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(54) **MULTILAYER IMAGEABLE ELEMENTS**

MEHRLAGIGE ABBILDBARE ELEMENTE

ELEMENTS DE FORMATION D'IMAGE MULTICOUCHES

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Description

Field of the Invention

[0001] The invention relates to lithographic printing. In particular, this invention relates to multi-layer, positive-working, thermally imageable elements that are useful in forming lithographic printing plates.

Background of the Invention

[0002] In conventional or "wet" lithographic printing, ink receptive regions, known as image areas, are generated on a hydrophilic surface. When the surface is moistened with water and ink is applied, the hydrophilic regions retain the water and repel the ink, and the ink receptive regions accept the ink and repel the water. The ink is transferred to the surface of a material upon which the image is to be reproduced. Typically, the ink is first transferred to an intermediate blanket, which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

[0003] Imageable elements useful as lithographic printing plate precursors typically comprise an imageable layer applied over the hydrophilic surface of a substrate. The imageable layer includes one or more radiation-sensitive components, which may be dispersed in a suitable binder. Alternatively, the radiation-sensitive component can also be the binder material. Following imaging, either the imaged regions or the unimaged regions of the imageable layer are removed by a suitable developer, revealing the underlying hydrophilic surface of the substrate. If the imaged regions are removed, the precursor is positive-working. Conversely, if the unimaged regions are removed, the precursor is negative-working. In each instance, the regions of the imageable layer (*i.e.*, the image areas) that remain are ink-receptive, and the regions of the hydrophilic surface revealed by the developing process accept water and aqueous solutions, typically a fountain solution, and repel ink.

[0004] Imaging of the imageable element with ultraviolet and/or visible radiation is typically carried out through a mask, which has clear and opaque regions. Imaging takes place in the regions under the clear regions of the mask but does not occur in the regions under the opaque regions. If corrections are needed in the final image, a new mask must be made. This is a time-consuming process. In addition, dimensions of the mask may change slightly due to changes in temperature and humidity. Thus, the same mask, when used at different times or in different environments, may give different results and could cause registration problems.

[0005] Direct digital imaging, which obviates the need for imaging through a mask, is becoming increasingly important in the printing industry. Imageable elements for the preparation of lithographic printing plates have been developed for use with infrared lasers. Thermally imageable, multi-layer elements are disclosed, for example, in Shimazu, U.S. Pat. No. 6,294,311, U.S. Pat. No. 6,352,812, and U.S. Pat. No. 6,593,055; Patel, U.S. Pat. No. 6,352,811; Savariar-Hauck, U.S. Pat. No. 6,358,669, and U.S. Pat. No. 6,528,228; and Pat. Pub. No. US 2004/0067432 A1.

[0006] EP-A-1 312 483 discloses an imaging element comprising:

a substrate;
an underlayer over the substrate; and
a top layer over the underlayer;

in which:

the element comprises a photothermal conversion material;
the top layer is free of the photothermal conversion material;
the top layer is ink receptive;
before thermal imaging, the top layer is not removable by alkaline developer;
the underlayer is removable by alkaline developer;
the underlayer comprises a copolymer of N-substituted maleimides/methacrylic acid/methacrylamides.

[0007] Despite the progress in thermally imageable elements, there is a desire for positive working, thermally imageable elements that are both bakable and resistant to press chemistries, such as inks, fountain solution, and the solvents used in washes, such as UV washes. Bakability is highly desirable because baking increases the press runlength.

Summary of the Invention

[0008] The invention is a positive-working, thermally imageable element that is resistant to press chemistry and can be baked to increase press runlength. The imageable element comprises a substrate; an underlayer over the substrate; and a top layer over the underlayer;

in which:

the element comprises a photothermal conversion material;
the top layer is substantially free of the photothermal conversion material;
the top layer is ink receptive;
before thermal imaging, the top layer is not removable by an alkaline developer;
after thermal imaging to form imaged regions in the top layer, the imaged regions are removable by the alkaline developer;
the underlayer is removable by the alkaline developer, and
the underlayer comprises a polymeric material that comprises, in polymerized form:

about 5 mol% to about 30 mol% of methacrylic acid;
about 20 mol% to about 75 mol% of N-phenylmaleimide, N-cyclohexylmaleimide, N-benzylmaleimide, or a mixture thereof, preferably N-phenylmaleimide;
optionally, about 5 mol% to about 50 mol% of methacrylamide; and
about 3 mol% to about 50 mol% of a compound (a), represented by the formula:

$$CH_2C(R_2)C(O)NHCH_2OR_1,$$

in which R_1 is C_1 to C_{12} alkyl, phenyl, C_1 to C_{12} substituted phenyl, C_1 to C_{12} aralkyl, or $Si(CH_3)_3$; and R_2 is H or methyl.

[0009] The underlayer may additionally comprise a resin having activated methylol or activated alkylated methylol groups, preferably a resole resin. In addition, the underlayer may further additionally comprise (1) a first added copolymer or (2) the first added copolymer, and a second added copolymer. The first added copolymer is a copolymer of N-phenylmaleimide; methacrylamide; acrylonitrile; and compound (b), represented by the formula represented by the formula:

$$CH_2C(R_4)CO_2CH_2CH_2\text{-NH-CO-NH-}p\text{-}C_6H_4\text{-}R_3,$$

in which R_3 is OH, COOH, or SO_2NH2; and R_4 is H or methyl;
and, optionally, 1 to 30 wt%, preferably, when present, 3 to 20 wt% of compound (c), represented by the formula represented by the formula:

$$CH_2C(R_6)CONH\text{-}p\text{-}C_6H_4\text{-}R_5$$

in which R_5 is OH, COOH, or SO_2NH_2; and R_6 is H or methyl.

[0010] The second added copolymer is a copolymer of N-phenylmaleimide, methacrylamide, and methacrylic acid.

[0011] In another aspect, the invention is a method for forming an image by imaging and developing the imageable element. In yet another aspect, the invention is an image useful as a lithographic printing plate formed by imaging and developing the imageable element.

[0012] The imageable elements are positive working thermally imageable multi-elements that are resistant to the press chemistries used in lithographic printing, especially in printing processes using ultraviolet-curing inks, where rinsing agents with a high content of esters, ethers or ketones are used. In addition, they can be baked to increase press run length.

Detailed Description of the invention

[0013] Unless the context indicates otherwise, in the specification and claims, the terms binder, resole resin, surfactant, dissolution inhibitor, novolac resin, resin having activated methylol or activated alkylated methylol groups, photothermal conversion material, polymeric material, first added copolymer, second added copolymer, coating solvent, compound (a), compound (b), compound (c), and similar terms also include mixtures of such materials. Unless otherwise specified, all percentages are percentages by weight. Thermal imaging refers to imaging with a hot body, such as a thermal head, or with infrared radiation.

[0014] The invention is an imageable element as defined in claim 1 useful as precursor for a lithographic printing plate. The imageable element comprises a substrate with a hydrophilic surface, an underlayer, and a top layer. A photothermal conversion material is present, either in the underlayer and/or in a separate absorber layer.

[0015] The substrate comprises a support, which may be any material conventionally used to prepare imageable elements useful as lithographic printing plates. The support is preferably strong, stable and flexible. It should resist dimensional change under conditions of use so that color records will register in a full-color image. Typically, it can be

any self-supporting material, including, for example, polymeric films such as polyethylene terephthalate film, ceramics, metals, or stiff papers, or a lamination of any of these materials. Metal supports include aluminum, zinc, titanium, and alloys thereof.

[0016] Typically, polymeric films contain a sub-coating on one or both surfaces to modify the surface characteristics to enhance the hydrophilicity of the surface, to improve adhesion to subsequent layers, and the like. The nature of this layer or layers depends upon the substrate and the composition of subsequent layers. Examples of subbing layer materials are adhesion-promoting materials, such as alkoxysilanes, aminopropyltriethoxysilane, glycidoxypropyltriethoxysilane and epoxy functional polymers, as well as conventional subbing materials used on polyester bases in photographic films.

[0017] The surface of an aluminum support may be treated by techniques known in the art, including physical graining, electrochemical graining, chemical graining, and anodizing. The substrate should be of sufficient thickness to sustain the wear from printing and be thin enough to wrap around a cylinder in a printing press, typically about 100 μm to about 600 μm. Typically, the substrate comprises an interlayer between the aluminum support and the underlayer. The interlayer may be formed by treatment of the aluminum support with, for example, silicate, dextrine, hexafluorosilicic acid, phosphate/fluoride, polyvinyl phosphonic acid (PVPA), a vinyl phosphonic acid copolymer, or a water-soluble diazo resin.

[0018] The back side of the support (*i.e.*, the side opposite the underlayer and top layer) may be coated with an antistatic agent and/or a slipping layer or matte layer to improve handling and "feel" of the imageable element.

[0019] The underlayer comprises a polymeric material that, after baking, surprisingly provides resistance to solvents and common printing room chemicals, such as fountain solution, inks, plate cleaning agents, rejuvenators, and rubber blanket washing agents, as well as to alcohol substitutes, which are used in fountain solutions. The underlayer also is resistant to rinsing agents with a high content of esters, ethers, and ketones, which are used with ultraviolet curable inks.

