0080] Suitable materials for forming the oleophilic top layer **206** according to the invention include many aqueous epoxy-resin dispersions. Commercial examples include, but are not limited to, EPI-REZ 3510 W-60, a low-molecular-weight bisphenol A epoxy resin; EPI-REZ 3515 W-60, a semi-solid bisphenol A epoxy resin; EPI-REZ 3519 W-50, a butadiene-acrylonitrile-modified epoxy resin; EPI-REZ 3522 W-60, a solid bisphenol A epoxy resin; EPI-REZ 5003 W-55, an epoxidized bisphenol A novalac with an average functionality of 3; EPI-REZ 5520 W-60, a urethane-modified bisphenol A epoxy resin; EPI-REZ 6006 W-70, an epoxidized o-cresylic novolac with an average functionality of 6 (all available from Shell Chemicals, Houston, Tex.), and various combinations thereof.

[0081] Other components that can also be included in the epoxy-resin dispersion top layer include colorants (e.g., dyes and/or pigments), plasticizers, glycols, surfactants, water-soluble oleophilic resins, other water dispersible resins, inorganic salts, and anionic and/or cationic materials.

[0082] The coating weight of the epoxy resin top layer ranges from about 0.25 to about 2.7 g/$m^2$, more preferably from about 0.4 to about 1.3 g/$m^2$ and most preferably from about 0.55 to about 0.85 g/$m^2$.

[0083] Certain additive components facilitate removal of the non-image areas of the imaged top layer in the water development step without any significant effect on the crosslinking reaction that insolubilizes the top layer. This is an unexpected and desirable result. Such additives are water-soluble or water-dispersible and are believed to improve development by facilitating the re-dispersion of the epoxy-resin microparticles; specifically, their presence may help water penetrate into the coating which, in turn, may help epoxy-resin particles re-disperse. If the additives re-disperse at a faster rate than the epoxy-resin particles, the net effect will be faster development.

[0084] Additives that were found to enhance the development of the epoxy resin top layer include Vinac XX-210 (available from Air products, Allentown, Pa.), an aqueous polyvinyl acetate dispersion; LUTANOL M-40 (from BASF, Ludwigshafen, Germany), a polyvinylmethyl ether; propylene glycol; ethylene glycol; cetyltrimethylammonium bromide; tetramethylammonium chloride; sodium chloride; IRGASPERSE BLUE B-W (from Ciba Specialties, St. Louis, Mo.), a water-soluble copper phthalocyanine dye; VICTORIA BLUE BO, a triphenylmethane dye; BONJET CW-**1** (from Orient Chemical, Korea), an aqueous carbon black dispersion; UNISPERSE BLUE (from Ciba Specialties, St. Louis, Mo.), an aqueous dispersion of a phthalocyanine pigment; acid dyes such as Acid Green 25 (C.I. 61570), Acid Blue 92 (C.I. 13390), Acid Red 183 (C.I. 18800), Acid Yellow 25 (C.I. 18835), BASACID Blue NB 755 (from BASF, Ludwigshafen, Germany); and various combinations thereof.

[0085] The addition of additives enables the use of thicker coatings which otherwise cannot be satisfactorily developed. Additionally, top layers without any additives may also become more difficult to develop after oven-aging. The addition of a preferred additive, such as IRGASPERSE BLUE B-W, to the top layer eliminates the potentially detrimental effect of oven-aging on development.

[0086] It was found that several epoxy-resin dispersions such as EPI-REZ 3510 W-60 and EPI-Rez 3515 W-60 produced tacky coatings which can be reduced through combination with other epoxy dispersions that do not produce tacky coatings. Additives may also be incorporated into the coating to reduce tackiness. For this purpose, VINAC XX-210 was found to be useful.

[0087] Suitable compositions for inkjet imaging fluid **208** include various crosslinking agents that are chemically reactive with epoxide fluctionalities. Preferred crosslinking agents include, but are not limited to, multifunctional amines and tetra-carboxylic acids.

[0088] Suitable multifunctional amines for preparing the imaging fluid **208** according to the invention include, but are not limited to, polyethylenimine; JEFFAMINE T 403 (available from Huntsman, West Footscray, Victoria, Australia), a triamine based on the reaction of trimethylolpropane with propylene oxide followed by amination of the terminal hydroxyl groups; pentaethylenehexamine, and related materials. The concentration of the multifunctional amine in the imaging fluid ranges from about 0.5% to 10% by weight, and preferably from about 1% to 3% by weight.

[0089] To promote and/or to complete the crosslinking reaction, the imaged plate **200** may be heated. Preferred heating temperature ranges from about 90° C. to about 150° C., and more preferably from about 110° C. to about 120° C. The imaged plate **200** may be heated for a period between about 15 seconds to 5 minutes, and preferably from about 1 minute to about 2 minutes. The heating step may be carried out in a conventional oven or by other heating methods, such as by exposure to infrared radiation.

