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(71) Applicant: **Eastman Kodak Company**
Rochester, New York 14650-2201 (US)

(72) Inventor: **Savariar-Hauck, Celin, Dr.**
37534 Badenhausen (DE)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4
81675 München (DE)

(54) Dual-layer heat-sensitive imageable elements with phosphorous containing polymers in the top layer

(57) Heat-sensitive positive working element comprising:
a) a substrate;
b) a bottom layer, which is soluble or swellable in aqueous alkaline developers and comprises at least one first polymeric material soluble or swellable in aqueous alkaline developers and insoluble inorganic solvents of low polarity; and
c) an ink-accepting top layer which is not soluble or dispersible in and not penetrable by an aqueous alkaline developer but is rendered soluble or dispersible in or penetrable by the developer upon exposure to heat and/or IR radiation, and which comprises a second polymeric material which is different from the first polymeric material, comprises a polymer backbone and pendant phosphonic acid groups and/or phosphate groups and has an acid number of up to 60 mg KOH/g polymer.

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Description

[0001] The present invention relates to heat-sensitive positive working elements, in particular heat-sensitive printing plate precursors comprising two layers on the substrate wherein the top layer comprises a polymer comprising phosphate or phosphonic acid groups. The invention furthermore relates to a process for the production of such elements and a process for imaging such elements.

[0002] Lithographic printing is based on the immiscibility of oil and water, wherein the oily material or the printing ink is preferably accepted by the image area, and the water or fountain solution is preferably accepted by the non-image area. When an appropriately produced surface is moistened with water and a printing ink is applied, the background or non-image area accepts the water and repels the printing ink, while the image area accepts the printing ink and repels the water. The printing ink in the image area is then transferred to the surface of a material such as paper, fabric and the like, on which the image is to be formed. Generally, however, the printing ink is first transferred to an intermediate material, referred to as blanket, which then in turn transfers the printing ink onto the surface of the material on which the image is to be formed; this technique is referred to as offset lithography.

[0003] A frequently used type of lithographic printing plate precursor (the term printing plate precursor refers to a coated printing plate prior to exposure and developing) comprises a photosensitive coating applied onto a substrate on aluminum basis. The coating can react to radiation such that the exposed portion becomes so soluble that it is removed during the developing process. Such a plate is referred to as positive working. On the other hand, a plate is referred to as negative working if the exposed portion of the coating is hardened by the radiation. In both cases, the remaining image area accepts printing ink, i.e. is oleophilic, and the non-image area (background) accepts water, i.e. is hydrophilic. The differentiation between image and non-image areas takes place during exposure.

[0004] In conventional plates, a film containing the information to be transferred is attached to the printing plate precursor under vacuum in order to guarantee good contact. The plate is then exposed by means of a radiation source, part of which is comprised of UV radiation. When a positive plate is used, the area on the film corresponding to the image on the plate is so opaque that the light does not affect the plate, while the area on the film corresponding to the non-image area is clear and allows light to permeate the coating, whose solubility increases. In the case of a negative plate, the opposite takes place: The area on the film corresponding to the image on the plate is clear, while the non-image area is opaque. The coating beneath the clear film area is hardened due to the incident light, while the area not affected by the light is removed during developing. The light-hardened surface of a negative working plate is therefore oleophilic and accepts printing ink, while the non-image area that used to be coated with the coating removed by the developer is desensitized and therefore hydrophilic.

[0005] For several decades, positive working commercial printing plate precursors were characterized by the use of alkali-soluble phenolic resins and naphthoquinone diazide derivatives; imaging was carried out by means of UV radiation.

[0006] Recent developments in the field of lithographic printing plate precursors have led to radiation-sensitive compositions suitable for the production of printing plate precursors which can be addressed directly by lasers. The digital image-forming information can be used to convey an image onto a printing plate precursor without the use of a film, as is common in conventional plates.

[0007] One example of a positive working, direct laser addressable printing plate precursor is described in US 4,708,925. The patent describes a lithographic printing plate precursor whose imaging layer comprises a phenolic resin and a radiation-sensitive onium salt. As described in the patent, the interaction between the phenolic resin and the onium salt results in an alkali solvent resistance of the composition, which restores the alkali solubility by photolytic decomposition of the onium salt. The printing plate precursor can be used as a precursor of a positive working printing plate or as a precursor of a negative printing plate, if additional process steps are added between exposure and developing, as described in detail in British patent no. 2,082,339. The printing plate precursors described in US 4,708,925 are UV-sensitive per se and can additionally be sensitized to visible and IR radiation.

[0008] Another example of a direct laser addressable printing plate precursor that can be used as a positive working system is described in US 5,372,907 and US 5,491,046. These two patents describe the decomposition of a latent Bronsted acid by radiation in order to increase solubility of the resin matrix upon image-wise exposure. As in the case of the printing plate precursor described in US 4,708,925, these systems can also be used as negative working systems in combination with additional process steps between imaging and developing. In the case of the negative working printing plate precursors, the decomposition by-products are subsequently used to catalyze a crosslinking reaction between the resins in order to render the layer of the irradiated areas insoluble, which requires a heating step prior to developing. As in US 4,708,925, these printing plate precursors are UV-sensitive per se due to the used acid-forming materials.

[0009] Heat-sensitive dual-layer lithographic printing plate precursors are for instance described in US 6,294,311 B1, US 6,358,669 B1, US 6,555,291 B1, US 6,528,228 B2, US 6,352,811 B1, EP 864 420 B1, EP 908 305 B1, EP 960 728 B1, EP 950 518 B1, EP 940 266 B1, EP 1 023 994 B1, JP 99-213585, JP 99-213586, US 2003-0129532 A2, EP 1439 058 A2, EP 1 275 498, EP 1 433 594 A2 and EP 1 262 318 B1.

[0010] DE 2 500 489 A1 describes phosphate copolymers for protective coatings for metal surfaces.

[0011] EP 883 835 B1 describes the use of tripolyphosphates as additives in the aqueous overcoat of radical polymerizable systems to give better humidity resistance and non-tackiness.

[0012] US 6,232,038 B1 describes phosphate containing compounds in photopolymerizable compositions in the basecoat.

[0013] It is the object of the present invention to provide a positive working thermally imageable element characterized by a high degree of resistance to organic solvents; at the same time, the element should exhibit excellent sensitivity, and resolution and the formation of sludge in the processor should be avoided.

[0014] This object is surprisingly achieved by an element comprising:

a) a substrate;
b) a bottom layer, which is soluble or swellable in aqueous alkaline developers and comprises at least one first polymeric material soluble or swellable in aqueous alkaline developers and insoluble in organic solvents of low polarity; and
c) an ink-accepting top layer which is not soluble or dispersible in and not penetrable by an aqueous alkaline developer but is rendered soluble or dispersible in or penetrable by the developer upon exposure to heat and/or IR radiation, and which comprises a second polymeric material which is different from the first polymeric material, comprises a polymer backbone and pendant phosphonic acid groups and/or phosphate groups and has an acid number of up to 60 mg KOH/g polymer.

[0015] As used in the present invention, the term "(meth)acrylate" encompasses both "acrylate" and "methacrylate"; analogously, the same applies to the term "(meth)acrylic acid".

[0016] For the purpose of the present invention, a polymer is considered soluble in an aqueous alkaline developer (with a pH of about 8 to 14) if 1 g or more dissolve in 100 ml of developer at room temperature.

[0017] Unless defined otherwise, the term "alkyl group" as used in the present invention refers to a straight-chain, branched or cyclic saturated hydrocarbon group which preferably comprises 1 to 18 carbon atoms, more preferred 1 to 10 carbon atoms and most preferred 1 to 6 carbon atoms. The alkyl group can optionally comprise one or more substituents (preferably 0 or 1 substituent), for example selected from halogen atoms (fluorine, chlorine, bromine, iodine), CN, NO_2, NR^7_2, $COOR^7$ and OR^7 (R^7 independently represents a hydrogen atom, an alkyl group or aryl group). The above definition also applies to the alkyl unit of an aralkyl group and an alkoxy group. The definition also applies to alkenyl groups, except that they comprise a C-C double bond in the hydrocarbon group.

[0018] Unless defined otherwise, the term "aryl group" as used in the present invention refers to an aromatic carbocyclic group with one or more fused rings, which preferably comprises 5 to 14 carbon atoms. The aryl group can optionally comprise one or more substituents (preferably 0 to 3) selected for example from halogen atoms, alkyl groups, alkoxy groups, CN, NO_2, NR^7_2, $COOR^7$ and OR^7 (wherein each R^7 is independently selected from hydrogen, alkyl and aryl). The above definition also applies to an arylene group and the aryl unit of an aralkyl group. Preferred examples include a phenyl group and a naphthyl group which can optionally be substituted. In a heteroaryl group at least one ring carbon atom is replaced with a heteroatom selected from O, S and N; substituents include the ones described above.

[0019] A fused ring or ring system as referred to in the present invention is a ring that shares two atoms with the ring to which it is fused.

[0020] Unless defined otherwise, the term "carbocyclic" ring as used in the present invention refers to a saturated, unsaturated (non-aromatic) or aromatic ring which only comprises C atoms as ring atoms.

[0021] Unless defined otherwise, the term "heterocyclic ring" as used in the present invention refers to a 5- to 7-membered (preferably 5- or 6-membered) saturated, unsaturated (non-aromatic) or aromatic ring, wherein one or more ring carbon atoms are replaced with heteroatoms selected from N, NR^8, S and O (preferably N or NR^8). The heterocyclic or carbocyclic ring can optionally comprise one or more substituents, selected for example from alkyl groups, aryl groups, aralkyl groups, halogen atoms, $-OR^8$, $-NR^8_2$, $-C(O)OR^8$, $C(O)NR^8_2$ and CN (wherein each R^8 is independently selected from hydrogen, alkyl, aryl and aralkyl).

SUBSTRATE

[0022] In the production of the printing plate precursors, a dimensionally stable plate or foil-shaped material that has already been used as a substrate for printing forms is preferably used as a substrate; for lithographic printing plate precursors the substrate has a hydrophilic surface (sometimes a specific surface treatment known to those skilled in the art is necessary to obtain such a surface). Examples of such substrates include paper, paper coated with plastic materials (such as polyethylene, polypropylene, polystyrene), a metal plate or foil, such as e.g. aluminum (including aluminum alloys), zinc and copper plates, plastic films made e.g. from cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose acetate, cellulose acetatebutyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate and polyvinyl acetate, and a laminated material made from paper or a plastic film and one of the above-mentioned metals, or a paper/plastic film that has been metallized by vapor deposition. Among these substrates, an aluminum plate or foil is especially preferred since it shows a remarkable degree of dimensional stability, is inexpensive, thermally stable and furthermore exhibits excellent adhesion to the coating. Furthermore, a composite film can be used wherein an aluminum foil has been laminated onto a polyethylene terephthalate film.

[0023] A metal substrate, in particular an aluminum substrate, is preferably subjected to a surface treatment, for example graining by brushing in a dry state or brushing with abrasive suspensions, or electrochemical graining, e.g. by means of a hydrochloric acid electrolyte, and optionally anodizing.

[0024] Furthermore, in order to improve the hydrophilic properties of the surface of the metal substrate that has been grained and optionally anodized in sulfuric acid or phosphonic acid, the metal substrate can be subjected to a posttreatment with an aqueous solution of e.g. sodium silicate, calcium zirconium fluoride, polyvinylphosphonic acid or phosphonic acid. Within the framework of the present invention, the term "substrate" also encompasses an optionally pretreated substrate exhibiting, for example, a hydrophilizing layer (also referred to as "interlayer") on its surface.

[0025] The details of the above-mentioned substrate pre-treatment are well known to the person skilled in the art.

BOTTOM LAYER

[0026] The first layer comprises at least one first polymer which is soluble or swellable in aqueous alkaline developers and insoluble in organic solvents of low polarity.