[0020] The underlayer is between the hydrophilic surface of the substrate and the top layer. After imaging, it is removed by the developer in the imaged regions to reveal the underlying hydrophilic surface of the substrate. The underlayer comprises a polymeric material that is preferably soluble in the developer to prevent sludging of the developer. In addition, the polymeric material is preferably insoluble in the solvent used to coat the top layer so that the top layer can be coated over the underlayer without dissolving the underlayer. Other ingredients, such as resins that have activated methylol and/or activated alkylated methylol groups, added copolymers, photothermal conversion materials, and surfactants, may also be present in the underlayer.

[0021] The polymeric material in the underlayer comprises, in polymerized form, about 5 mol% to about 30 mol%, preferably about 10 mol% to about 30 mol% of methacrylic acid; about 20 mol% to about 75 mol%, preferably about 35 mol% to about 60 mol% of N-phenylmaleimide; N- cyclohexylmaleimide, N-benzylmaleimide, or a mixture thereof, preferably N-phenylmaleimide; optionally, about 5 mol% to about 50 mol%, preferably when present about 15 mol% to about 40 mol% of methacrylamide; and about 3 mol% to about 50 mol%, preferably about 10 mol% to about 40 mol% of one or more monomers of the structure:

$$CH_2=C(R_2)\text{-}C(O)\text{-}NH\text{-}CH_2\text{-}OR_1;$$

in which R_1 is C_1 to C_{12} alkyl, phenyl, C_1 to C_{12} substituted phenyl, C_1 to C_{12} aralkyl, or $Si(CH_3)_3$; and R_2 is H or methyl. Methods of preparation of certain of these polymeric materials are disclosed in Jarek, U.S. Pat. No. 6,475,692.

[0022] R_1 is C_1 to C_{12} alkyl, preferably C_1 to C_4 alkyl, phenyl, C_1 to C_{12} substituted phenyl, C_1 to C_{12} aralkyl, or $Si(CH_3)_3$. Typical C_1 to C_{12} alkyl groups are 2-methylbutyl, 3-methylbutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, 4-methylpentyl, 3-methylpentyl, 2-methylpentyl, 2-methylhexyl, 2-ethylpentyl, 5-methylhexyl, 2,2,4-trimethylpentyl, cyclopentyl, cyclohexyl, and alkyl groups of one to four carbon atoms, such as methyl, ethyl, *i*-propyl, *n*-propyl, cyclopropyl, cyclobutyl, *i*-butyl, *s*-butyl, *t*-butyl, and *n*-butyl. Typical C_1 to C_{12} substituted phenyl groups are *p*-methylphenyl, m-methylphenyl, o-methylphenyl, *p*-methoxyphenyl, *m*-methoxyphenyl, *o*-methoxyphenyl, *p*-ethoxyphenyl, *p*-ethylphenyl, *p*-*i*-propylphenyl, *p*-chlorophenyl, *p*-bromophenyl, *p*-cyanophenyl, *m*-cyanophenyl, *p*-fluorophenyl, *p*-nitrophenyl, *p*-thiomethoxyphenyl, *p*-(N,N-dimethylamino)phenyl, pentafluorophenyl, pentachlorophenyl, *p*-trifluoromethylphenyl, 3,5-dichlorophenyl, 3,5-dimethylphenyl, 3,5-diethylphenyl, and 2,4,6-trimethylphenyl. Typical C_1 to C_{12} aralkyl groups are benzyl, 1-phenylethyl, 2-phenylethyl, 1-phenylpropyl, and 3-phenyl propyl. Preferably, R_1 is an alkyl group of one to four carbon atoms, phenyl, benzyl, 2-phenylethyl, or trimethylsilyl. Preferred alkyl groups of one to four carbon atoms are *i*-butyl, *s*-butyl, *t*-butyl, and *n*-butyl. R_2 is hydrogen or methyl, preferably methyl.

[0023] The polymeric material comprises about 20 mol% to about 75 mol%, preferably about 35 mol% to about 60 mol%, of N-phenylmaleimide, N-cyclohexylmaleimide, N-benzylmaleimide, or a mixture thereof. N-Phenylmaleimide is preferred.

[0024] The underlayer may additionally comprise a resin or resins having activated methylol and/or activated alkylated methylol groups. Such resins include, for example: resole resins and their alkylated analogs; methylol melamine resins and their alkylated analogs, for example melamine-formaldehyde resins; methylol glycoluril resins and alkylated analogs, for example, glycoluril-formaldehyde resins; thiourea-formaldehyde resins; guanamine-formaldehyde resins; and ben-

zoguanamine-formaldehyde resins. Commercially available melamine-formaldehyde resins and glycoluril-formaldehyde resins include, for example, CYMEL® resins (Dyno Cyanamid Co., Ltd.) and NIKALAC® resins (Sanwa Chemical Co., Ltd.). The resin or resins having activated methylol and/or activated alkylated methylol groups is preferably a resole resin or a mixture of resole resins. Resole resins are well known to those skilled in the art. They are prepared by reaction of a phenol with an aldehyde under basic conditions using an excess of phenol. Commercially available resole resins include, for example, GP649D99 resole (Georgia Pacific) and BKS-5928 resole resin (Union Carbide).

[0025] Additionally, the underlayer may comprise a first added copolymer. The first added copolymer comprises, in polymerized form, about 1 to about 30 wt%, preferably about 3 to about 20 wt%, more preferably about 5 wt% of N-phenylmaleimide; about 1 to about 30 wt%, preferably about 5 to about 20 wt%, more preferably about 10 wt% of methacrylamide, about 20 to about 75 wt%, preferably about 35 to about 60 wt% of acrylonitrile and about 20 to about 75 wt%, preferably about 35 to about 60 wt% of:

$$CH_2=C\text{-}(R_4)\text{-}CO_2\text{-}CH_2CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}p\text{-}C_6H_4\text{-}R_3$$

in which R_3 is OH, COOH, or SO_2NH2; and R_4 is H or methyl;
and, optionally, about 1 to about 30 wt%, preferably, when present, about 3 to about 20 wt% of

$$CH_2=C(R_6)\text{-}CO\text{-}NH\text{-}p\text{-}C_6H_4\text{-}R_5$$

in which R_5 is OH, COOH, or SO_2NH_2; and R_6 is H or methyl.

[0026] Additionally, the underlayer may also comprise a second added copolymer. The second added copolymer comprises, in polymerized form, N-phenylmaleimide, methacrylamide, and methacrylic acid. These copolymers comprise about 25 to about 75 mol%, preferably about 35 to about 60 mol% of N-phenylmaleimide; about 10 to about 50 mol%, preferably about 15 to about 40 mol% of methacrylamide; and about 5 to about 30 mol%, preferably about 10 to about 30 mol%, of methacrylic acid. These copolymers are disclosed in Shimazu, U.S. Pat. No. 6,294,311, and Savariar-Hauck, U.S. Pat. No. 6,528,228.

[0027] The polymeric materials and the added copolymers can be prepared by methods, such as free radical polymerization, which are well known to those skilled in the art and which are described, for example, in Chapters 20 and 21, of Macromolecules, Vol. 2, 2nd Ed., H.G. Elias, Plenum, New York, 1984. Useful free radical initiators are peroxides such as benzoyl peroxide (BPO), hydroperoxides such as cumyl hydroperoxide and azo compounds such as 2,2'-azobis (isobutyronitrile) (AIBN). Suitable solvents include liquids that are inert to the reactants and which will not otherwise adversely affect the reaction. Typical solvents include, for example, esters such as ethyl acetate and butyl acetate; ketones such as methyl ethyl ketone, methyl isobutyl ketone, methyl propyl ketone, and acetone; alcohols such as methanol, ethanol, isopropyl alcohol, and butanol; ethers such as dioxane and tetrahydrofuran, and mixtures thereof.

[0028] When a photothermal conversion material is present, it typically comprises about comprises 0.1 wt% to about 25 wt%, preferably about 5 wt% to about 20 wt%, more preferably about 10 wt% to 15 wt%, of the underlayer, based on the total weight of the underlayer. When a surfactant is present in the underlayer, it typically comprises 0.05 wt% to about 1 wt%, preferably about 0.1 wt% to about 0.6 wt%, more preferably about 0.2 wt% to 0.5 wt%, based on the total weight of the underlayer. The resole resin typically comprises about 7 wt% to about 15 wt%, preferably about 8 wt% to about 12 wt%, more preferably about 10 wt% of the underlayer, based on the total weight of the underlayer.

[0029] When the underlayer does not comprise either the resin having activated methylol or activated alkylated methylol groups, the first added copolymer, or the second added copolymer, the underlayer typically comprises about 5 wt% to about 20 wt% of the photothermal conversion material and about 80 wt% to about 95 wt% the polymeric material. When the photothermal conversion material is not present, the underlayer typically comprises about 95 wt% to about 100 wt% of the polymeric material.

[0030] When the underlayer does not comprise either the first or second added copolymers, the underlayer typically comprises the resole resin, the photothermal conversion material, optionally the surfactant, and about 60 wt% to about 90 wt%, preferably about 65 wt% to about 80 wt%, of the polymeric material. When the photothermal conversion material is not present, the underlayer typically comprises the resole resin, optionally the surfactant, and about 85 wt% to abut 93 wt%, preferably about 88 wt% to about 92 wt% of the polymeric material.