[0090] After imaging and the optional heat treatment, top layer **206** can be developed by rubbing with a WEBRIL wipe (manufactured by Kimberly Clark, Neenah, Wisc.). The WEBRIL wipe can be wetted with water, treated with ink, or both. It was found that the WEBRIL wipe that contained both water and ink developed the imaged plate significantly faster than the other two WEBRIL wipes. The combination of water and ink was found to produce a synergistic effect in improving development.

[0091] It will be seen that the foregoing techniques provide a basis for improved lithographic printing and superior plate constructions. The terms and expressions employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof. Instead, it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

**1**. A lithographic printing member comprising a soluble and top layer having a first lithographic affinity and a layer thereunder also having the first lithographic affinity, the top layer being responsive to an imaging fluid by undergoing a phase change to an insoluble state having a second lithographic affinity opposite to the first lithographic affinity.

**2**. The printing member of claim 1, wherein the top layer is water-soluble and hydrophilic prior to the phase change and water-insoluble and oleophilic following the phase change.

**3**. The printing member of claim 1, wherein the top layer is water-soluble and oleophilic prior to the phase change and water-insoluble and hydrophilic following the phase change.

**4**. The printing member of claim 1, wherein the top layer comprises a polymer selected from the group consisting of polyvinyl phosphonic acid, polyvinyl alcohol comprising amino-moieties, and any polymer comprising at least one of carboxylic acid moieties, sulfonic acid moieties, and phosphonic acid moieties.

**5**. The printing member of claim 1, wherein the imaging fluid to which the printing member is responsive comprises an esterifying agent.

**6**. The printing member of claim 5, wherein the esterifying agent comprises a chemical compound selected from the group consisting of tetramethylammonium hydroxide, phenyltrimethylammonium hydroxide, trimethylsulfonium hydroxide, trimethylsulfoxonium hydroxide, and 1,3-(bistripropylammonium)xylene hydroxide.

**7**. The printing member of claim 1, wherein the imaging fluid to which the printing member is responsive comprises an alkylating agent.

**8**. The printing member of claim 1, wherein the imaging fluid to which the printing member is responsive comprises a polymer comprising a quaternary ammonium salt.

**9**. The printing member of claim 1 further comprising a crosslinked hydrophilic intermediate layer disposed between the top layer and the underlying layer.

**10**. A system for lithographic printing comprising:

(a) a printing member comprising a soluble top layer and a layer thereunder, the top layer having a first lithographic affinity and the underlying layer also having the first lithographic affinity, and

(b) an imaging fluid;

wherein the top layer responds to the imaging fluid by undergoing a phase change to an insoluble state having having a second lithographic affinity opposite to the first lithographic affinity.

**11**. The system of claim 10, wherein the top layer is water-soluble and hydrophilic prior to the phase change and water-insoluble and oleophilic following the phase change.

**12**. The system of claim 10, wherein the top layer is water-soluble and oleophilic prior to the phase change and water-insoluble and hydrophilic following the phase change.

**13**. The system of claim 10, wherein the top layer comprises a polymer selected from the group consisting of polyvinyl phosphonic acid, polyvinyl alcohol comprising amino-moieties, and any polymer comprising at least one of carboxylic acid moieties, sulfonic acid moieties, and phosphonic acid moieties.

**14**. The system of claim 10, wherein the imaging fluid comprises an esterifying agent.

**15**. The system of claim 14, wherein the esterifying agent comprises a chemical compound selected from the group consisting of tetramethylammonium hydroxide, phenyltrimethylammonium hydroxide, trimethylsulfonium hydroxide, trimethylsulfoxonium hydroxide, and 1,3-(bistripropylammonium)xylene hydroxide.

**16**. The system of claim 10, wherein the imaging fluid comprises an alkylating agent.

**17**. The system of claim 10, wherein the imaging fluid comprises a polymer comprising a quaternary ammonium salt.

**18**. The system of claim 8, wherein the printing member further comprises a crosslinked hydrophilic intermediate layer disposed between the top layer and the underlying layer.

**19**. A method of imaging a lithographic printing member, the method comprising the steps of:

(a) providing a printing member comprising a soluble and top layer having a first lithographic affinity and a layer thereunder also having the first lithographic affinity, the top layer being responsive to an imaging fluid by undergoing a phase change to an insoluble state having a second lithographic affinity opposite to the first lithographic affinity;

(b) dispensing the imaging fluid in an imagewise pattern, the imaging fluid chemically reacting with the top layer and inducing the phase change;

(c) subjecting the printing member to a solvent, the solvent dissolving soluble portions of the top layer; and

(d) removing the soluble portions of the top layer, thereby creating an imagewise lithographic pattern on the printing member.

20. The method of claim 19, wherein the top layer is water-soluble and hydrophilic prior to the phase change and water-insoluble and oleophilic following the phase change, the solvent comprising an aqueous fluid.

21. The method of claim 19, wherein the top layer is water-soluble and oleophilic prior to the phase change and water-insoluble and hydrophilic following the phase change, the solvent comprising an aqueous fluid.

22. The method of claim 19, wherein the top layer comprises a polymer selected from the group consisting of polyvinyl phosphonic acid, polyvinyl alcohol comprising amino-moieties, and any polymer comprising at least one of carboxylic acid moieties, sulfonic acid moieties, and phosphonic acid moieties.