[0027] Solvents of low polarity wherein the first polymer is insoluble include for example butyl acetate, ethyl acetate, methyl isobutyl ketone, propylene glycol monomethylether acetate and propylene glycol monoethylether acetate.

[0028] Examples of the first polymeric material include acrylic polymers and copolymers with carboxyl functions, copolymers of vinyl acetate, crotonate and vinyl neodecanoate, copolymers of styrene and maleic acid anhydride, wood rosin esterified with maleic acid, and combinations thereof.

[0029] Particularly suitable polymers are derived from N-substituted maleimides, in particular N-phenylmaleimide, (meth)acrylamides, in particular methacrylamide, and acrylic acid and/or methacrylic acid, in particular methacrylic acid. Copolymers of two of these monomers are more preferred, and it is particularly preferred that all three monomers be present in polymerized form. Preferred polymers of that type are copolymers of N-phenylmaleimide, (meth)acrylamide and (meth)acrylic acid and optional further comonomers, more preferred those comprising 25 to 75 mole-% (more preferred 35 to 60 mole-%) N-phenylmaleimide, 10 to 50 mole-% (more preferred 15 to 40 mole-%) (meth)acrylamide and 5 to 30 mole-% (more preferred 10 to 30 mole-%) (meth)acrylic acid. Other hydrophilic monomers, such as hydroxyethyl(meth)acrylate, can be used instead of a portion of the (meth)acrylamide. Other monomers soluble in aqueous alkaline media can be used instead of (meth)acrylic acid. Such polymers are for example described in DE 199 36 331 A1.

[0030] Another group of suitable first polymeric materials include copolymers comprising the following monomers in polymerized form:

> 5 to 30 mole-% methacrylic acid, 20 to 75 mole-% N-phenylmaleimide, N-cyclohexylmaleimide, N-benzylmaleimide or a mixture thereof and 3 to 50 mole-% $CH_2C(R)C(O)NHCH_2OR'$ (wherein R is C_1-C_{12} alkyl, phenyl, substituted phenyl, aralkyl or $Si(CH_3)_3$ and R' represents H or CH_3). Such copolymers are described in detail for example in WO 2005/018934.

[0031] Another group of first polymeric materials for the bottom layer include copolymers comprising a monomer in polymerized form which contains a urea group in its side chain; such copolymers are for example described in US 5,731,127 B. These copolymers comprise 10 to 80 wt.% (preferably 20 to 80 wt.%) of at least one monomer of the following formula (I):

$$CH_2{=}CR\text{-}CO_2\text{-}X\text{-}NH\text{-}CO\text{-}NH\text{-}Y\text{-}Z \qquad \text{(I)}$$

wherein

R	is a hydrogen atom or a methyl group,
X	is a divalent linking group,
Y	is a divalent substituted or unsubstituted aromatic group, and
Z	is selected from OH, COOH and SO_2NH_2.
R	is preferably a methyl group.
X	is preferably a substituted or unsubstituted alkylene group, a substituted or unsubstituted phenylene group (C_6H_4) or a substituted or unsubstituted naphthalene group $(C_{10}H_6)_n$, such as $-(CH_2)_n-$ (wherein n is an integer from 2 to 8), 1,2-, 1,3- and 1,4-phenylene and 1,4-, 2,7- and 1,8-naphthalene. More preferred, X is an unsubstituted alkylene

group -$(CH_2)_n$- wherein n = 2 or 3, and most preferred, X represents -(CH_2CH_2)-.

Y is preferably a substituted or unsubstituted phenylene group or a substituted or unsubstituted naphthalene group. More preferred, Y is an unsubstituted 1,4-phenylene group.

Z is preferably OH.

[0032] A preferred monomer of this group is

$$CH_2{=}C(CH_3)\text{ -}CO_2\text{-}CH_2CH_2\text{-NH-CO-NH-(p-}C_6H_4\text{)-Z} \qquad \text{(Ia)},$$

wherein Z is selected from OH, COOH and SO_2NH_2, and is preferably OH.

[0033] Monomers comprising one or more urea groups can be used in the synthesis of the copolymers. The copolymers furthermore comprise 20 to 90 wt.% of other polymerizable monomers such as maleimide, acrylic acid, methacrylic acid, acrylic acid esters, methacrylic acid esters, acrylonitrile, methacrylonitrile, acrylamides and methacrylamides, in polymerized form. Preferably, the copolymers soluble in alkaline solutions comprise 30 to 70 wt.% of the monomer with urea group, 20 to 60 wt.% acrylonitrile or methacrylonitrile (preferably acrylonitrile) and 5 to 25 wt.% acrylamide or methacrylamide (preferably methacrylamide).

[0034] The polymers described above are soluble in aqueous alkaline developers; they are furthermore soluble in polar solvents such as ethylene glycol monomethylether, which can be used as coating solvent for the production of the bottom layer, or mixtures of methyl lactate, methanol and dioxolane. The polymers described above can be prepared using known methods of free-radical polymerization.

[0035] Derivatives of methylvinylether/maleic acid anhydride copolymers comprising an N-substituted cyclic imide unit and derivatives of styrene/maleic acid anhydride copolymers comprising an N-substituted cyclic imide unit can also be used as first polymeric material for the bottom layer if they are soluble in aqueous alkaline media. Such copolymers can for example be prepared by reacting maleic acid anhydride copolymer and an amine such as p-aminobenzene sulfonamide or p-aminophenol and subsequent cyclization by means of an acid.

[0036] Another group of polymers that can be used as first polymeric material are copolymers containing 1 to 90 mole-% of a sulfonamide monomer unit, in particular N-(p-aminosulfonylphenyl)methacrylamide, N-(m-aminosulfonylphenol) methacrylamide, N-(o-aminosulfonylphenyl)methacrylamide and/or corresponding acrylamides. Suitable polymers containing a sulfonamide group in their side chain, processes for their production and suitable monomers are described in US 5,141,838 B. Especially suitable polymers comprise (1) a sulfonamide monomer unit, in particular N-(p-aminosulfonylphenyl)methacrylamide, (2) acrylonitrile and/or methacrylonitrile and (3) methylmethacrylate and/or methylacrylate. Some of these copolymers are available from Kokusan Chemical, Gumma, Japan under the tradename PU Copolymers.

[0037] Furthermore, polyacrylates can be used as first polymeric material which contain structural units of the following formulas (IIa) and/or (IIb):

$$\text{-[}CH_2\text{-CH(CO-}X^1\text{-}R^1\text{-}SO_2NH\text{-}R^2\text{)]-} \qquad \text{(IIa)}$$

$$\text{-[}CH_2\text{-CH(CO-}X^1\text{-}R^1\text{-NH}SO_2\text{-}R^{2a}\text{)]-} \qquad \text{(IIb)}$$

wherein

X^1 in both formulas represents O or NR^3;

R^1 in both formulas represents a substituted or unsubstituted alkylene group (preferably C_1-C_{12}), cycloalkylene group (preferably C_6-C_{12}), arylene group (preferably C_6-C_{12}) or aralkylene group (preferably C_7-C_{14});

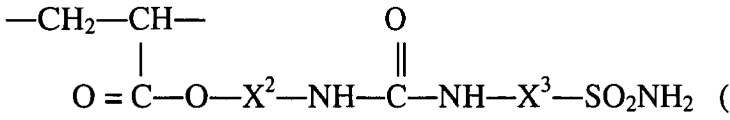
R^2 and R^3 each independently represent a hydrogen atom or a substituted or unsubstituted alkyl group (preferably C_1-C_{12}); cycloalkyl group (preferably C_6-C_{12}), aryl group (preferably C_6-C_{12}) or aralkyl group (preferably C_7-C_{14}); and

R^{2a} represents a substituted or unsubstituted alkyl group (preferably C_1-C_{12}), cycloalkyl group (preferably C_6-C_{12}), aryl group (preferably C_6-C_{12}) or aralkyl group (preferably C_7-C_{14}).

[0038] Such polyacrylates and starting monomers and comonomers for their production are described in detail in EP-A-0 544 264 (pages 3 to 5).

[0039] According to the present invention, polymethacrylates analogous to the polyacrylates of formulas (IIa) and (IIb) can be used as well for the bottom layer.

[0040] Polyacrylates with sulfonamide side groups which additionally contain a urea group in the side chains can also be used as first polymeric material. Such polyacrylates are for example described in EP-A-0 737 896 and comprise the following structural unit (IIc):



$$\begin{array}{l} -CH_2-CH- \\ \qquad\quad | \\ O=C-O-X^2-NH-\overset{\overset{O}{\|}}{C}-NH-X^3-SO_2NH_2 \end{array}$$

(IIc)

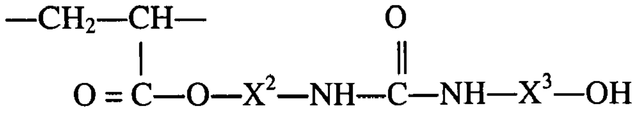
wherein

X² is a substituted or unsubstituted alkylene group (preferably C_1-C_{12}), cycloalkylene group (preferably C_6-C_{12}), arylene group (preferably C_6-C_{12}) or aralkylene group (preferably C_7-C_{14}), and

X³ is a substituted or unsubstituted arylene group (preferably C_6-C_{12}).

[0041] According to the present invention, polymethacrylates analogous to the polyacrylates of formula (IIc) can be used as well in the bottom layer.

[0042] The polyacrylates of formulas (IId) with urea groups and phenolic OH mentioned in EP-A-0 737 896 can also be used as first polymeric material:



$$\begin{array}{l} -CH_2-CH- \\ \qquad\quad | \\ O=C-O-X^2-NH-\overset{\overset{O}{\|}}{C}-NH-X^3-OH \end{array}$$

(IId)

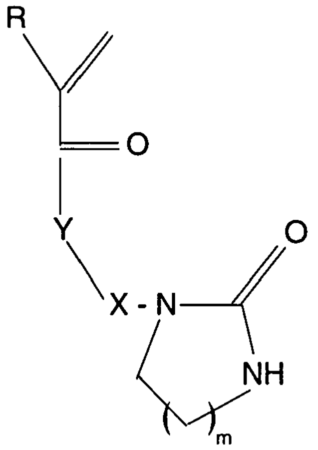
wherein

X^2 and X^3 are as defined above.

[0043] According to the present invention, polymethacrylates analogous to the polyacrylates of formula (IId) can be used as well in the bottom layer.

[0044] The weight average of the molecular weight of suitable poly(meth)acrylates with sulfonamide side groups and/or phenolic side groups is preferably 2,000 to 300,000.

[0045] Further copolymers suitable as first polymeric material are described in US 6,893,783 B2 and US 2005/0,244,749 A1. The copolymers described therein comprise in polymerized form: 5 to 40 mole% (meth)acrylic acid or vinyl benzoic acid, 20 to 75 mole% N-phenylmaleimide, N-cyclohexylmaleimide, N-benzylmaleimide or N-(p-carboxyphenyl)maleimide, and 3 to 50 mole% of a monomer having a cyclic urea group represented by the following formula (IIe)



(IIe)

wherein

R is H or CH_3;
X is selected from $-(CH_2)_n-$ with n being an integer from 2. to 12, $-(CH_2-CH_2-O)_p-CH_2-CH_2-$ with p being an integer from 1 to 3, and -Si(R')(R")- with R' and R" being independently selected from methyl and ethyl; and
Y is -O- or -NH-.

[0046] Of course, mixtures of different first polymeric materials can be used as well.

[0047] Based on the dry layer weight of the bottom layer, the first polymeric material is present in an amount of at least 50 wt.%, preferably at least 60 wt.%, more preferred at least 70 wt.% and particularly preferred at least 80 wt.%.