[0031] When the first added copolymer is present, the underlayer typically comprises the resole resin, the photothermal conversion material, optionally the surfactant, about 40 wt% to about 80 wt%, preferably about 50 wt% to about 70 wt%, of the polymeric material, and about 5 wt% to about 25 wt%, preferably about 10 wt% to about 20 wt%, of the first added copolymer. When the photothermal conversion material is not present, the underlayer typically comprises the resole resin, optionally the surfactant, and about 60 wt% to 85 wt%, preferably about 65 wt% to about 80 wt% of the polymeric material, and about 5 wt% to about 30 wt%, preferably about 10 wt% to about 25 wt%, of the first added copolymer.

[0032] When the first added copolymer and the second added copolymer are present, the underlayer typically comprises the resole resin, the photothermal conversion material, optionally the surfactant, about 15 wt% to about 45 wt%,

preferably about 20 wt% to about 40 wt%, of the polymeric material, about 5 wt% to about 25 wt%, preferably about 10 wt% to about 20 wt%, of the first added copolymer, and about 15 wt% to about 45 wt%, preferably about 20 wt% to about 40 wt%, of the second added copolymer. When the photothermal conversion material is not present, the underlayer typically comprises the resole resin, optionally the surfactant, and about 15 wt% to about 50 wt%, preferably about 20 wt% to about 45 wt% of the polymeric material, about 5 wt% to about 30 wt%, preferably about 10 wt% to about 20 wt%, of the first added copolymer, and about 15 wt% to about 50 wt%, preferably about 20 wt% to about 45 wt%, of the second added copolymer.

[0033] The top layer, sometimes known as the imageable layer, is over the underlayer. The top layer becomes soluble or dispersible in the developer following thermal exposure. It typically comprises an ink-receptive polymeric material, known as the binder, and a dissolution inhibitor. Alternatively, or additionally, the polymeric material comprises polar groups and acts as both the binder and dissolution inhibitor.

[0034] Any top layer used in multi-layer thermally imageable elements may be used with in the imageable elements of the invention. These are described for example in Savariar-Hauck, U.S. Pat. No. 6,358,669, and Hauck, U.S. Pat. No. 6,555,291.

[0035] Preferably, the binder in the top layer is a light-stable, water-insoluble, developer-soluble, film-forming phenolic resin. Phenolic resins have a multiplicity of phenolic hydroxyl groups, either on the polymer backbone or on pendent groups. Novolac resins, resol resins, acrylic resins that contain pendent phenol groups, and polyvinyl phenol resins are preferred phenolic resins. Novolac resins are more preferred. Novolac resins are commercially available and are well known to those skilled in the art. They are typically prepared by the condensation reaction of a phenol, such as phenol, *m*-cresol, o-cresol, *p*-cresol, etc, with an aldehyde, such as formaldehyde, paraformaldehyde, acetaldehyde, etc. or a ketone, such as acetone, in the presence of an acid catalyst. Typical novolac resins include, for example, phenol-formaldehyde resins, cresol-formaldehyde resins, phenol-cresol-formaldehyde resins, *p*-*t*-butylphenol-formaldehyde resins, and pyrogallol-acetone resins. Particularly useful novolac resins are prepared by reacting m-resol, mixtures of *m*-cresol and *p*-cresol, or phenol with formaldehyde using conventional conditions.

[0036] A solvent soluble novolac resin is one that is sufficiently soluble in a coating solvent to produce a coating solution that can be coated to produce a top layer. In some cases, it may be desirable to use a novolac resin with the highest weight average molecular weight that maintains its solubility in common coating solvents, such as acetone, tetrahydrofuran, and 1-methoxypropan-2-ol. Top layers comprising novolac resins, including for example m-cresol only novolac resins (*i.e.* those that contain at least about 97 mol% m-cresol) and *m*-cresol/*p*-cresol novolac resins that have up to 10 mol% of p-cresol, having a weight average molecular weight of about 10,000 to at least about 25,000, may be used. Top layers comprising *m*-cresol/*p*-cresol novolac resins with at least 10 mol% p-cresol, having a weight average molecular weight of about 8,000 to about 25,000, may also be used. In some instances, novolac resins prepared by solvent condensation may be desirable. Top layers comprising these resins are disclosed in Pat. Pub. No. US 2004/0067432 A1.

[0037] The top layer typically comprises a dissolution inhibitor, which functions as a solubility-suppressing component for the binder. Dissolution inhibitors have polar functional groups that are believed to act as acceptor sites for hydrogen bonding with the hydroxyl groups present in the binder. The acceptor sites comprise atoms with high electron density, preferably selected from electronegative first row elements, especially carbon, nitrogen, and oxygen. Dissolution inhibitors that are soluble in the developer are preferred.

[0038] Useful polar groups for dissolution inhibitors include, for example, diazo groups; diazonium groups; keto groups; sulfonic acid ester groups; phosphate ester groups; triarylmethane groups; onium groups, such as sulfonium, iodonium, and phosphonium; groups in which a nitrogen atom is incorporated into a heterocyclic ring; and groups that contain a positively charged atom, especially a positively charged nitrogen atom, typically a quaternized nitrogen atom, *i.e.*, ammonium groups. Compounds that contain a positively charged (*i.e.*, quaternized) nitrogen atom useful as dissolution inhibitors include, for example, tetraalkyl ammonium compounds, and quaternized heterocyclic compounds such as quinolinium compounds, benzothiazolium compounds, pyridinium compounds, and imidazolium compounds. Compounds containing other polar groups, such as ether, amine, azo, nitro, ferrocenium, sulfoxide, sulfone, and disulfone may also be useful as dissolution inhibitors.

[0039] The dissolution inhibitor may be a monomeric and/or polymeric compound that comprises a diazobenzoquinone moiety and/or a diazonaphthoquinone moiety. Other useful dissolution inhibitors are triarylmethane dyes, such as ethyl violet, crystal violet, malachite green, brilliant green, Victoria blue B, Victoria blue R, Victoria blue BO, BASONYL® Violet 610, and D11 (PCAS, Longjumeau, France). These dyes can also act as contrast dyes, which distinguish the unimaged regions from the imaged regions in the developed imageable element.

[0040] When a dissolution inhibitor is present in the top layer, it typically comprises at least about 0.1 wt%, typically about 0.5 wt% to about 30 wt%, preferably about 1 wt% to 15 wt%, based on the dry weight of the layer.

[0041] Alternatively, or additionally, the polymeric material in the top layer can comprise polar groups that act as acceptor sites for hydrogen bonding with the hydroxy groups present in the polymeric material and, thus, act as both the polymeric material and dissolution inhibitor. The level of derivatization should be high enough that the polymeric

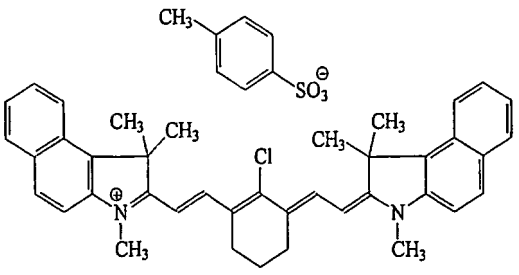
material acts as a dissolution inhibitor, but not so high that, following thermal imaging, the polymeric material is not soluble in the developer. Although the degree of derivatization required will depend on the nature of the polymeric material and the nature of the moiety containing the polar groups introduced into the polymeric material, typically about 0.5 mol% to about 5 mol%, preferably about 1 mol% to about 3 mol%, of the hydroxyl groups will be derivatized. Derivatization of phenolic resins with compounds that contain the diazonaphthoquinone moiety is well known and is described, for example, in West, U.S. Pat. Nos. 5,705,308, and 5,705,322.

[0042] One group of polymeric materials that comprise polar groups and function as dissolution inhibitors are derivatized phenolic polymeric materials in which a portion of the phenolic hydroxyl groups have been converted to sulfonic acid esters, preferably phenyl sulfonates or *p*-toluene sulfonates. Derivatization can be carried out by reaction of the polymeric material with, for example, a sulfonyl chloride such as *p*-toluene sulfonyl chloride in the presence of a base such as a tertiary amine. A useful material is a novolac resin in which about 1 mol% to 3 mol%, preferably about 1.5 mol% to about 2.5 mol%, of the hydroxyl groups have been converted to phenyl sulfonate or *p*-toluene sulfonate (tosyl) groups.

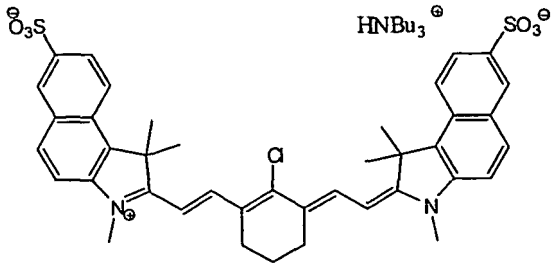
[0043] Imageable elements that are to be imaged with infrared radiation typically comprise an infrared absorber, known as a photothermal conversion material. Photothermal conversion materials absorb radiation and convert it to heat. Although a photothermal conversion material is not necessary for imaging with a hot body, imageable elements that contain a photothermal conversion material may also be imaged with a hot body, such as a thermal head or an array of thermal heads.