23. The method of claim 19, wherein the imaging fluid comprises an esterifying agent.

24. The method of claim 23, wherein the esterifying agent comprises a chemical compound selected from the group consisting of tetramethylammonium hydroxide, phenyltrimethylammonium hydroxide, trimethylsulfonium hydroxide, trimethylsulfoxonium hydroxide, and 1,3-(bistripropylammonium)xylene hydroxide.

25. The method of claim 19, wherein the imaging fluid comprises an alkylating agent.

26. The method of claim 19, wherein the imaging fluid comprises a polymer comprising a quaternary ammonium salt.

27. The method of claim 19, wherein the printing member further comprises a crosslinked hydrophilic intermediate layer disposed between the top layer and the underlying layer.

28. The method of claim 19, flurther comprising a step of heating the printing member between steps (b) and (c).

29. A lithographic printing member comprising a dispersible top layer having a first lithographic affinity and a layer thereunder having a second lithographic affinity opposite to the first lithographic affinity, the top layer being responsive to an imaging fluid by undergoing a phase change from a dispersible state to an insoluble state.

30. The printing member of claim 29, wherein the top layer is water-dispersible and oleophilic, and responsive to an imaging fluid by undergoing a phase change to a water-insoluble state.

31. The printing member of claim 29, wherein the top layer is water-dispersible and hydrophilic, and responsive to an imaging fluid by undergoing a phase change to a water-insoluble state.

32. The printing member of claim 29, wherein the top layer comprises a water-dispersible polymer.

33. The printing member of claim 32, wherein the water-dispersible polymer comprises an epoxy resin.

34. The printing member of claim 29, wherein the imaging fluid comprises a multiflnctional amine.

35. The printing member of claim 29, wherein the imaging fluid comprises a tetra-carboxylic acid.

36. The printing member of claim 29, wherein the printing member fiuther comprises a crosslinked hydrophilic intermediate layer disposed between the top layer and the underlying layer.

37. The printing member of claim 36, wherein the intermediate layer comprises PVOH—ZrOH.

38. A system for lithographic printing comprising:

(a) a printing member comprising a dispersible top layer and a layer thereunder, the top layer having a first lithographic affinity and the underlying layer having a second lithographic affinity opposite to the first lithographic affinity, and

(b) an imaging fluid;

wherein the top layer responds to the imaging fluid by undergoing a phase change from a dispersible state to an insoluble state.

39. The system of claim 38, wherein the top layer is water-dispersible and oleophilic, and responsive to an imaging fluid by undergoing a phase change to a water-insoluble state.

40. The system of claim 38, wherein the top layer is water-dispersible and hydrophilic, and responsive to an imaging fluid by undergoing a phase change to a water-insoluble state.

41. The system of claim 38, wherein the top layer comprises a water-dispersible polymer.

42. The system of claim 41, wherein the water-dispersible polymer comprises an epoxy resin.

43. The system of claim 38, wherein the imaging fluid comprises a multifunctional amine.

44. The system of claim 38, wherein the imaging fluid comprises a tetra-carboxylic acid.

45. The system of claim 38, wherein the printing member flurther comprises a crosslinked hydrophilic intermediate layer disposed between the top layer and the substrate.

46. The system of claim 45, wherein the intermediate layer comprises PVOH—ZrOH.

47. A method of imaging a lithographic printing member, the method comprising the steps of:

(a) providing a printing member comprising a dispersible top layer having a first lithographic affinity and a layer thereunder having a second lithographic affinity opposite to the first lithographic affinity, the top layer being responsive to an imaging fluid by undergoing a phase change from a dispersible state to an insoluble state;

(b) dispensing the imaging fluid in an imagewise pattern, the imaging fluid chemically reacting with the top layer and inducing the phase change;

(c) subjecting the printing member to a solvent, the solvent dissolving dispersible portions of the top layer; and

(d) removing the dispersible portions of the top layer, thereby creating an imagewise lithographic pattern on the printing member.

48. The method of claim 47, wherein the solvent comprises an aqueous fluid.

49. The method of claim 48, wherein the top layer is water-dispersible and oleophilic, and responsive to an imaging fluid by undergoing a phase change to a water-insoluble state.

50. The method of claim 48, wherein the top layer is water-dispersible and hydrophilic, and responsive to an imaging fluid by undergoing a phase change to a water-insoluble state.

**51**. The method of claim 47, wherein the top layer comprises a water-dispersible polymer.

**52**. The method of claim 51, wherein the water-dispersible polymer comprises an epoxy resin.

**53**. The method of claim 47, wherein the imaging fluid comprises a multifunctional amine.

**54**. The method of claim 47, wherein the imaging fluid comprises a tetra-carboxylic acid.

**55**. The method of claim 47, wherein the printing member further comprises a crosslinked hydrophilic intermediate layer disposed between the top layer and the substrate.

**56**. The method of claim 55, wherein the intermediate layer comprises PVOH—ZrOH.

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