[0048] The bottom layer can furthermore comprise dyes or pigments having a high absorption in the visible spectral range in order to increase the contrast ("contrast dyes and pigments"). Particularly suitable dyes and pigments are those that dissolve well in the solvent or solvent mixture used for coating or are easily introduced in the disperse form of a pigment. Suitable contrast dyes include *inter alia* rhodamine dyes, triarylmethane dyes such as Victoria blue R and Victoria blue BO, crystal violet and methyl violet, anthraquinone pigments, azo pigments and phthalocyanine dyes and/or pigments. The colorants are preferably present in the bottom layer in an amount of 0 to 15 wt.%, more preferred 0.5 to 10 wt.%, particularly preferred 1.5 to 7 wt.%, based on the dry layer weight.

[0049] Furthermore, the bottom layer can comprise surfactants (e.g. anionic, cationic, amphoteric or non-ionic tensides or mixtures thereof). Suitable examples include fluorine-containing polymers, polymers with ethylene oxide and/or propylene oxide groups, sorbitol-tri-stearate and alkyl-di-(aminoethyl)-glycines. They are preferably present in an amount of 0 to 10 wt.%, based on the dry layer weight, especially preferred 0.2 to 5 wt.%.

[0050] The bottom layer can furthermore comprise print-out dyes such as crystal violet lactone or photochromic dyes (e.g. spiropyrans etc.). They are preferably present in an amount of 0 to 15 wt.%, based on the dry layer weight, especially preferred 0.5 to 5 wt.%.

[0051] Also, coating enhancers can be present in the bottom layer, such as poly(glycol)ether-modified siloxanes; they are preferably present in an amount of 0 to 1 wt.%, based on the dry layer weight.

[0052] The bottom layer can furthermore comprise antioxidants such as e.g. mercapto compounds (2-mercaptobenzimidazole, 2-mercaptobenzthiazole, 2-mercaptobenzoxazole and 3-mercapto-1,2,4-triazole), and triphenylphosphate. They are preferably used in an amount of 0 to 15 wt.%, based on the dry layer weight, especially preferred 0.5 to 5 wt.%.

[0053] Other coating additives can of course be present as well.

[0054] As an optional component, the bottom layer can comprise up to 25 wt.% (more preferably up to 15 wt.%) of one or more other polymers, for example novolac and resol 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 benzoguanamine-formaldehyde resins. Commercially available melamine-formaldehyde resins and glycoluril-formaldahyde resins include, for example, CYMEL® resins (Dyno Cyanamid) and NIKALAC® resins (Sanwa Chemical).

[0055] Suitable phenolic resins are for instance condensation products of one or more suitable phenols, e.g. phenol itself, m-cresol, o-cresol, p-cresol, 2,5-xylenol, 3,5-xylenol, resorcinol, pyrogallol, phenylphenol, diphenols (e.g. bisphenol-A), trisphenol, 1-naphthol and 2-naphthol with one or more suitable aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde and furfuraldehyde and/or ketones such as e.g. acetone, methyl ethyl ketone and methyl isobutyl ketone. The type of catalyst and the molar ratio of the reactants determine the molecular structure and thus the physical properties of the resin. Phenylphenol, xylenols, resorcinol and pyrogallol are preferably not used as the single phenol for condensation but rather in admixture with other phenols. An aldehyde/phenol ratio of about 0.5:1 to 1:1, preferably 0.5:1 to 0.8:1, and an acid catalyst are used in order to produce those phenolic resins known as "novolaks" and having a thermoplastic character. Phenolic resins known as "resols" are obtained at higher aldehyde/phenol ratios and in the presence of alkaline catalysts. Commercially available resol resins include, for example, GP649D99 resole (Georgia Pacific) and BKS-5928 resole resin (Union Carbide).

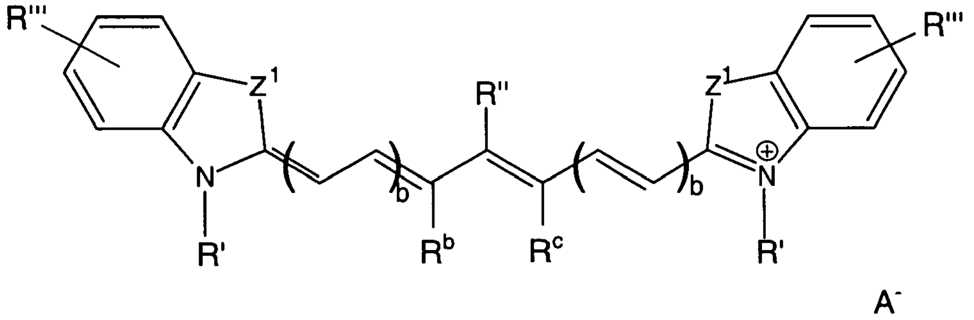
[0056] Suitable phenolic resins can be prepared according to known processes or are commercially available. Preferably, the molecular weight (weight average determined by means of gel permeation chromatography using polystyrene as standard) is between 1,000 and 15,000, especially preferred between 1,500 and 10,000.

[0057] In addition to the novolaks and resols mentioned above, modified novolaks/resols and (meth)acrylates with phenolic groups (e.g. terpolymers or tetrapolymers) can be used as optional components as well.

[0058] If the element of the present invention is to be imaged by exposure to IR radiation the bottom layer furthermore comprises at least one photothermal conversion material (in the following also referred to as "IR absorber").

[0059] The photothermal conversion material is capable of absorbing IR radiation and converting it into heat. The chemical structure of the IR absorber is not particularly restricted, as long as it is capable of converting the radiation it absorbed into heat. It is preferred that the IR absorber show essential absorption in the range of 650 to 1,300 nm, preferably 750 to 1,120 nm, and it preferably shows an absorption maximum in that range. IR absorbers showing an absorption maximum in the range of 800 to 1,100 nm are especially preferred. It is furthermore preferred that the IR absorber not or not essentially absorb radiation in the UV range. The absorbers are for example selected from carbon black, phthalocyanine pigments/dyes and pigments/dyes of the polythiophene; squarylium, thiazolium; croconate, merocyanine, cyanine, indolizine, pyrylium or metaldithiolin classes, especially preferred from the cyanine class. Suitable IR absorbers include for example the compounds listed in Table 1 of US-A-6,326,122. Additional examples can be found in US 4,327,169, US 4,756,993, US 5,156,938, WO 00/29214, US 6,410,207 B and EP 1 176 007 A1.

[0060] According to one embodiment, a cyanine dye of the formula (III) is used



(III)

wherein

each Z^1	independently represents S, O, NR^a or $C(alkyl)_2$;
each R'	independently represents an alkyl group, an alkylsulfonate group or an alkylammonium group;
R''	represents a halogen atom, SR^a, OR^a, SO_2R^a or NR^a_2 (preferably a halogen atom, SR^a or NR^a_2);
each R'''	independently represents a hydrogen atom, an alkyl group, $-COOR^a$, $-OR^a$, $-SR^a$, $-NR^a_2$ or a halogen atom; or represents a benzofused ring;
A^-	represents an anion;
R^b and R^c	either both represent hydrogen atoms or, together with the carbon atoms to which they are bonded, form a carbocyclic five- or six-membered ring;
R^a	represents a hydrogen atom, an alkyl or aryl group (in SR^a R^a is preferably an aryl in NR^a_2 each R^a is preferably an aryl group);
each b	is independently 0, 1, 2 or 3.

[0061] If R' represents an alkylsulfonate group, an internal salt can form so that no anion A- is necessary. If R' represents an alkylammonium group, a second counterion is needed which is the same as or different from A-.

Z^1	is preferably a $C(alkyl)_2$ group.
R'	is preferably an alkyl group with 1 to 4 carbon atoms.
R''	is preferably a halogen atom or SR^a.
R'''	is preferably a hydrogen atom.
R^a	is preferably an optionally substituted phenyl group or an optionally substituted heteroaromatic group.

[0062] Preferably, R^b and R^c, together with the carbon atoms to which they are bonded, form a 5- or 6-membered carbocyclic ring.

[0063] The counterion A^- is preferably a chloride ion, trifluoromethylsulfonate or a tosylate anion.

[0064] Of the IR dyes of formula (III), dyes with a symmetrical structure are especially preferred. Examples of especially preferred dyes include:

2-[2-[2-Phenylsulfonyl-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,3,3-trimethyl-3H-indoliumchloride,

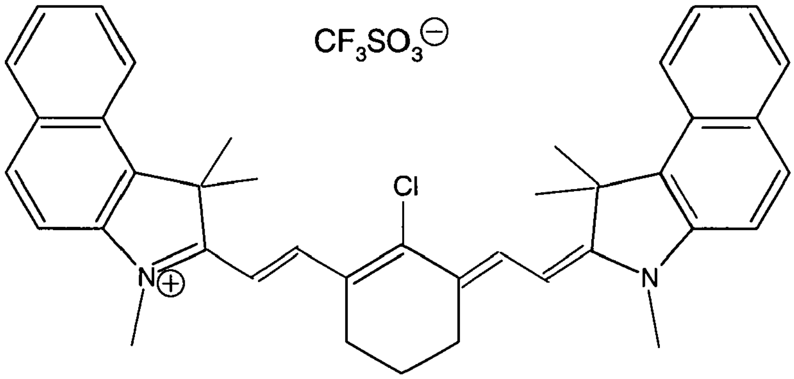
2-[2-[2-thiophenyl-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,3,3-trimethyl-3H-indoliumchloride,

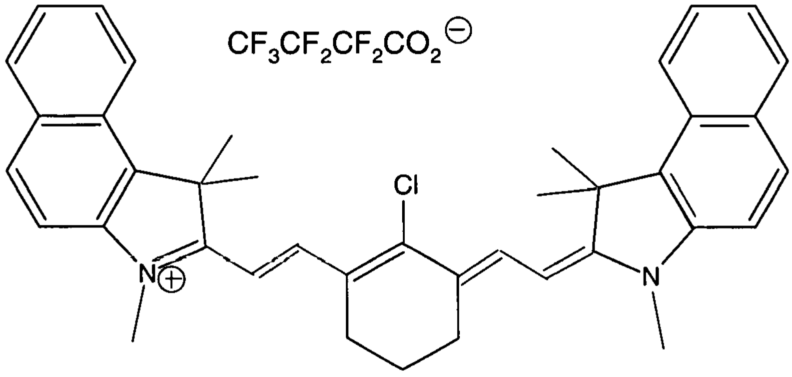
2-[2-[2-thiophenyl-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indole-2-ylidene)-ethylidene]-1-cyclopentene-1-yl]-ethenyl]-1,3,3-trimethyl-3H-indoliumtosylate, 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-benzo[e]-indole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,3,3-trimethyl-1H-benzo[e]-indolium-tosylate,

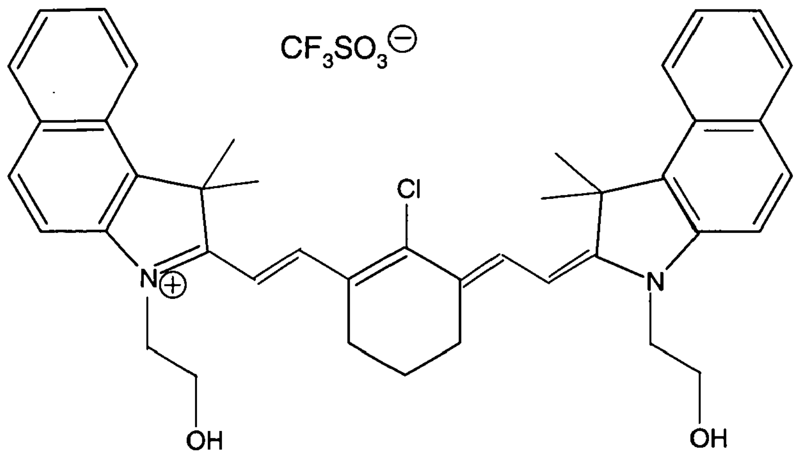
5-chloro-2-(2-{3-[2-(5-chloro-1-ethyl-3,3-dimethyl-1,3-dihydro-indole-2-ylidene)ethylidene]-2-diphenylamino-cyclopent-1-enyl}-vinyl)-1-ethyl-3,3-dimethyl-3H-indolium salt (e.g. tetrafluoroborate) and