[0044] The photothermal conversion material may be any material that can absorb radiation and convert it to heat. Suitable materials include, for example, dyes and pigments. Suitable pigments include, for example, carbon black, Heliogen Green, Nigrosine Base, iron (III) oxide, manganese oxide, Prussian Blue, and Paris blue. Because of its low cost and wide absorption bands that allow it to be used with imaging devices having a wide range of peak emission wavelengths, one particularly useful pigment is carbon black. The size of the pigment particles should not be more than the thickness of the layer that contains the pigment. Preferably, the size of the particles will be half the thickness of the layer or less.

[0045] To prevent sludging of the developer by insoluble material, photothermal conversion materials that are soluble in the developer are preferred. The photothermal conversion material may be a dye with the appropriate absorption spectrum and solubility. Dyes, especially dyes with a high extinction coefficient in the range of 750 nm to 1200 nm, are preferred. Examples of suitable dyes include dyes of the following classes: methine, polymethine, arylmethine, cyanine, hemicyanine, streptocyanine, squarylium, pyrylium, oxonol, naphthoquinone, anthraquinone, porphyrin, azo, croconium, triarylamine, thiazolium, indolium, oxazolium, indocyanine, indotricarbocyanine, oxatricarbocyanine, phthalocyanine, thiocyanine, thiatricarbocyanine, merocyanine, cryptocyanine, naphthalocyanine, polyaniline, polypyrrole, polythiophene, chalcogenopyryloarylidene and bis(chalcogenopyrylo)-polymethine, oxyindolizine, pyrazoline azo, and oxazine classes. Absorbing dyes are disclosed in numerous publications, for example, Nagasaka, EP 0,823,327; DeBoer, U.S. Pat. No. 4,973,572; Jandrue, U.S. Pat. No. 5,244,771; Patel, U.S. Pat. No. 5,208,135; and Chapman, U.S. Pat. No. 5,401,618. Other examples of useful absorbing dyes include: ADS-830A and ADS-1064 (American Dye Source, Montreal, Canada), EC2117 (FEW, Wolfen, Germany), Cyasorb IR 99 and Cyasorb IR 165 (Glendale Protective Technology), Epolite IV-62B and Epolite III-178 (Epoline), SpectraIR 830A and SpectraIR 840A (Spectra Colors), as well as IR Dye A, and IR Dye B, whose structures are shown below.



IR Dye A



IR Dye B

[0046] To prevent ablation during imaging with infrared radiation, the top layer is substantially free of photothermal conversion material. That is, the photothermal conversion material in the top layer, if any, absorbs less than about 10% of the imaging radiation, preferably less than about 3% of the imaging radiation, and the amount of imaging radiation absorbed by the top layer, if any, is not enough to cause ablation of the top layer.

[0047] The amount of infrared absorber is generally sufficient to provide an optical density of at least 0.05, and preferably, an optical density of from about 0.5 to at least about 2 to 3 at the imaging wavelength. As is well known to those skilled in the art, the amount of compound required to produce a particular optical density can be determined from the thickness of the underlayer and the extinction coefficient of the infrared absorber at the wavelength used for imaging using Beer's law.

[0048] When an absorber layer is present, it is between the top layer and the underlayer. The absorber layer preferably consists essentially of the photothermal conversion material and, optionally, a surfactant. It may be possible to use less of the photothermal conversion material if it is present in a separate absorber layer. The absorber layer preferably has a thickness sufficient to absorb at least 90%, preferably at least 99%, of the imaging radiation. Typically, the absorber layer has a coating weight of about 0.02 g/m^2 to about 2 g/m^2, preferably about 0.05 g/m^2 to about 1.5 g/m^2. Elements that comprise an absorber layer are disclosed in Shimazu, U.S. Pat. No. 6,593,055.

[0049] To further minimize migration of the infrared absorber from the underlayer to the top layer during manufacture and storage of the imageable element, the element may comprise a barrier layer between the underlayer and the top layer. The barrier layer comprises a polymeric material that is soluble in the developer. If this polymeric material is different from the polymeric material in the underlayer, it is preferably soluble in at least one organic solvent in which the polymeric material in the underlayer is insoluble. A preferred polymeric material for the barrier layer is polyvinyl alcohol. When the polymeric material in the barrier layer is different from the polymeric material in the underlayer, the barrier layer should be less than about one-fifth as thick as the underlayer, preferably less than a tenth of the thickness of the underlayer.

[0050] The imageable element may be prepared by sequentially applying the underlayer over the hydrophilic surface of the substrate; applying the absorber layer or the barrier layer if present, over the underlayer; and then applying the top layer using conventional techniques. The terms "solvent" and "coating solvent" include mixtures of solvents. These terms are used although some or all of the materials may be suspended or dispersed in the solvent rather than in solution. Selection of coating solvents depends on the nature of the components present in the various layers.

[0051] The underlayer may be applied by any conventional method, such as coating or lamination. Typically the ingredients are dispersed or dissolved in a suitable coating solvent, and the resulting mixture coated by conventional methods, such as spin coating, bar coating, gravure coating, die coating, or roller coating. The underlayer may be applied, for example, from mixtures of methyl ethyl ketone, 1-methoxypropan-2-ol, butyrolactone, and water; from mixtures of diethyl ketone, water, methyl lactate, and γ-butyrolactone; and from mixtures of diethyl ketone, water, and methyl lactate.

[0052] When neither a barrier layer nor an absorber layer is present, the top layer is coated on the underlayer. To prevent the underlayer from dissolving and mixing with the top layer, the top layer should be coated from a solvent in which the underlayer layer is essentially insoluble. Thus, the coating solvent for the top layer should be a solvent in which the components of the top layer are sufficiently soluble that the top layer can be formed and in which any underlying layers are essentially insoluble. Typically, the solvents used to coat the underlying layers are more polar than the solvent used to coat the top layer. The top layer may be applied, for example, from diethyl ketone, or from mixtures of diethyl ketone and 1-methoxy-2-propyl acetate. An intermediate drying step, *i.e.*, drying the underlayer, if present, to remove coating solvent before coating the top layer over it, may also be used to prevent mixing of the layers.

[0053] Alternatively, the underlayer, the top layer or both layers may be applied by conventional extrusion coating methods from a melt mixture of layer components. Typically, such a melt mixture contains no volatile organic solvents.

[0054] The element may be thermally imaged with a laser or an array of lasers emitting modulated near infrared or

infrared radiation in a wavelength region that is absorbed by the imageable element. Infrared radiation, especially infrared radiation in the range of about 800 nm to about 1200 nm, is typically used for imaging. Imaging is conveniently carried out with a laser emitting at about 830 nm, about 1056 nm, or about 1064 nm. Suitable commercially available imaging devices include image setters such as the CREO® Trendsetter (Creo, Burnaby, British Columbia, Canada), the Screen PlateRite model 4300, model 8600, and model 8800 (Screen, Rolling Meadows, Chicago, Illinois, USA), and the Gerber Crescent 42T (Gerber).

[0055] Alternatively, the imageable element may be thermally imaged using a hot body, such as a conventional apparatus containing a thermal printing head. A suitable apparatus includes at least one thermal head but would usually include a thermal head array, such as a TDK Model No. LV5416 used in thermal fax machines and sublimation printers. the GS618-400 thermal plotter (Oyo Instruments, Houston, TX, USA), or the Model VP-3500 thermal printer (Seikosha America, Mahwah, NJ, USA).

[0056] Imaging produces an imaged element, which comprises a latent image of imaged regions and complementary unimaged regions. Development of the imaged element to form a printing plate, or printing form, converts the latent image to an image by removing the imaged regions, revealing the hydrophilic surface of the underlying substrate.

[0057] Suitable developers depend on the solubility characteristics of the ingredients present in the imageable element. The developer may be any liquid or solution that can penetrate and remove the imaged regions of the imageable element without substantially affecting the complementary unimaged regions. While not being bound by any theory or explanation, it is believed that image discrimination is based on a kinetic effect. The imaged regions of the top layer are removed more rapidly in the developer than the unimaged regions. Development is carried out for a long enough time to remove the imaged regions of the top layer and the underlying regions of the other layer or layers of the element, but not long enough to remove the unimaged regions of the top layer. Hence, the top layer is described as being "not removable" by, or "insoluble" in, the developer prior to imaging, and the imaged regions are described as being "soluble" in, or "removable" by, the developer because they are removed, *i.e.* dissolved and/or dispersed, more rapidly in the developer than the unimaged regions. Typically, the underlayer is dissolved in the developer and the top layer is dissolved and/or dispersed in the developer.