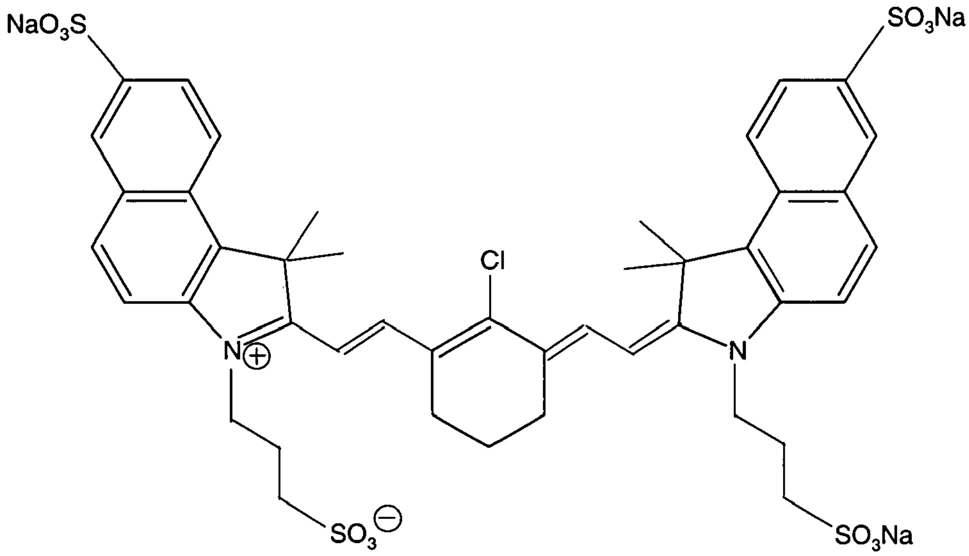
2-[2-[2-chloro-3-[2-ethyl-(3H-benzthiazole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-3-ethyl-benzthiazolium-tosylate.

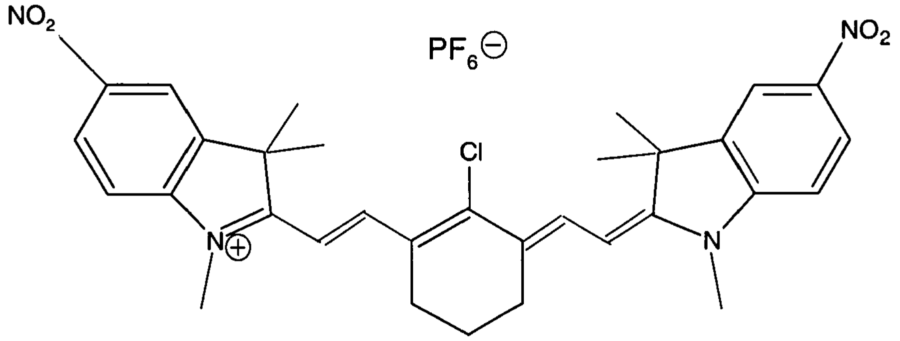
[0065] The following compounds are also IR absorbers suitable for use in the present invention:

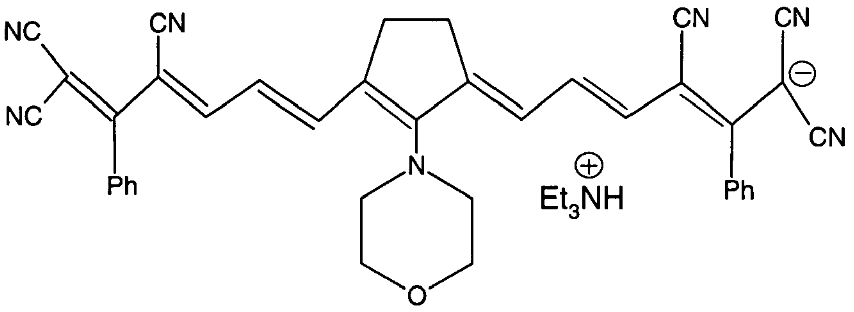


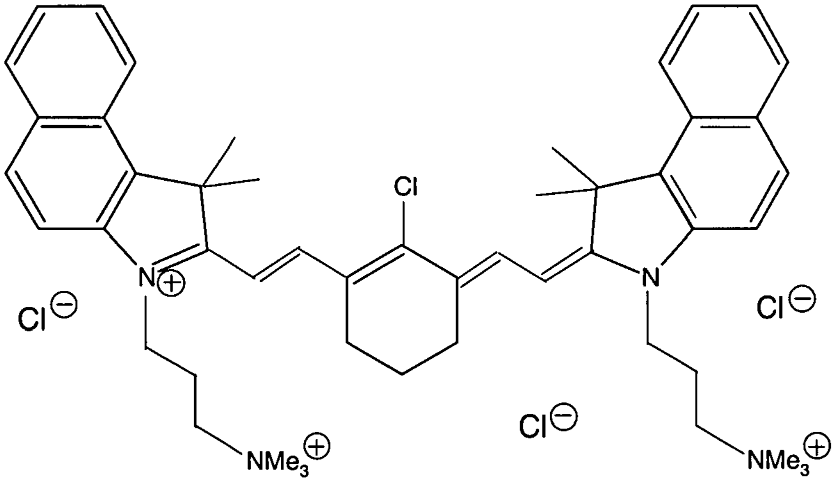


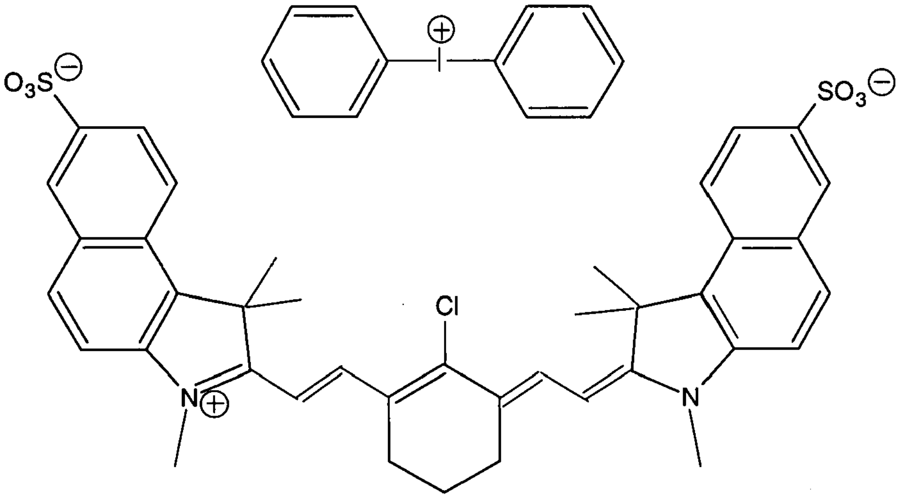

$CF_3SO_3^{\ominus}$
Cl
N⊕
N
OH
OH

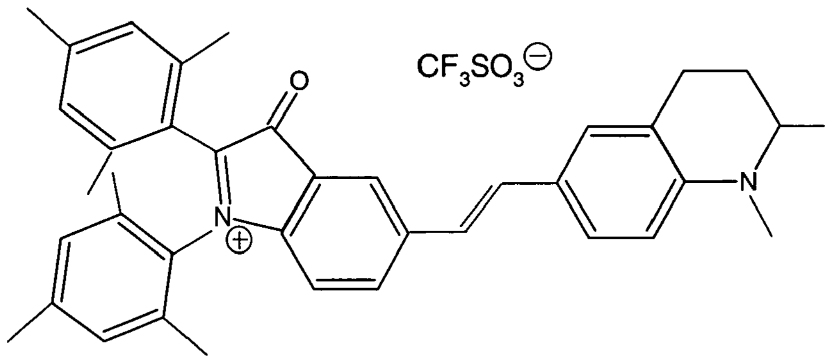

NaO_3S
SO_3Na
Cl
N⊕
N
$SO_3^{\ominus}$
SO_3Na

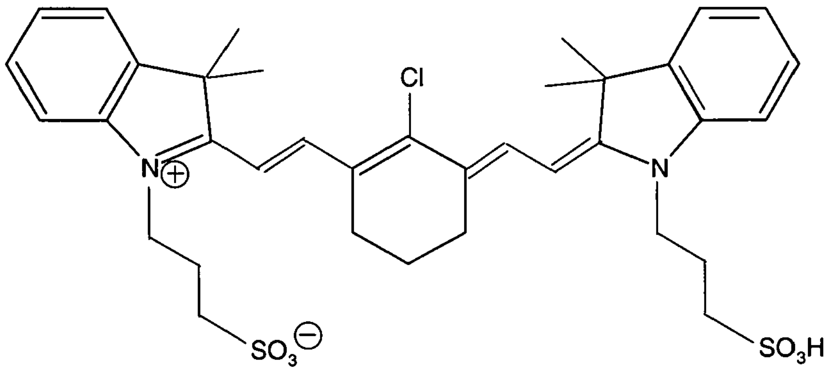

NO_2
$PF_6^{\ominus}$
NO_2
Cl
N⊕
N

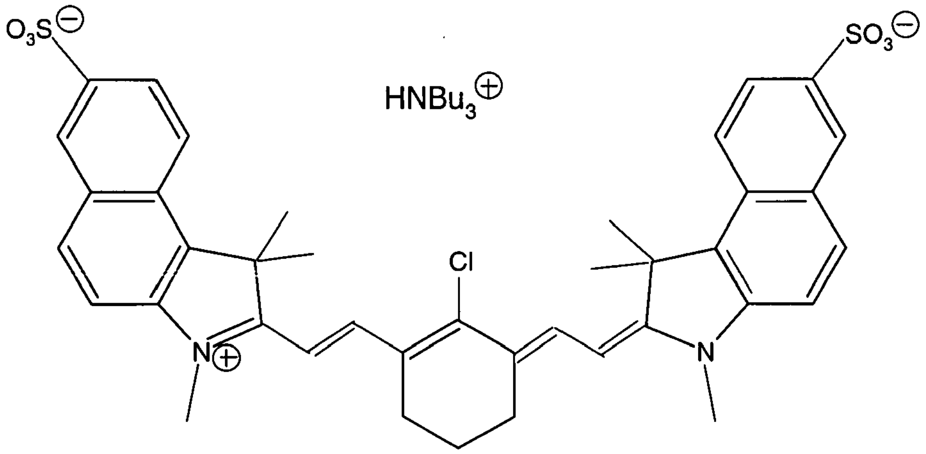

NC
NC
CN
Ph
N
O
$Et_3NH^{\oplus}$
CN
CN
CN
Ph

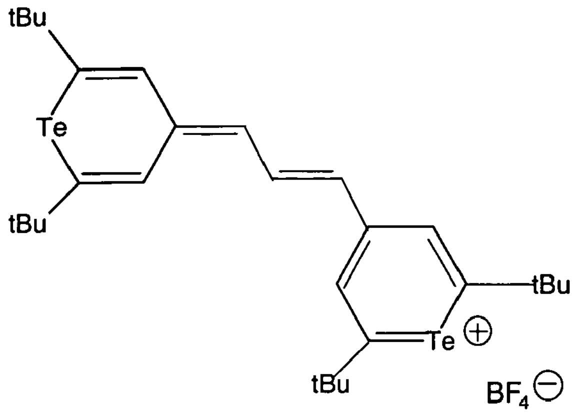

Cl
N⊕
$Cl^{\ominus}$
$NMe_3^{\oplus}$
$Cl^{\ominus}$
N
$Cl^{\ominus}$
$NMe_3^{\oplus}$

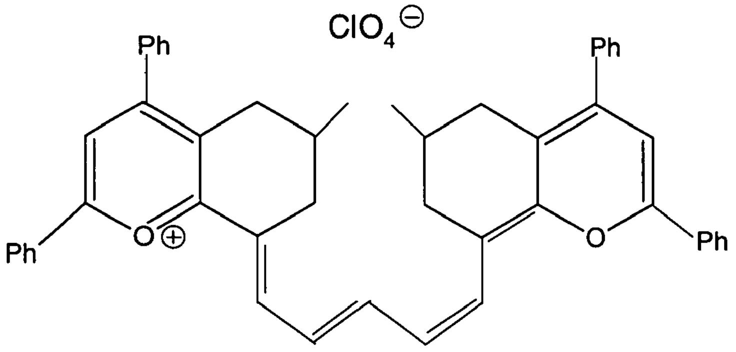

$I^{\oplus}$
$O_3S^{\ominus}$
$SO_3^{\ominus}$
Cl
N⊕
N

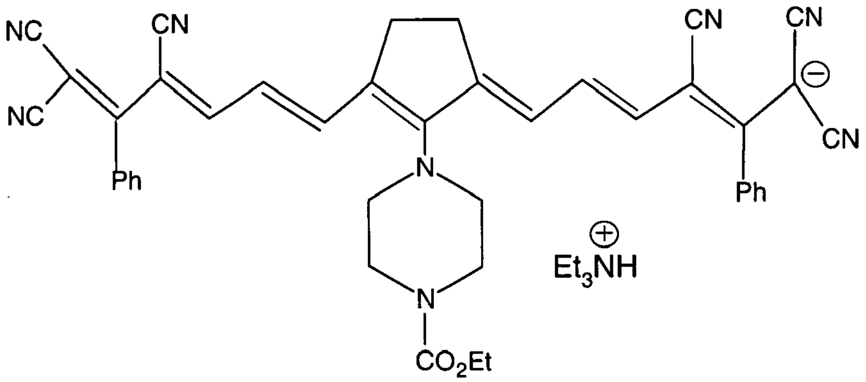

CF$_3$SO$_3^\ominus$
O
N$^\oplus$
N

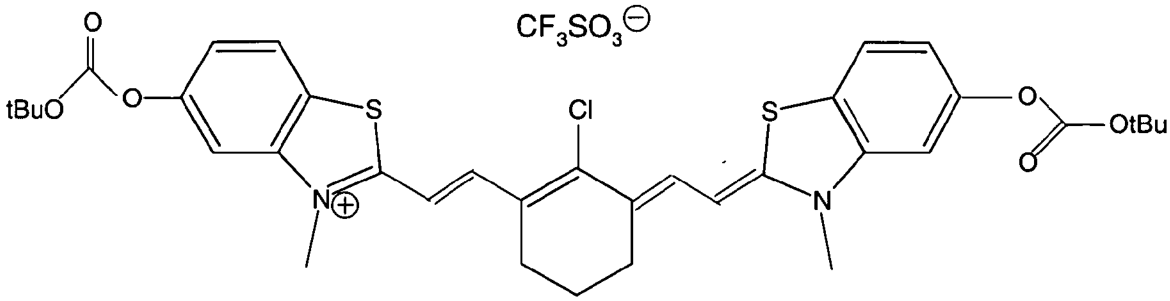

Cl
N$^\oplus$
N
SO$_3^\ominus$
SO$_3$H

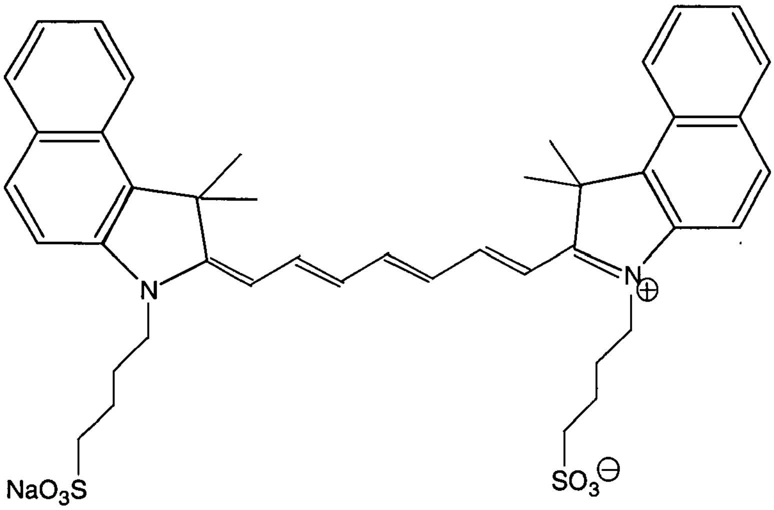

O$_3$S$^\ominus$
HNBu$_3^\oplus$
SO$_3^\ominus$
Cl
N$^\oplus$
N

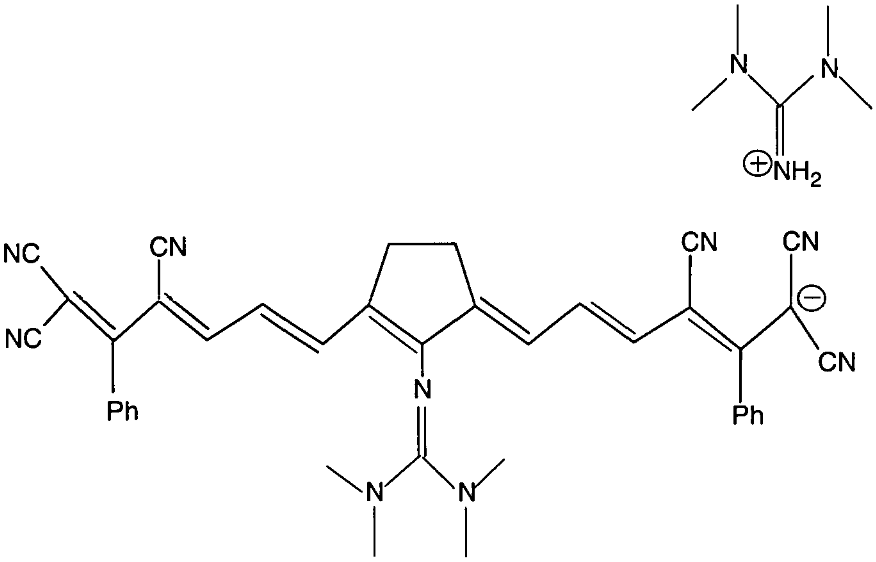

tBu
Te
tBu
tBu
Te ⊕
tBu
BF₄⊖

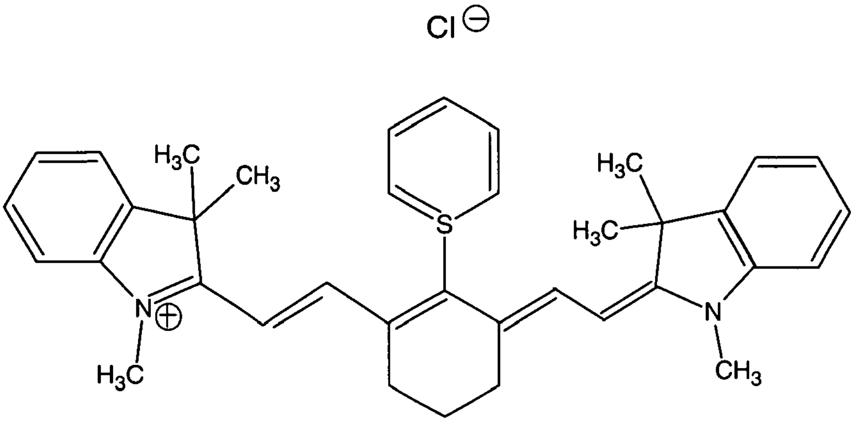

ClO₄⊖
Ph
Ph
Ph
O⊕
O
Ph

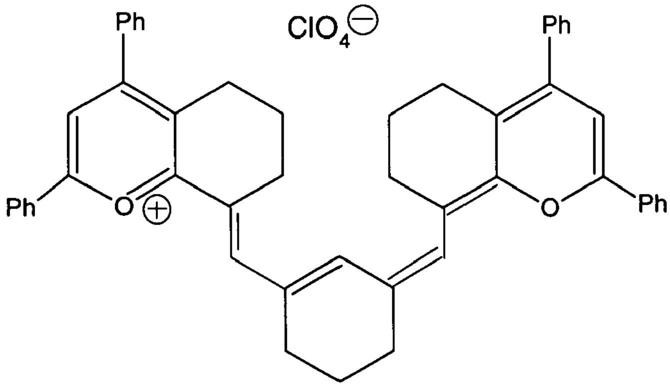

NC
CN
NC
Ph
CN
CN
⊖
CN
Ph
N
N
CO₂Et
⊕
Et₃NH

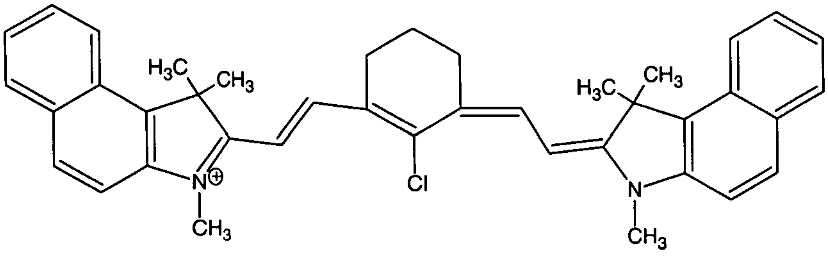

CF3SO3⊖
O
tBuO
O
S
Cl
N⊕
S
N
O
OtBu
O

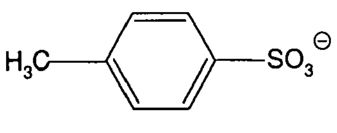

N
N⊕
NaO3S
SO3⊖


N
N
⊕NH2
NC
CN
NC
Ph
N
N
N
CN
CN
⊖
CN
Ph









[0066] If present, the amount of IR absorber in the bottom layer is preferably at least 0.1 wt.% based on the dry layer weight of the bottom layer, more preferably at least 1 wt.%, most preferably at least 1.5 wt.%. Usually, the amount of IR absorber does not exceed 50 wt.%, preferably 30 wt.% and most preferably 20 wt.%. The IR absorber can for example be present in an amount of 0.2 to 50 wt.%. The preferred range is 8 to 20 %. If carbon black is used as IR absorber, it is preferably used in an amount of no less than 40%. Either a single IR absorber or a mixture of two or more can be present; in the latter case, the amounts given refer to the total amount of all IR absorbers.

[0067] The dry layer weight of the bottom layer is preferably 0.1 to 5 g/m^2, more preferred 0.5 to 2.5 g/m^2, most preferred 1.0 to 2.0 g/m^2.

TOP LAYER

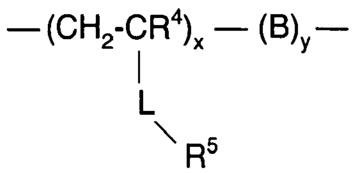
[0068] The top layer protects the bottom layer from being dissolved by an aqueous alkaline developer. It is therefore necessary that the top layer itself is not soluble or dispersible in or penetrable by an aqueous alkaline developer. By the wording "not soluble in, dispersible in or penetrable by an aqueous alkaline developer", it is meant that the top layer can resist the attack of an aqueous alkaline developer having a pH of at least 8 for at least 2 minutes. However, upon exposure to IR radiation the top layer becomes removable by an aqueous alkaline developer (necessary dwell time: less than 2 minutes).

[0069] The top layer comprises a second polymeric material (preferably at least 30 wt.%, more preferably at least 50 wt.%, most preferably at least 70 wt.% of the dry layer weight of the top layer) which is different from the first polymeric material and comprises a polymer backbone and pendant phosphonic acid groups and/or phosphate groups (in the following abbreviated as phosphorous derivatized polymers); preferred polymers can be represented by the following structure (IV):

$$-(A)_x-(B)_y- \qquad (IV)$$

wherein A and B together represents the polymer backbone in which A further comprises recurring units comprising pendant phosphonic acid groups and/or phosphate groups, B further represents different recurring units, x represents 3 to 15 mole% and y represents 85 to 97 mole%.