[0058] High pH developers can be used. High pH developers typically have a pH of at least about 11, more typically at least about 12, even more typically from about 12 to about 14. High pH developers also typically comprise at least one alkali metal silicate, such as lithium silicate, sodium silicate, and/or potassium silicate, and are typically substantially free of organic solvents. The alkalinity can be provided by using a hydroxide or an alkali metal silicate, or a mixture. Preferred hydroxides are ammonium, sodium, lithium and, especially, potassium hydroxides. The alkali metal silicate has a SiO_2 to M_2O weight ratio of at least 0.3 (where M is the alkali metal), preferably this ratio is from 0.3 to 1.2, more preferably 0.6 to 1.1, most preferably 0.7 to 1.0. The amount of alkali metal silicate in the developer is at least 20 g SiO_2 per 100 g of composition and preferably from 20 to 80 g, most preferably it is from 40 to 65 g. High pH developers can be used in an immersion processor. Typical high pH developers include PC9000, PC3000, Goldstar™, Greenstar™, ThermaIPro™, PROTHERM®, MX 1813, and MX1710, aqueous alkaline developers, all available from Kodak Polychrome Graphics LLC. Another useful developer contains 200 parts of Goldstar™ developer, 4 parts of polyethylene glycol (PEG) 1449, 1 part of sodium metasilicate pentahydrate, and 0.5 part of TRITON® H-22 surfactant (phosphate ester surfactant).

[0059] Alternatively, the imaged imageable elements can be developed using a solvent based developer in an immersion processor or a spray on processor. Typical commercially available solvent based developers include 956 Developer, 955 Developer and SP200 (Kodak Polychrome Graphics, Norwalk, CT, USA). Commercially available spray on processors include the 85 NS (Kodak Polychrome Graphics). Commercially available immersion processors include the Mercury™ Mark V processor (Kodak Polychrome Graphics); the Global Graphics Titanium processor (Global Graphics, Trenton, NJ, USA); and the Glunz and Jensen Quartz 85 processor (Glunz and Jensen, Elkwood, VA, USA).

[0060] Following development, the resulting printing plate is rinsed with water and dried. Drying may be conveniently carried out by infrared radiators or with hot air. After drying, the printing plate may be treated with a gumming solution comprising one or more water-soluble polymers, for example polyvinylalcohol, polymethacrylic acid, polymethacrylamide, polyhydroxyethylmethacrylate, polyvinylmethylether, gelatin, and polysaccharide such as dextrine, pullulan, cellulose, gum arabic, and alginic acid. A preferred material is gum arabic.

[0061] The developed and gummed plate is baked to increase the press runlength of the plate. Baking can be carried out, for example, at about 220°C to about 260°C for about 5 minutes to about 15 minutes, or at a temperature of about 110°C to about 130°C for about 25 to about 35 min.

Industrial Applicability

[0062] The imageable elements of the invention are a multi-layer, positive working, thermally imageable, bakeable lithographic printing precursors that produce lithographic printing plates that have a long press runlength and are resistant to press chemistries. They are especially useful for use with ultraviolet curable inks, in which aggressive washes that contain organic solvents (UV wash) are used. Once a lithographic printing plate precursor has been imaged and developed

to form a lithographic printing plate, printing can then be carried out by applying a fountain solution and then lithographic ink to the image on its surface. The fountain solution is taken up by the unimaged regions, *i.e.*, the surface of the hydrophilic substrate revealed by the imaging and development process, and the ink is taken up by the imaged regions, *i.e.*, the regions not removed by the development process. The ink is then transferred to a suitable receiving material (such as cloth, paper, metal, glass or plastic) either directly or indirectly using an offset printing blanket to provide a desired impression of the image thereon.

EXAMPLES

[0063] In the Examples, "coating solution" refers to the mixture of solvent or solvents and additives coated, even though some of the additives may be in suspension rather than in solution, and "total solids" refers to the total amount of nonvolatile material in the coating solution even though some of the additives may be nonvolatile liquids at ambient temperature. Except where indicated, the indicated percentages are percentages by weight based on the total solids in the coating solution.

Glossary

[0064]

956 Developer	Solvent based (phenoxyethanol) alkaline negative developer (Kodak Polychrome Graphics, Norwalk, CT, USA)
BC	1-Butoxyethanol (BUTYL CELLOSOLVE®)
BYK-307	Polyethoxylated dimethylpolysiloxane copolymer (BYK Chemie, Wallingford, CT, USA
CREO® Trendsetter 3230	Commercially available platesetter, using Procom Plus software and operating at a wavelength of 830 nm (Creo Products, Burnaby, BC, Canada)
Copolymer 1	Copolymer of 5 wt% N-phenylmaleimide, 10 wt% methacrylamide, 45 wt% acrylonitrile; and 40 wt% $CH_2C(CH_3)CO_2CH_2CH_2$-NH-CO-NH-*p*-C_6H_4-OH
Copolymer 2	Copolymer of 5 wt% N-phenylmaleimide, 10 wt% methacrylamide, 6 wt% benzoic acid methacrylamide, 48 wt% acrylonitrile, and 31 wt% $CH_2C(CH_3)CO_2CH_2CH_2$-NH-CO-NH-*p*-C_6H_4-OH
DAA	Diacetone alcohol
Deletion Fluid 243	Deletion fluid (Kodak Polychrome Graphics, Norwalk, CT, USA)
ELECTRA EXCEL®	Thermally sensitive, positive working, single layer, conditioned, inhibited novolac-containing plate printing plate precursor (Kodak Polychrome Graphics, Norwalk, CT, USA).
Ethyl violet	C.I. 42600; CAS 2390-59-2 ($lambda_{max}$ = 596 nm) [(*p*-$(CH_3CH_2)_2NC_6H_4)_3C^+$ Cl^-] (Aldrich, Milwaukee, WI, USA)
GOLDSTAR™ Developer	Sodium metasilicate based aqueous alkaline developer (Kodak Polychrome Graphics, Norwalk, CT, USA)
IR Dye A	Infrared absorbing dye ($lambda_{max}$ = 830 nm) (Eastman Kodak, Rochester, NY, USA) (see structure above)
N-13	Novolac resin; 100% *m*-cresol; MW 13,000 (Eastman Kodak Rochester, NY, USA)
PM	DOWANOL® PM (propylene glycol methyl ether; 1-methoxy-2-propanol) (Dow, Midland, MI, USA)
Resole resin	GP649D99 (Georgia-Pacific, Atlanta, GA, USA)
Substrate A	0.3 gauge, aluminum sheet which had been electrograined, anodized and treated with a solution of sodium dihydrogen phosphate/sodium fluoride
Substrate B	Aluminum sheet that had been electrochemically grained, anodized, and coated with polyvinyl phosphonic acid

Example 1

[0065] This example illustrates preparation of a copolymer containing 41.5 mol% N-phenylmaleimide, 21 mol% methacrylic acid, and 37.5 mol% N-(isobutoxymethyl)acrylamide. N-Phenylmaleimide (19.31 g), methacrylic acid (4.86 g), N-(*iso*-butoxymethyl)acrylamide (15.84 g) (Cytec Industries, Charlotte, NC, USA), and 50:50 (v:v) dioxolane/ethanol

(126.01 g) were placed in a 1 L reaction kettle fitted with a reflux condenser, nitrogen supply, thermometer, stirrer, and heating mantle. Nitrogen was bubbled through the reaction mixture for one hour. The reaction was heated to 60°C under nitrogen and 2,2-azobisisobutyronitrile (AIBN) (0.054 g in 10 g of dioxolane/ethanol) was added. The reaction mixture was stirred under nitrogen at 60°C for about 20 hr. The reaction mixture was slowly added to water (about 1 L), and the resulting precipitate filtered. The precipitate was washed with about 1 L of 80:20 ethanol/water, filtered again, and dried for two days at 50°C. Yield: 79%

Example 2

[0066] This example illustrates preparation of a copolymer containing 41.5 mol% N-phenylmaleimide, 21 mol% methacrylic acid, 19 mol% methacryamide, and 18.5 mol% N-(*iso*-butoxymethyl)acrylamide. The procedure of Example 1 was repeated except that N-phenylmaleimide (21.26 g), methacrylic acid (5.35 g), methacrylamide (4.78 g), N-(isobutoxymethyl)acrylamide (8.60 g) and 50:50 (v:v) dioxolane/ethanol (126.01 g) were used to prepare the copolymer. Yield: 75%.

Example 3

[0067] This example illustrates preparation of a copolymer containing 41.5 mol% N-phenylmaleimide, 21 mol% methacrylic acid, 19 mol% methacryamide, and 18.5 mol% N-(butoxymethyl)acrylamide. The procedure of Example 1 was repeated except that N-phenylmaleimide (21.26 g), methacrylic acid (5.35 g), methacrylamide (4.78 g), N-(butoxymethyl)-acrylamide (8.60 g) (Cytec Industries, Charlotte, NC, USA) and 50:50 (v:v) dioxolane/ethanol (126.01 g) were used to prepare the copolymer. Yield: 72%.

Example 4

[0068] This example illustrates preparation of a functionalized novolac resin. N-13 (24 g, 199.75 millimoles) was added in acetone (66 g) with stirring and the resulting mixture cooled 10°C in an ice/water bath. *p*-Toluene sulfonyl chloride (20.02 millimoles) at 10°C over 1 min. Triethylamine (19.63 millimoles) was added at 10°C over 2 min. The reaction mixture was stirred for 10 min at less than 15°C. Acetic acid (8.33 millimoles) was added at 10°C over 10 sec, and the reaction mixture stirred for 15 min. Water/ice (160 g), and acetic acid (1.2 g, 20.02 millimoles) was added over several minutes at 15°C and the reaction mixture stirred below 15°C for 5 min.