[0070] More preferably, the phosphate polymer can be represented by the following structure (V):



$$-(CH_2-\underset{\underset{\diagdown R^5}{L}}{\underset{|}{C}}R^4)_x-(B)_y- \qquad (V)$$

[0071] The copolymers of formulae (IV) and (V) can be block copolymers with A blocks and B blocks or can be random copolymers where units A and units B, respectively do not form blocks within the copolymer.

[0072] R^4 represents hydrogen, a substituted or unsubstituted lower alkyl group having 1 to 4 carbon atoms (such as methyl, ethyl, *n*-propyl, or *t*-butyl), or a halogen atom (such as fluoro, chloro, bromo, or iodo); preferably R^4 represents hydrogen or methyl.

[0073] L represents a direct bond or a linear, branched or cyclic linking group comprising 1 or more carbon atoms and optionally 1 or more heteroatoms. Useful linking groups can include, but are not limited to, substituted or unsubstituted, linear or branched alkylene groups having 1 to 10 carbon atoms (such as methylene, methoxymethylene, ethylene, isopropylene, *n*-butylene, *t*-butylene, and n-hexylene), substituted or unsubstituted cycloalkylene groups having 5 to 10 carbon atoms in the cyclic group (such as 1,3-cyclopentylene and 1,4-cyclohexylene), substituted or unsubstituted arylene groups having 6 to 10 carbon atoms in the cyclic group (such as 1,4-phenylene, 3-methyl-1,4-phenylene, or naphthylene), or combinations thereof, such as arylenealkylene, alkylenearylene (for example, methylene-1,4-phenylene), and alkylenearylenealkylene groups. The L linking groups can also include one or more oxy, thio, amido, carbonyl, oxycarbonyl, carbonyloxy, carbonamido, sulfonamido, urea, urethane, and carbonate [-O-C(O)-O-] groups within the linking chain, with or without any of the alkylene, cycloalkylene, and arylene groups described above. L can include combinations of two or more of these groups.

[0074] Preferably, L is a direct bond or one or more of alkylene groups having 1 to 4 carbon atoms in the linking chain, carbonyloxy, urea, urethane, alkylenecarbonyloxy, and carboxyalkylene groups, $-(OCH_2CH_2)n-$, $-(OCH_2CHCH_3)n-$, where n = 0 to 20 (preferably 0 to 7).

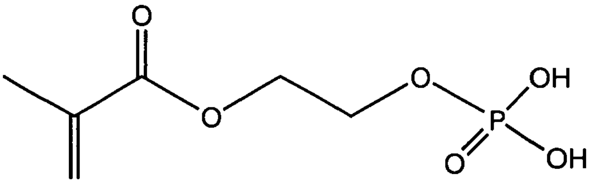
[0075] More preferably, L comprises $-(OCH_2CH_2)_n-$, $-(OCH_2CHCH_3)_n$ or mixtures thereof where n = 0 to 5.

[0076] In structure (V), R^5 represents a pendant $P(O)(OH)_2$ group. The polymer can comprise one or more different recurring units with pendant $P(O)(OH)_2$ group.

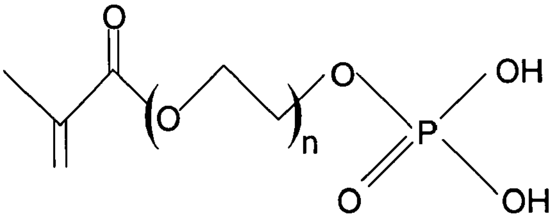
[0077] In referring to phosphorous derivatized groups, it is also intended to include the corresponding salts of the phosphonic acid, including but not limited to, alkali metal salts and ammonium salts. Any suitable positive counterion can be used with the pendant phosphonic acid groups as long as the counterion does not adversely affect the performance of the resulting polymer or other desired imaging properties.

[0078] In more preferred embodiments of Structures IV and V, x is from about 5 to about 10 mole% and y is from about 90 to about 95 mole%.

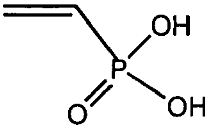
[0079] Particularly useful ethylenically unsaturated polymerizable monomers that can be used to provide the "A" recurring units described above include, but are not limited to the following compounds represented by the following Structures A1 through A5:



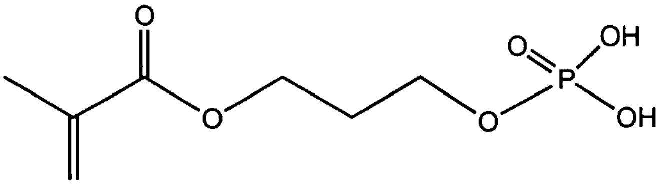
Ethylene glycol methacrylate phosphate (A1)



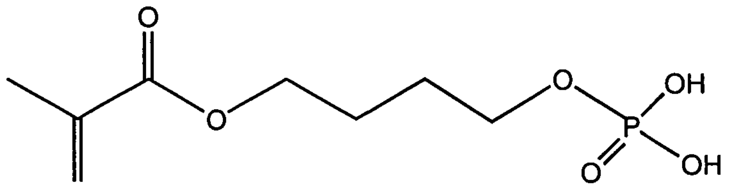
Polyethylenglycol methacrylate phosphate (A2)



Vinyl phosphonic acid (A3)



1,3-Propylene glycol methacrylate phosphate (A4)



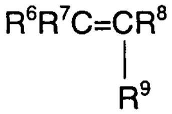
1,4-n-Butylene glycol methacrylate phosphate (A5)

and suitable salts thereof

[0080] In structures (IV) and (V), B represents recurring units derived from one or more ethylenically unsaturated polymerizable monomers that do not have pendant phosphonic acid groups and phosphate groups. A variety of ethylenically unsaturated monomers which are copolymerizable with the monomers from which the A recurring units are derived can be used for providing B recurring units, including acrylates and methacrylates each having an aliphatic hydroxy group (like 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate), alkyl acrylates (like methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, glycidyl acrylate and N-dimethylaminoethyl acrylate), and alkyl methacrylates (like methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate, glycidyl methacrylate and N-dimethylaminoethyl methacrylate), acrylamides and methacrylamides (like acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide and N-ethyl-N-phenylacrylamide), vinyl ethers (like ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether and phenyl vinyl ether), vinyl esters (like vinyl acetate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate), styrenes (like styrene, α-methylstyrene, β-methylstyrene, halostyrene, and halomethylstyrene), vinyl ketones (like methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone and phenyl vinyl ketone), olefins (like ethylene, propylene, isobutylene, butadiene and isoprene), N-vinylpyrrolidone, N-vinylcarbazol, 4-vinylpyridine, (meth)acrylonitrile, unsaturated imides (like maleimide, N-(meth)acryloyl(meth)acrylamide, N-acetyl(meth) acrylamide, N-propionyl(meth)acrylamide and N-(p-chlorobenzoyl)methacrylamide), unsaturated anhydrides (like maleic anhydrides), and combinations thereof. Specific monomers of these and similar classes are described for example, in paragraphs [0044] through [0054] of US Patent Application 2004/0137366 (corresponding to EP 1 433 594 A).

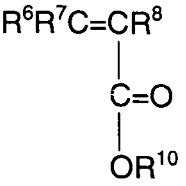
[0081] Preferably, B represents recurring units for Structure (IV) that are derived from one or more (meth)acrylates, (meth)acrylonitriles, N-phenylmaleimide, or (meth)acrylamides such as N-alkoxyalkylmethacrylamides, or combinations of two or more of such monomers. Some particularly useful monomers from which B recurring units are derived include methyl methacrylate, styrene, ethylenically unsaturated polymerizable monomers having pendant cyclic urea groups, and combinations thereof.

[0082] More particularly useful monomers for obtaining units B are represented by the following Structures (VI) through (X):



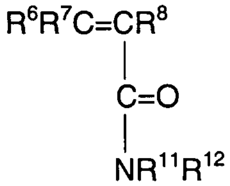
$$\begin{array}{r} R^6R^7C{=}CR^8 \\ | \\ R^9 \end{array}$$

(VI)



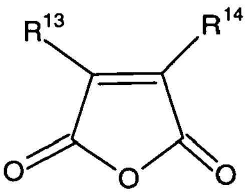
$$\begin{array}{r} R^6R^7C{=}CR^8 \\ | \\ C{=}O \\ | \\ OR^{10} \end{array}$$

(VII)

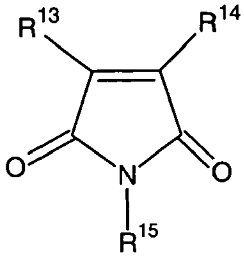


$$\begin{array}{r} R^6R^7C{=}CR^8 \\ | \\ C{=}O \\ | \\ NR^{11}R^{12} \end{array}$$

(VIII)



(IX)



(X)

[0083] R^6 and R^7 are independently hydrogen, substituted or unsubstituted alkyl groups having 1 to 6 six carbon atoms, substituted or unsubstituted alkenyl groups having 1 to 6 carbon atoms, substituted or unsubstituted phenyl groups, halogen atoms; substituted or unsubstituted alkoxy groups having 1 to 6 carbon atoms, substituted or unsubstituted acyl groups having 1 to 6 carbon atoms, substituted or unsubstituted acyloxy groups having 1 to 6 carbon atoms, or R^6 and R^7 together can form a cyclic group, such as a cyclopentyl or cyclohexyl group or form one of the following divalent groups: $-NHC(O)CH_2CH_2CH_2-$, $-NHC(O)CH_2CH_2-$, $-CH_2C(O)OC(O)-$, $-(CH_2)_2C(O)OC(O)-$, and $-CH_2C(O)OC(O)CH_2-$. R^6 and R^7 are preferably independently hydrogen or unsubstituted alkyl, more preferably hydrogen or methyl.

[0084] R^8 is hydrogen or a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms, substituted or unsubstituted phenyl group, or halogen atom. R^8 is preferably hydrogen or an unsubstituted alkyl group; more preferred R^8 is hydrogen or methyl.

[0085] R^9 is hydrogen or a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms, substituted or unsubstituted phenyl group, or halogen atom. R^9 is preferably a substituted or unsubstituted phenyl group (that is, to provide a styrenic monomer).

[0086] R^{10} is hydrogen or a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, substituted or unsubstituted alkenyl group having 1 to 20 carbon atoms, substituted or unsubstituted cycloalkyl group, substituted or unsubstituted cycloalkenyl group, substituted or unsubstituted phenyl group, or substituted or unsubstituted alkoxyalkylene group having 1 to 20 carbon atoms. R^{10} is preferably a substituted or unsubstituted alkyl group, more preferably methyl or ethyl.

[0087] R^{11} and R^{12} are independently hydrogen or substituted or unsubstituted alkyl groups having 1 to 20 carbon atoms, substituted or unsubstituted alkenyl groups having 1 to 20 carbon atoms, substituted or unsubstituted cycloalkyl groups, substituted or unsubstituted cycloalkenyl groups, substituted or unsubstituted phenyl groups, or substituted or unsubstituted alkoxyalkylene groups having 1 to 12 carbon atoms. R^{11} and R^{12} are preferably independently hydrogen or unsubstituted alkyl, more preferably hydrogen or methyl.

[0088] R^{13} and R^{14} are independently hydrogen or substituted or unsubstituted alkyl groups having 1 to 6 carbon atoms, substituted or unsubstituted alkenyl groups having 1 to 6 carbon atoms, substituted or unsubstituted phenyl groups, halogen atoms, cyano groups, substituted or unsubstituted alkoxy groups having 1 to 6 carbon atoms, substituted or unsubstituted acyl groups having 1 to 6 carbon atoms, or substituted or unsubstituted acyloxy groups having 1 to 6 carbon atoms. R^{13} and R^{14} are independently preferably hydrogen, unsubstituted alkyl or phenyl, more preferably hydrogen, methyl or phenyl.

[0089] R^{15} is hydrogen or a substituted or unsubstituted alkyl group having 1 to 7 carbon atoms (including a benzyl group), substituted or unsubstituted phenyl group, or hydroxy group. R^{15} is preferably hydrogen or a substituted or unsubstituted phenyl group.

[0090] Preferably, the recurring units represented by B are derived from styrenes, N-phenylmaleimide, (meth)acrylic acid, (meth)acrylonitrile, (meth)acrylamides, alkyl (meth)acrylates, monomers having pendant cyclic urea groups or mixtures of two or more of these monomers.

[0091] In some preferred embodiments for the multi-layer imageable elements, the phosphorous derivatized polymer is represented by Structure (V) described above in which the x is from about 3 to about 15 mole% (more preferably, from about 5 to about 10 mole%) and B represents recurring units derived from: styrene, N-phenylmaleimide, (meth) acrylic acid, and alkyl methacrylate, wherein these recurring units comprise from 85 to about 97 mole% (more preferably from about 90 to about 95 mole%) of all recurring units in the phosphorous derivatized polymer.

[0092] The phosphorous derivatized polymers useful in this invention can be prepared using known polymerization techniques depending upon the starting materials. If condensation polymers are prepared and used, the starting materials are generally dibasic carboxylic acids and dibasic alcohols, either of which can include the desired pendant phosphonic acid group.

[0093] More preferably, the phosphorous derivatized polymers are prepared from ethylenically unsaturated polymerizable monomers using conditions, reactants, and catalysts suitable for free radical (or "addition") polymerization that are well known to those skilled in the art and that 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, hydroperoxides such as cumyl hydroperoxide and azo compounds such as 2,2'-azobis(isobutyronitrile) (AIBN). Suitable reaction solvents include liquids that are inert to the reactants and that will not otherwise adversely affect the reaction.

[0094] The phosphorous derivatized polymers used in the present invention show an acid number of 60 mg KOH/g polymer or less, more preferably 50 mg KOH/g polymer or less, especially preferred 40 mg KOH/g polymer or less. The term "acid number" denotes the number of mg KOH determined by titration which is necessary for neutralizing 1 g polymer. Preferably, the phosphorous derivatized polymers have an acid number of 10 to 60 mg KOH/g polymer, more preferably 10 to 40 mg KOH/g phosphate polymer.

[0095] The phosphorous derivatized polymers preferably have a weight average molecular weight from 5,000 to 500,000, more preferably 10,000 to 200,000 (determined by GPC with polystyrene standards).

[0096] Furthermore, the top layer can comprise dyes or pigments having a high absorption in the visible spectral range. Those mentioned above in connection with the bottom layer are for example suitable. The colorants are preferably present in an amount of 0 to 5 wt.%, more preferred 0.5 to 3 wt.%, based on the dry layer weight of the top layer.

[0097] The surfactants mentioned in connection with the bottom layer can be present in the top layer as well. Here, they are preferably present in an amount of 0 to 2 wt.%, more preferred 0 to 0.5 wt.%, based on the dry layer weight of the top layer.

[0098] The top layer can also comprise acid formers which release acids upon application of heat.

[0099] Examples include triazines, diazonium, iodonium, sulphonium, phosphonium, ammonium, oxysulphoxonium, oxysulphonium and sulphoxonium salts with non-nucleophilic anions such as tetrafluoroborate, hexafluorophosphate, hexafluoroarsenate, hexafluoro-antimonate, triflate, tetrakis(pentafluorophenyl)borate, pentafluoroethylsulfonate, p-methylbenzylsulfonate, ethylsulfonate, trifluoromethylacetate and pentafluoroethylacetate anions. But also C_1-C_5 alkylsulfonates, arylsulfonates, N-C_1-C_5 alkylsulfonylsulfonamides, such as for example benzoin tosylate, 2-hydroxymethylbenzoin tosylate and N-methanesulfonyl-2,4-dimethylbenzolsulfonamide and combinations of two or more of the above. They are preferably present in an amount of 0 to 25 wt.%, more preferred 0 to 10 wt.%, particularly preferred 0 to 5 wt.%, based on the dry layer weight of the top layer. According to one embodiment, no acid former is present.

[0100] Furthermore, the top layer composition can comprise coating enhancers such as poly(glycol)ether-modified siloxanes. They are preferably present in an amount of 0 to 1 wt.%, based on the dry layer weight of the top layer.

[0101] The dry layer weight of the top layer is preferably 0.1 to 5 g/m^2, more preferred 1 to 3 g/m^2, and especially preferred 0.2 to 1.5 g/m^2.

PRODUCTION OF THE ELEMENTS

[0102] The compositions for the bottom layer and the top layer can be applied to the surface of the substrate by means of common coating processes, e.g. spin coating, dip coating, roller coating, spray coating, coating with a slot coater and coating by means of a doctor blade. It is possible to apply the coating compositions for the bottom layer and the top layer on both sides of the substrate; however, it is preferred that the radiation-sensitive coating be only applied to one side of the substrate.

IMAGING

[0103] Imaging of the lithographic printing plate precursors according to the present invention can be carried out by the application of IR irradiation; in this case, it is required that the bottom layer comprises an IR absorber. As a radiation source, semiconductor lasers or laser diodes which emit in the range of 650 to 1,300 nm, preferably 750 to 1,120 nm, are for example used. The laser radiation can be digitally controlled via a computer, i.e. it can be turned on or off so that an image-wise exposure of the plates can be effected via stored digitized information in the computer which results in so-called computer-to-plate (ctp) printing plates. All image-setting units with IR lasers known to the person skilled in the art can be used for this purpose. The IR radiation causes the top layer of the present invention, which was originally insoluble in the developer, to become soluble or dispersible in and/or penetrable by the aqueous alkaline developer.

[0104] Suitable radiation sources are e.g. semi-conductor lasers or laser diodes which emit in the range of 750 to 1200 nm, for example Nd:YAG lasers (1,064 nm), laser diodes which emit between 790 and 990 nm, and Ti:sapphire lasers. The laser radiation can be digitally controlled via a computer, i.e. it can be turned on or off so that an image-wise exposure of the plates can be effected via stored digitized information in the computer; this way, so-called computer-to-plate (ctp) printing plates can be obtained. Any image-setters equipped with IR lasers that are known to the person skilled in the art can be used.

[0105] Instead of applying IR radiation to the imageable element heat can be directly applied imagewise by imagewise contacting the imageable element with a hot body like a hot stylus or thermal printing head; in this case, the presence of an IR absorber in the coating is not required. It is preferred that IR radiation is applied.

[0106] The image-wise irradiated/heated elements such as e.g. printing plate precursors are developed with an aqueous alkaline developer, which typically has a pH value in the range of 10 to 14. For this purpose, commercially available developers and mixtures thereof can be used. To the person skilled in the art, it goes without saying that the developer composition can be optimized for specific printing plate precursors based on the polymers used in the bottom layer and top layer.

[0107] Generally, the alkaline developer is applied to the element by rubbing or wiping the top layer with an applicator containing the developer. Alternatively, the imaged element can be brushed with the developer or the developer may be applied by spraying it onto the top layer with sufficient force to remove the exposed regions. Also the imaged element can be immersed in the developer. Although the elements of the present invention are positive working, they can be developed with conventional "negative developers", i.e. developers which are initially designed for developing negative working precursors; this is an advantage as due to the usually lower pH of negative developers, there is less substrate attack, and the developer leaves a more hydrophilic surface with less problems of restart toning. The developer removes the bottom layer and the top layer in the exposed areas so that the hydrophilic surface of the substrate is revealed. Hybrid developers containing organic solvents and having a high pH would also be possible, i.e. those containing sodium metasilicate, Dowanol EPH and diethanolamine (pH = 13).

[0108] The developed elements can be treated with a preservative ("gumming"). The preservatives are aqueous solutions of hydrophilic (co)polymers, wetting agents and other known additives.

[0109] For certain applications, it is furthermore advantageous to increase the mechanical strength of the obtained image areas by subjecting them to a heat treatment (what is referred as "baking") and/or overall exposure (e.g. to UV light). For this purpose, prior to the treatment, the imaged plate is treated with a solution that protects the non-image areas such that the heat treatment does not cause these areas to accept ink. A solution suitable for this purpose is e.g. described in US-A-4,355,096. Baking usually takes place at a temperature in the range of 150 to 250°C. When both baking and overall exposure are carried out, the two treatment steps can be performed simultaneously or one after the other.

[0110] Under typical processing conditions for e.g. printing plates, the elements of the present invention like printing plate precursors are preferably not sensitive to visible light and the UV portion of daylight so that they can be processed under white light, i.e. do not require yellow light conditions.

[0111] The present invention is described in more detail in the following examples; however, they are not intended to restrict the invention in any way.

Examples

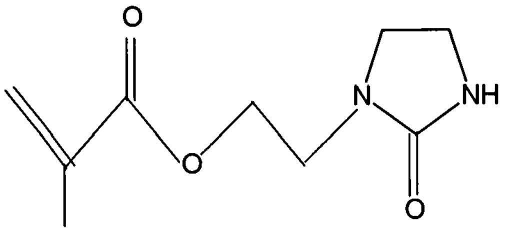
[0112] The following abbreviations are used:

AC432:

[0113] A copolymer of N-phenylmaleimide (40 mole%), methacrylamide (19 mole%), methacrylic acid (15 mole%) and N-(2-methacryloyloxyethyl)ethylene urea (26 mole%) with an acid number of 57.

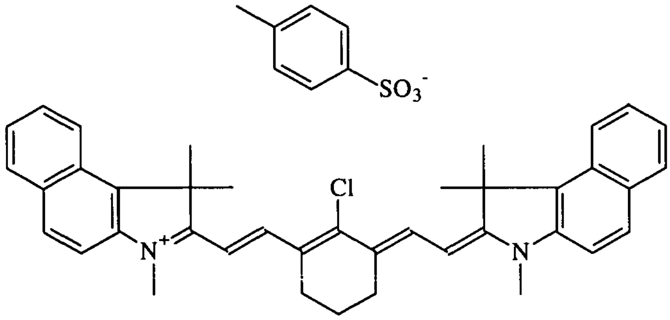
N-(2-methacryloyloxyethyl)ethylene urea: methacrylic monomer available from Degussa

[0114]



IR dye A: Trump Dye

[0115]



BYK307:

[0116] A polyethoxylated dimethylpolysiloxane surfactant as supplied by BYK Chemie of Wallingford, CT

Ethyl Violet:

[0117] Contrast dye, C.I. 42600; CAS 2390-59-2 [$(p-(CH_3CH_2)_ZNC_6H_4)_3C^+Cl^-$]

Developers 956 and 980	are negative developers available from Eastman Kodak Company
AIBN	2,2'-azobis(isobutyronitrile)
DEK	diethyl ketone
MEK	methyl ethyl ketone
Dowanol PM	propylene glycol monomethylether (PGME), 1-methoxy-propan-2-ol
BLO	γ-butyrolactone
GP Resol	GP649D99 resol resin from Georgia Pacific, Atlanta
D11	triarylmethane dye (CAS 433334-19-1)
PAM 100	polyethylene glycol methacrylate phosphate
Dowanol PMA	1-methoxy-2-propyl acetate
Polymer A	copolymer having recurring units derived from N-phenyl-maleimide (41.5 mole%), methacrylamide (37.5 mole%) and methacrylic acid (21 mole%), obtained from AZ Electronics (Germany)

Preparation Example 1

Synthesis of a copolymer of ethylene glycol methacrylate phosphate and methylmethacrylate (Copolymer 1)

[0118] 150g n-Propanol, 36.84 g methylmethacrylate and 6.72 g ethyleneglycol methacrylate phosphate were added to a 3-necked round bottom flask fitted with stirrer, nitrogen inlet and condenser and heated to 70°C. After flushing thoroughly for 15 mins with nitrogen, 0.66g AIBN dissolved in 100 ml n-propanol was added dropwise over 2 hours. The reaction was carried out further for 2 hour at 70°C under nitrogen atmosphere. The copolymer was precipitated in 600 ml petrol ether (Waschbenzin 135/180). The copolymer was filtered and dried at 40°C in a vacuum oven. The acid number of this copolymer was found to be 37.