[0069] The supernatant was decanted from the tacky solid that formed in the bottom of the reaction flask. Acetone (354 g) was added, and the reaction mixture stirred until a clear solution was obtained. Water/ice (160 g) and acetic acid (1.2 g, 20.02 millimoles) were added over several minutes and the reaction mixture stirred for 5 min below 15°C. The supernatant was decanted from the tacky solid. Additional acetone (354 g) was added and the reaction mixture stirred until a clear solution was obtained. 25% of the acetone solution was added to a mixture of ice (460 g), water (460 g) and acetic acid (0.5 g). The resulting mixture was stirred for 20 minutes, the precipitate allowed to settle, and the supernatant decanted. The process was repeated with the rest of the acetone solution. The damp polymer fractions were combined, washed twice with water (460 g), and dried. Yield: 88%.

Comparative Example 1

[0070] This example illustrates preparation of a copolymer containing 41.5 mol% N-phenylmaleimide, 21 mol% methacrylic acid, and 37.5% methacrylamide The procedure of Example 1 was repeated except that N-phenylmaleimide (23.59 g), methacrylic acid (5.93 g), methacrylamide (10.48 g) and dioxolane/ethanol (50:50 (v:v); 126.01 g). After precipitation of the copolymer in water, the copolymer was washed with about 1 L of 80:20 ethanol/water containing about 5 drops of concentrated hydrochloric acid, filtered again, washed with about 1 L of 80:20 ethanol/water, filtered again, and dried for two days at 50°C. Yield: 80%.

Comparative Examples 2 to 4 and Examples 5 to 10

[0071] Comparative Example 2 is an ELECTRA EXCEL® thermally sensitive, positive working, single layer, conditioned, inhibited novolac-containing plate printing plate precursor. It develops in high pH developer, is bakeable, but has poor resistance to press chemicals. Comparative Examples 3 and 4 and Examples 5 to 10 were prepared by the following procedure.

[0072] Underlayer Coating solutions containing the components listed in Table 1 in methyl ethyl ketone/1-methoxypropan-2-ol/butyrolactone/water (65/15/10/10, w:w:w:w) were coated onto substrate A using a wire wound bar. The resulting element comprising the underlayer and the substrate was dried at 135°C for 35 sec. The coating weight of

each of the resulting underlayers was 1.3 g/m^2.

[0073] Top Layer A coating solution containing 99.35 parts by weight of the functionalized novolac resin prepared in Example 4, 0.3 parts by weight of ethyl violet, and 0.35 parts by weight of BYK-307 in diethyl ketone/1-methoxy-2-propyl acetate (92/8, w:w) was coated onto each underlayer, using a wire wound bar. Each resulting imageable element was dried at 135°C for 35 seconds. The coating weight of each of the resulting top layers was 0.9 g/m^2.

Table 1

	Example			
	C3	C4	5	6
Component	Parts by Weight			
Copolymer of Comparative Example 1	59.65	74.65	-	-
Copolymer of Example 1	-	-	59.65	74.65
Copolymer 1	15	-	15	-
GP649D99	10	10	10	10
IR Dye A	15	15	15	15
BYK-307	0.35	0.35	0.35	0.35

Table 1 (continued)

	Example			
	7	8	9	10
Component	Parts by Weight			
Copolymer of Example 2	59.65	74.65	-	-
Copolymer of Example 3	-	-	59.65	74.65
Copolymer 1	15	-	15	-
GP649D99	10	10	10	10
IR Dye A	15	15	15	15
BYK-307	0.35	0.35	0.35	0.35

[0074] The imageable elements from Comparative Examples 2 to 4 (C2 to C4) and Examples 5 to 10 were evaluated with the following tests. The results are given in Table 2.

[0075] Developer drop test on underlayer only. A large drop of Goldstar™ developer was placed on the underlayer of each element at 22°C, and the time required to dissolve the layer ("coating") was noted.

[0076] Developer drop test on complete imageable element. A large drop of Goldstar™ developer was placed on each imageable element at 22°C and the time required to dissolve the layers is noted.

[0077] Cleanout and Resolution Each imageable element was imaged with 830 nm radiation with an internal test pattern (plot 0), on a CREO® 3230 Trendsetter at 100 to 180 mJ/cm^2, in 20 mJ/cm^2 increments (at 9W). Each imaged imageable element was machine processed with Goldstar™ developer in a Kodak Polychrome Graphics Mercury™ Mark V Processor (750 mm/min processing speed, 23°C developer temperature). The resulting printing plates were evaluated for cleanout (first imaging exposure where exposed regions dissolve completely in developer) and best resolution (imaging exposure where plate performs best).

[0078] Solvent resistance drop test on complete imageable element. A large drop of either diacetone alcohol/water (80:20, v:v) or 2-butoxyethanol/water (80:20, v:v) was placed on each imageable element at 22°C. The time required to dissolve the layers was noted, and the amount of material removed after 1 min was assessed.

[0079] Baking test Each imageable elements was baked at 210°C and 230°C for 8 minutes in a Mathis LTE labdryer oven (Werner Mathis, Switzerland) (fan speed of 1000 rpm). After the element was baked, a 6 minute drop test was carried out with methyl lactate/diethyl ketone/butyrolactone/water (45/36/10/9, w:w) a typical coating solvent composition for this type of element, and the amount of material removed was assessed.

[0080] Deletion gel test A Kodak Polychrome Graphics positive deletion gel (contains hydrofluoric acid) was applied to the baked imageable elements for up to 3 min, and the amount of time required for removal of the baked layer ("coating") was noted.

Table 2

Example	Goldstar^{tm} Developer Drop Test (sec)		Minimum exposure required for (mJ/cm^2)	
	Under-layer	Complete element	Clean out	Best Resolution
C2	n/a	50	100	160
C3	8	180	125	135
C4	5	90	120	125
5	>60	300	180	>180
6	>60	90	180	>180
7	25	240	155	160
8	18	150	155	160
9	25	240	150	160
10	16	120	150	150

Table 2 (continued)

Example	Solvent resistance drop test (sec)		Weight loss after 1 minute (%)	
	DAA/water	BC/water	DAA/water	BC/water
C2	<10	<10	100	100
C3	>180	>180	25	20
C4	>180	>180	25	35
5	20	20	100	100
6	20	20	100	100
7	90	>180	80	35
8	60	60	100	100
9	90	>180	80	20
10	60	>180	100	40

Table 2 (continued)

Example	Baked plates at 210°C		Baked plates at 230°C	
	6 Minute drop test	Deletion gel	6 Minute drop test	Deletion gel
C2	A little coating removed	A little coating removed	No coating removed	No coating removed
C3	Most coating removed	Most coating removed	A little coating removed	A little coating removed
C4	All coating removed	All coating removed	All coating removed	All coating removed
5	No coating removed	No coating removed	No coating removed	No coating removed
6	No coating removed	No coating removed	No coating removed	No coating removed
7	No coating removed	No coating removed	No coating removed	No coating removed
8	A little coating removed	A little coating removed	A little coating removed	A little coating removed
9	No coating removed	A little coating removed	No coating removed	No coating removed
10	A little coating removed	A little coating removed	A little coating removed	A little coating removed

Example 11

[0081] This example illustrates preparation of a copolymer having 40 mol% N-phenylmaleimide, 25 mol% methacrylic acid, 25 mol% methacrylamide and 10 mol% N-(Isobutoxymethyl)acrylamide. The procedure of Example 1 was repeated except that N-phenylmaleimide (21.68 g), methacrylic acid (6.74 g), methacrylamide (6.66 g), N-(*iso*-butoxymethyl) acrylamide (4.92 g) and dioxolane/ethanol (50:50 (v:v); 126.01 g) were used to prepare the copolymer. Yield: 79%

Example 12

[0082] This example illustrates preparation of a copolymer having 40 mol% N-phenylmaleimide, 25 mol% methacrylic acid, 25 mol% methacrylamide and 10 mol% N-(butoxymethyl)acrylamide. The procedure of Example 1 was repeated except that N-phenylmaleimide (21.68 g), methacrylic acid (6.74 g), methacrylamide (6.66 g), N-(butoxymethyl)acryla-

mide (4.92 g), and dioxolane/- ethanol (50:50 (v:v); 126.01 g) were used to prepare the copolymer. Yield: 82%.

Example 13

[0083] This example illustrates preparation of a copolymer having 30 mol% N-phenylmaleimide, 20 mol% methacrylic acid, 35 mol% methacrylamide and 15 mol% N-(isobutoxymethyl)acrylamide. The procedure of Example 1 was repeated except that N-phenylmaleimide (16.96 g), methacrylic acid (5.62 g), methacrylamide (9.72 g), N-(butoxymethyl)acrylamide (7.70 g), and dioxolane/- ethanol (50:50 (v:v); 126.01 g) were used to prepare the copolymer. Yield: 83%.

Examples 14 to 19

[0084] Imageable elements were prepared as in Examples 5 to 10, except that the ingredients listed in Table 3 were used in the underlayer.

Table 3

	Example			
	14	15	16	17
Component	Parts by Weight			
Copolymer of Example 11	59.65	74.65	-	-
Copolymer of Example 12	-	-	59.65	74.65
Copolymer 2	15	-	15	-
GP649D99	10	10	10	10
IR Dye A	15	15	15	15
BYK-307	0.35	0.35	0.35	0.35

Table 3 (continued)

	Example	
	18	19
	Parts by Weight	
Copolymer of Example 13	59.65	74.65
Copolymer 2	15	-
GP649D99	10	10
IR Dye A	15	15
BYK-307	0.35	0.35

[0085] The resulting imageable elements were evaluated as in Examples 5 to 10, except that the 6 minute drop test was not carried out and the baking test was assessed on a 10 point scale in which 1 = no removal, and 10 = complete removal. The results are given in Table 4.

Table 4

Example	Goldstar™ Developer Drop Test (sec)		Minimum exposure required for (mJ/cm²)	
	Under-layer	Complete Element	Clean Out	Best Resolution
14	15	180	<120	<120
15	5	60	<120	<120
16	15	120	<120	<120
17	5	80	<120	<120
18	30	150	<100	100
19	5	90	<100	100

Table 4 (continued)

Example	Solvent resistance drop test (sec)		Weight loss after 1 minute (%)	
	DAA/water	BC/water	DAA/water	BC/water
14	180	>180	30	10
15	180	180	35	30
16	>180	>180	20	5
17	180	>180	30	15
18	>180	>180	25	20
19	180	180	30	40

Table 4 (continued)

Example	Baked plates at 210°C	Baked plates at 230°C
	Deletion gel[a]	Deletion gel[a]
14	3	1
15	5	3
16	3	2
17	5	3
18	1	1
19	4	1

[a]1 = no removal; 10 = complete removal

Comparative Example 5

[0086] This example illustrates preparation of a copolymer containing 40 mol% N-phenylmaleimide, 25 mol% methacrylic acid, and 35 mol% methacrylamide.

[0087] To a 1:1 mixture of dioxolane/methanol (250 ml) in a 500 ml 3-necked round-bottomed flask equipped with a stirrer, thermometer, nitrogen inlet and reflux condenser was added a 250 ml of a mixture of methacrylic acid (21.52 g), N-phenylmaleimide (69.27 g), and methacrylamide (29.79 g). After the monomers dissolved with stirring, AIBN (1.50 g) was added and the reaction mixture heated at 60°C with stirring for 22 hr. The resulting polymer was by precipitated in 2000 ml of water, filtered, and dried in the oven at 40°C for 2 days.

Example 20

[0088] This example illustrates preparation of a polymeric material containing 35 mol% N-phenylmaleimide, 20 mol% methacrylic acid, 20 mol% methacrylamide, and 25 mol% N-methoxymethylmethacrylamide. The procedure of Comparative Example 5 was repeated except that 250 ml of a mixture of methacrylic acid (17.22 g), N-phenylmaleimide (60.61 g), methacrylamide (17.02 g) and N-methoxymethymethacrylamide (32.25g) and 1.65 g of AIBN was used.

Comparative Example 6 and Example 21

[0089] These examples show evaluation of the copolymers formed in Comparative Example 5 and the polymeric material formed Example 20 in the underlayer of an imageable element.

[0090] The copolymer formed in Comparative Example 5 (2.12 g) and IR Dye A (0.38 g) were dissolved in 30 g of a mixture of 2-butanol (65%), PM (15%), γ-butyrolatone (10%), and water (10%), coated onto a Substrate B, and dried to give an underlayer with a coating weight of 1.40 g/m^2. 10 g of a 15 mol% tosylated novolac resin (Diversitec, Fort Collins, CO, USA) and 0.025 g of ethyl violet were dissolved in 50 g of a mixture of diethyl ketone/1-methoxy-2-propyl acetate (90:10 w%), coated on top of the underlayer, and dried at 92°C for 90 min. The coating weight of the top layer was 0.80 g/m^2. The imageable element was imaged in a CREO® Trendsetter with 9.5W and 225 rpm. The resulting imaged imageable element was developed in GOLDSTAR™ DC developer to form a lithographic printing plate. The image areas had good resistance to the developer. The plate showed good developability in the imaged areas, giving a clean background and good resolution. An additional imaged imageable element was developed in 956 Developer. The resulting printing plate showed a clean background and good resolution.

[0091] The procedure was repeated except that the polymeric material prepared in Example 20 was used in the underlayer. The coating weight of the underlayer was 1.51 g/m^2, and the coating weight of the top layer was 0.80 g/m^2. The imaged imageable element developed with GOLDSTAR™ DC Developer had good resistance to the developer. The element showed good developability in the imaged areas, giving a clean background and good resolution. The imaged imageable element developed with 956 Developer showed a clean background and good resolution.

[0092] The copolymer formed in Comparative Example 5 and the polymeric material formed in Example 20 were each coated onto Substrate B as described above to form an element consisting of the underlayer on the substrate. The underlayers were evaluated as follows.

[0093] To determine the solvent resistance of the underlayer, each element consisting of the underlayer on the substrate was soaked in BC/water (80/20) for 5 min and the weight loss determined. The soak losses were: 30% for the element containing the copolymer formed in Comparative Example 5, and 21% for the element containing the polymeric material formed in Example 20. Under the same conditions, the single layer of an ELECTRA EXCEL® printing plate precursor was completely removed (100% soak loss).

[0094] Bakeability of the underlayer was determined by baking the elements consisting of the underlayer on the substrate at 235°C for 8 min and applying Deletion Fluid 243 to the surface of the underlayer. The underlayer consisting of the copolymer formed in Comparative Example 5 deleted completely within 1 min. The underlayer consisting of the polymeric material formed in Example 20 showed no deletion after 8 min.

[0095] Having described the invention, we now claim the following

Claims

1. An imageable element comprising:

a substrate;
a underlayer over the substrate; and
a top layer over the underlayer;

in which:

the element comprises a photothermal conversion material;
the top layer is substantially free of the photothermal conversion material;
the top layer is ink receptive;
before thermal imaging, the top layer is not removable by an alkaline developer;
after thermal imaging to form imaged regions in the top layer, the imaged regions are removable by the alkaline developer;
the underlayer is removable by the alkaline developer, and
the underlayer comprises a polymeric material that comprises, in polymerized form:

about 5 mol% to about 30 mol% of methacrylic acid;
about 20 mol% to about 75 mol% of N-phenylmaleimide, N-cyclohexylmaleimide, N-benzylmaleimide, or a mixture thereof; and
about 3 mol% to about 50 mol% of a compound (a), represented by the formula:

$CH_2C(R_2)C(O)NHCH_2OR_1$,

in which R_1 is C_1 to C_{12} alkyl, phenyl, C_1 to C_{12} substituted phenyl, C_1 to C_{12} aralkyl, or $Si(CH_3)_3$; and R_2 is H or methyl.

2. The element of claim 1 in which R_1 is C_1 to C_4 alkyl, phenyl, benzyl, 2-phenylethyl, or $Si(CH_3)_3$; and R_2 is methyl and the polymeric material comprises about 10 mol% to about 30 mol% of methacrylic acid; about 35 mol% to about 60 mol% of N-phenylmaleimide; and about 10 mol% to about 40 mol% of compound (a).

3. The element of claim 2 in which the polymeric material additionally comprises about 15 mol% to about 40 mol% of methacrylamide.

4. The element of any preceding claim in which the underlayer additionally comprises a resin having activated methylol or activated alkylated methylol groups.

5. The element of any preceding claim in which the underlayer additionally comprises a first added copolymer, and the first added copolymer comprises, in polymerized form, about 1 wt% to about 30 wt% of N-phenylmaleimide; about 1 wt% to about 30 wt% of methacrylamide; about 20 wt% to about 75 wt% of acrylonitrile; and about 20 wt% to about 75 wt% of compound (b), represented by the formula:

$CH_2C(R_4)CO_2CH_2CH_2$-NH-CO-NH-*p*-C_6H_4-R_3,

in which R_3 is OH, COOH, or SO_2NH2; and R_4 is H or methyl.

6. The element of claim 5 in which the first added copolymer additionally comprises, in polymerized form, about 1 wt% to about 30 wt% of compound (c) represented by the formula:

$CH_2C(R_6)CO$-NH-*p*-C_6H_4-R_5

in which R_5 is OH, COOH, or SO_2NH_2; and R_6 is H or methyl.

7. The element of claim 5 in which the underlayer additionally comprises a second added copolymer, and the second added copolymer comprises, in polymerized form, about 25 mol% to about 75 mol% of N-phenylmaleimide; about 10 mol% to about 50 mol% of methacrylamide; and about 5 mol% to about 30 mol% of methacrylic acid.

8. A method for forming an image, the method comprising the steps of:

a) thermally imaging the imageable element of any of claims 1 to 7 and forming an imaged imageable element comprising imaged and complementary unimaged regions;
b) developing the imaged imageable element with the developer and removing the imaged regions without substantially affecting the unimaged regions.

9. The method of claim 8 additionally comprising the step of baking the imaged imageable element after step b).

10. An image formed by the method of claim 8.

Patentansprüche

1. Bebilderbares Element mit:

einem Substrat;
einer über dem Substrat angeordneten unteren Schicht; und
einer über der unteren Schicht angeordneten oberen Schicht;

worin:

das Element ein fotothermisches Umwandlungsmaterial umfasst;

die obere Schicht im Wesentlichen frei von fotothermischem Umwandlungsmaterial ist;
die obere Schicht Tinte aufzunehmen vermag;
die obere Schicht vor der thermischen Bebilderung nicht mithilfe eines alkalischen Entwicklers entfernbar ist;
nach der thermischen Bebilderung zur Ausbildung bebilderter Bereiche in der oberen Schicht die bebilderten Bereiche mithilfe eines alkalischen Entwicklers entfernbar sind;
die untere Schicht mithilfe des alkalischen Entwicklers entfernbar ist, und
die untere Schicht ein Polymermaterial umfasst, das in polymerisierter Form Folgendes umfasst:

etwa 5 Mol% bis etwa 30 Mol% Methacrylsäure;
etwa 20 Mol% bis ca. 75 Mol% N-Phenylmaleimid, N-Cyclohexylmaleimid, N-Benzylmaleimid oder eine Mischung daraus; und
etwa 3 Mol% bis etwa 50 Mol% einer Verbindung (a),
dargestellt durch folgende Formel:

$$CH_2C(R_2)C(O)NHCH_2OR_1,$$

worin R_1 für C_1 bis C_{12} Alkyl, Phenyl, C_1 bis C_{12} substituiertes Phenyl, C_1 bis C_{12} Aralkyl oder $Si(CH_3)_3$ steht und R_2 für H oder Methyl steht.

2. Element nach Anspruch 1, worin R_1 für C_1 bis C_4 Alkyl, Phenyl, Benzyl, 2-Phenylethyl oder $Si(CH_3)_3$ steht und R_2 für Methyl steht und das Polymermaterial etwa 10 Mol% bis etwa 30 Mol% Methacrylsäure, etwa 35 Mol% bis etwa 60 Mol% von N-Phenylmaleimid und etwa 10 Mol% bis etwa 40 Mol% einer Verbindung (a) umfasst.

3. Element nach Anspruch 2, worin das Polymermaterial zudem etwa 15 Mol% bis etwa 40 Mol% Methacrylamid umfasst.

4. Element nach einem der vorausgehenden Ansprüche, worin die untere Schicht zudem ein Harz mit aktivierten Methylol-oder aktivierten, alkylierten Methylolgruppen umfasst.

5. Element nach einem der vorausgehenden Ansprüche, worin die untere Schicht zudem ein erstes zugegebenes Copolymer umfasst, und worin das erste zugegebene Copolymer in polymerisierter Form etwa 1 Gew.-% bis etwa 30 Gew.-% N-Phenylmaleimid, etwa 1 Gew.-% bis etwa 30 Gew.-% Methacrylamid, etwa 20 Gew.-% bis etwa 75 Gew.-% Acrylonitril und etwa 20 Gew.-% bis etwa 75 Gew.-% einer Verbindung (b) umfasst, dargestellt durch folgende Formel:

$$CH_2C(R_4)CO_2CH_2CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}p\text{-}C_6H_4\text{-}R_3,$$

worin R_3 für OH, COOH oder SO_2NH2 und R_4 für H oder Methyl stehen.

6. Element nach Anspruch 5, worin das erste zugegebene Copolymer zudem in polymerisierter Form etwa 1 Gew.-% bis etwa 30 Gew.-% der Verbindung (c) umfasst, dargestellt durch die Formel:

$$CH_2C(R_6)CO\text{-}NH\text{-}p\text{-}C_6H_4\text{-}R_5$$

worin R_5 für OH, COOH oder SO_2NH_2 und R_6 für H oder Methyl stehen.

7. Element nach Anspruch 5, worin die untere Schicht zusätzlich ein zweites zugegebenes Copolymer umfasst und worin das zweite zugegebene Copolymer in polymerisierter Form etwa 25 Mol% bis etwa 75 Mol% N-Phenylmaleimid, etwa 10 Mol% bis etwa 50 Mol% Methacrylamid und etwa 5 Mol% bis etwa 30 Mol% Methacrylsäure umfasst.

8. Verfahren zur Ausbildung eines Bildes mit folgenden Schritten:

a) thermisches Bebildern des bebilderbaren Elements nach einem der Ansprüche 1 bis 7 und Ausbilden eines bebilderten, bebilderbaren Elements aus bebilderten Bereichen und komplementären unbebilderten Bereichen;
b) Entwickeln des bebilderten, bebilderbaren Elements mit einem Entwickler und Entfernen der bebilderten Bereiche, ohne im Wesentlichen die unbebilderten Bereiche zu beeinträchtigen.

9. Verfahren nach Anspruch 8 mit dem zusätzlichen Schritt des Einbrennens des bebilderten, bebilderbaren Elements nach Schritt b).

10. Bild, hergestellt gemäß dem Verfahren nach Anspruch 8.

Revendications

1. Elément apte à être imagé comprenant :

un substrat ;
une sous-couche appliquée par-dessus le substrat ; et
une surcouche appliquée par-dessus la sous-couche ;
dans lequel :

l'élément comprend un matériau de conversion photothermique ;
la surcouche est sensiblement exempte de matériau de conversion photothermique ;
la surcouche est une couche réceptrice d'encre ;
avant la mise en oeuvre du procédé de formation d'image thermique, la surcouche ne peut être éliminée par un révélateur alcalin ;
après la mise en oeuvre du procédé de formation d'image thermique afin de former des régions imagées dans la surcouche, les régions imagées peuvent être éliminées par le révélateur alcalin ;
la sous-couche peut être éliminée par le révélateur alcalin, et
la sous-couche comprend un matériau polymère contenant, sous forme polymérisée :

de 5% en moles environ à 30% en moles environ d'acide méthacrylique ;
de 20% en moles environ à 75% en moles environ de composé N-phénylmaléimide, de composé N-cyclohexylmaléimide, de composé N-benzylmaléimide ou de l'un de ces mélanges ; et
de 3% en moles environ à 50% en moles environ d'un composé (a) représenté par la formule :

$$CH_2C(R_2)C(O)NHCH_2OR_1,$$

dans laquelle R_1 est un groupe alkyle, phényle en C_1 à C_{12}, un groupe phényle substitué en C_1 à C_{12}, un groupe aralkyle en C_1 à C_{12} ou un groupe $Si(CH_3)_3$; et R_2 est H ou un groupe méthyle.

2. Elément selon la revendication 1, dans lequel R_1 est un groupe alkyle, phényle, benzyle, 2-phénéthyle ou $Si(CH_3)_3$ en C_1 à C_4 ; et R_2 est un groupe méthyle et le matériau polymère comprend de 10% en moles environ à 30% en moles environ d'acide méthacrylique ; de 35% en moles environ à 60% en moles environ de composé N-phénylmaléimide, et de 10% en moles environ à 40% en moles environ de composé (a).

3. Elément selon la revendication 2, dans lequel le matériau polymère comprend en outre de 15% en moles environ à 40% en moles environ de méthacrylamide.

4. Elément selon l'une quelconque des revendications précédentes, dans lequel la sous-couche comprend en outre une résine ayant des groupes méthylol activés ou des groupes méthylol alkylés activés.

5. Elément selon l'une quelconque des revendications précédentes, dans lequel la sous-couche comprend en outre un premier copolymère ajouté et le premier copolymère ajouté comprend, sous forme polymérisée, de 1% en poids environ à 30% en poids environ de composé N-phénylmaléimide ; de 1% en poids environ à 30% en poids environ de méthacrylamide, de 20% en poids environ à 75% en poids environ d'acrylonitrile et de 20% en poids environ à 75% en poids environ de composé (b), représenté par la formule :

$$CH_2C(R_4)CO_2CH_2CH_2\text{-NH-CO-NH-}p\text{-}C_6H_4\text{-}R_3,$$

dans laquelle R_3 est OH, COOH, ou SO_2NH_2 ; et R_4 est H ou un groupe méthyle.

6. Elément selon la revendication 5, dans lequel le premier copolymère ajouté comprend en outre, sous forme polymérisée, de 1% en poids environ à 30% en poids environ de composé (c), représenté par la formule :

$CH_2C(R_6)CO\text{-}NH\text{-}p\text{-}C_6H_4\text{-}R_5$,

dans laquelle R_5 est OH, COOH ou SO_2NH_2 ; et R_6 est H ou un groupe méthyle.

7. Elément selon la revendication 5, dans lequel la sous-couche comprend en outre un second copolymère ajouté et le second copolymère ajouté comprend, sous forme polymérisée, de 25% en moles environ à 75% en moles environ de composé N-phénylmaléimide ; de 10% en moles environ à 50% en moles environ de méthacrylamide, et de 5% en moles environ à 30% en moles environ d'acide méthacrylique.

8. Procédé de formation d'une image, lequel procédé comprend les étapes suivantes :

a) imager thermiquement l'élément apte à être imagé selon l'une quelconque des revendications 1 à 7 et former un élément apte à être imagé imagé comprenant des régions imagées et des régions non imagées complémentaires ;
b) développer l'élément apte à être imagé imagé au moyen du révélateur et éliminer les régions imagées sans affecter sensiblement les régions non imagées.

9. Procédé selon la revendication 8 comprenant en outre l'étape de cuisson de l'élément apte à être imagé imagé après la mise en oeuvre de l'étape (b).

10. Image formée au moyen du procédé selon la revendication 8.

REFERENCES CITED IN THE DESCRIPTION

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