[0119] The solubility of Copolymer 1 in 956 developer was tested by adding 0.3 g of the copolymer to 30 ml 956 developer under stirring. The resin dissolved completely without any residues.

Preparation Example 2

Synthesis of a copolymer of vinyl phosphonic acid and methylmethacrylate (Copolymer 2)

[0120] 5.3 g Vinyl phosphonic acid, 14.7 g methylmethacrylate, 40 ml Dowanol PM and 0.20 g AIBN were placed in a 200 ml bottle fitted with a rubber cap. The solution was flushed thoroughly with nitrogen, capped and allowed to react at 60°C for 18 hours. The copolymer was precipitated in 200 ml petrol ether (Waschbenzin 135/180). The copolymer was filtered and dried at 40°C in a vacuum oven. The acid number of this copolymer was found to be 30.

Preparation Example 3

Synthesis of a copolymer of polyethyleneglycol methacrylate phosphate and methylmethacrylate (Copolymer 3)

[0121] 150g n-Propanol, 38.85 g methylmethacrylate and 5.17 g polyethyleneglycol methacrylate phosphate PAM 100 were added to a 3-necked round bottom flask fitted with stirrer, nitrogen inlet and condenser and heated to 70°C. After flushing thoroughly for 15 mins with nitrogen, 0.66g AIBN dissolved in 100 ml n-propanol was added dropwise over 2 hours. The reaction was carried out further for 2 hour at 70°C under nitrogen atmosphere. The copolymer was precipitated in 600 ml petrol ether (Waschbenzin 135/180). The copolymer was filtered and dried at 40°C in a vacuum oven. The acid number of this copolymer was found to be 12.

[0122] The solubility of Copolymer 3 in 980 developer was tested by adding 0.3 g of the copolymer to 30 ml 980 developer while stirring. The resin dissolved completely without any residues.

Preparation Example 4

Synthesis of a copolymer of ethylene glycol methacrylate phosphate and methyl methacrylate (Copolymer 4)

[0123] 150 g n-Propanol, 34.04 g methyl methacrylate and 12.60 g ethyleneglycol methacrylate phosphate were added to a 3-necked round bottom flask fitted with stirrer, nitrogen inlet and condenser and heated to 70°C. After flushing thoroughly for 15 min with nitrogen, 0.66 g AIBN dissolved in 100 ml n-propanol was added dropwise over 2 hours. The reaction was carried out further for 2 hours at 70°C under nitrogen atmosphere. The copolymer was precipitated in 600 ml petrol ether (Waschbenzin 135/180). The copolymer was filtered and dried at 40°C in a vacuum oven. The acid number of this copolymer was found to be 65.

Example 1

[0124] A lithographic printing plate was prepared as follows:

Bottom layer

[0125] A solution of 6% solids was prepared by dissolving the components as given in the formulation below in a solvent mixture consisting of MEK 45 wt.%, PM 35 wt.%, BLO 10 wt.%, H_2O 10 wt.%:

Component	Parts by weight
AC 432	84.5
IR dye A	15
BYK 307	0.5

[0126] The solution was coated on an electrolytically grained, anodised and polyvinylphosphonic acid treated substrate and dried at 135°C for 45 s to obtain a dry coating weight of 1.35 g/m^2.

Top layer

[0127] 2.4 g Copolymer 1, 0.012 g Byk 307 and 0.013 g Ethyl Violet were dissolved in 20 g of a solvent mixture (diethylketone: Dowanol PMA: isopropylalcohol; 8:1:1 weight ratio) and coated over the bottom layer.

[0128] The thermally imageable element thus formed was dried at 135°C for 45s, the dry coating weight of the top layer was 0.55 g/m^2. The plate was imaged with test patterns at 9W and drum speeds between 150 rpm and 360 rpm (which corresponds to 67- 161 mJ/cm^2) in steps of 30 rpm with a Creo Quantum 800 platesetter. The plate was developed with 956 developer in a Mercury processor at 900 mm/min to provide a good image with excellent resolution and clean background at exposures above 80 mJ/cm^2.

Example 2

Top layer

[0129] 2.4 g Copolymer 3, 0.012 g Byk 307 and 0.013 g Ethyl Violet were dissolved in 20 g of a solvent mixture (diethylketone: Dowanol PMA; 9:1 weight ratio) and coated over the bottom layer described in Example 1 to give a dry coating weight of 0.65 g/m^2 for the top layer after drying at 135°C for 45s.

[0130] The plate was imaged with test patterns at 9W and drum speeds between 150 rpm and 360 rpm (which corresponds to 67- 161 mJ/cm^2) in steps of 30 rpm with a Creo Quantum 800 imagesetter. The plate was developed with 980 developer in a Glunz and Jensen Processor at 120 cm/min and provided a good image with excellent resolution and clean background at exposures above 93 mJ/cm^2.

Example 3

[0131] A lithographic printing plate was prepared as follows:

Bottom layer

[0132] A solution of 6% solids was prepared by dissolving the components as given in the table below in a solvent mixture consisting of MEK 45 wt.%, PM 35 wt.%, BLO 10 wt.%, H_2O 10 wt.%:

Components	Parts by weight
AC432	74.5
GP-Resol	7.5
IR dye A	15.0
D11	1.5

[0133] The solution was coated on an electrolytically grained, anodised and polyvinylphosphonic acid treated substrate and dried at 135°C for 45 s to obtain a dry coating weight of 1.35 g/m^2

Top layer

[0134] 2.4 g Copolymer 3, 0.012 g Byk 307 and 0.013 g Ethyl Violet were dissolved in 20 g of a solvent mixture (diethylketone : Dowanol PMA : isopropylalcohol; 8:1:1 weight ratio) and coated over the bottom layer to give a dry coating weight of 0.60 g/m^2 for the top layer after drying at 135°C for 45s.

[0135] The plate was imaged with test patterns at 9W and drum speeds between 150 rpm and 360 rpm (which corresponds to 67- 161 mJ/cm^2) in steps of 30 rpm with a Creo Quantum 800 imagesetter. The plate was developed with 956 developer in a Mercury processor at 90 cm/min and provided a good image with excellent resolution and clean background at exposures above 93 mJ/cm^2.

Example 4

Bottom Layer

[0136] A bottom layer formulation (6 % solids) was prepared by dissolving the components shown in the following table in a solvent mixture comprising MEK (45 wt.%), PM (35 wt.%), BLO (10 wt.%), and water (10 wt.%).

Bottom layer component	Parts by weight
Polymer A	84.5
IR dye A	15.0
Byk® 307	1.5

[0137] This bottom layer formulation solution was coated on substrate A and dried at 135°C for 45 seconds to provide a dry coating weight of 1.3 g/m^2.

Top layer

[0138] 2.4 g Copolymer 2, 0.012 g Byk 307 and 0.013 g ethyl violet were dissolved in 20 g of a solvent mixture (diethyl ketone: Dowanol PMA; 9:1 weight ratio) and coated over the bottom layer to give a dry coating weight of 0.65 g/m^2 for the top layer after drying at 135°C for 45s.

[0139] The plate was imaged with test patterns at 9W and drum speeds between 150 rpm and 360 rpm (which corresponds to 67 to 161 mJ/cm^2) in steps of 30 rpm with a Creo Quantum 800 imagesetter. The plate was developed with 980 developer in a Glunz and Jensen processor at 120 cm/min and provided a good image with excellent resolution and clean background at exposures above 93 mJ/cm^2.

[0140] The solubility of Copolymer 2 in 980 developer was tested by adding 0.3 g of the copolymer to 30 ml 980 developer while stirring. The resin dissolved completely without any residues.

Comparative Example 1:

[0141] A top layer formulation was prepared with TN13-15 which is a 15 m% tosylated m-Cresol Novolac (2.4 g), Byk® 307 (0.012 g) and Ethyl Violet (0.013 g) that were dissolved in 20 g of a solvent mixture of DEK and Dowanol PM (9:1 weight ratio) and coated over the first layer described in Example 3 to provide a dry top layer weight of 0.65 g/m^2.

[0142] The thermally imageable element thus formed was dried at 135 °C for 45 seconds. The element was imaged with test patterns at 9W and drum speeds between 150 rpm and 360 rpm in steps of 30 rpm using a Creo Quantum 800 imagesetter (67 to 161 mJ/cm^2). The resulting imaged printing plate was developed with 980 Developer for 30 seconds to give a good image with excellent resolution and clean background at exposures greater than 101 mJ/cm^2.

[0143] The solubility of the resin TN13-15 in 980 Developer was evaluated by stirring 0.3 g of TN13-15 in 30 ml of the developer. Insoluble residues were found in the developer; this shows that the used top layer composition can lead to filter blockage and redeposition problems in the processor.

Comparative Example 2:

[0144] A formulation for a top layer comprising the components described in the following table in diethyl ketone was prepared. The formulation concentration was selected to provide a dry film having a coating weight of 0.7 g/m^{-2}. The formulation was applied to the coated substrate described in Example 3 above by means of a wire-wound bar, and dried at 135 °C for 30 seconds to produce a two-layer imageable element.

Component	Parts by weight
PD 140A	69.1
P3000	30
Ethyl violet	0.4
Byk 307	0.5

[0145] The element was imaged with test patterns at 9W and drum speeds between 150 rpm and 360 rpm in steps of 30 rpm using a Creo Quantum 800 imagesetter (67 to 161 mJ/cm^2). The resulting imaged printing plate was developed with 980 Developer for 30 seconds to give a good image with excellent resolution and clean background at exposures greater than 101 mJ/cm^2.

[0146] The solubility of the resin components PD140A and P3000 in 980 Developer was evaluated by stirring 0.2 g of PD 140 A and 0.1 g P3000 in 30 ml of the developer. Insoluble residues were found in the developer; this shows that the used top layer composition can lead to filter blockage and redeposition problems in the processor.

Comparative Example 3:

[0147] A top layer formulation was prepared by dissolving Copolymer 4 (2.4 g), Byk® 307 (0.012 g) and Ethyl violet (0.013 g) in 20 g of a solvent mixture of DEK and Dowanol PM (9:1 weight ratio). The formulation was coated over the first layer which was as described in Example 3 to provide a top layer with a dry layer weight of 0.65 g/m^2. The thermally imageable element thus formed was dried at 135°C for 45 seconds. The element was imaged with test patterns at 9W and drum speeds between 150 rpm and 360 rpm in steps of 30 rpm using a Creo Quantum 800 imagesetter (67 to 161 mJ/cm^2). The resulting imaged printing plate was developed with 980 Developer for 30 seconds. Almost no image was found on the plate.

[0148] The solubility of Copolymer 4 in 980 Developer was evaluated by stirring 0.3 g of Copolymer 4 in 30 ml of the developer. The resin dissolved completely without any residues.

Solvent Resistance Test

[0149] The top layers described in Examples 1 to 4 and in the comparative examples were coated directly on the aluminum substrate as described in Example 1 and dried for 30 seconds at 135°C.

[0150] Drops of solvent Butylcellosolve and commercially available UV Wash (commercial cleaner for rollers and blanket) from Varn were placed on each coating at one minute intervals up to 5 minutes and then wiped off with tissue. The results are given in Table 1 below where the times for complete dissolution of the coating is noted.

Table 1

Example	UV Wash	Butylcellosolve
1	240 s	>300 s
2	240 s	>300 s
4	240 s	>300 s
Comparative Example 1	30 s	30 s
Comparative Example 2	10 s	10 s
Comparative Example 3	150 s	240 s

[0151] As can be derived from Table 1, the top layers according to the present invention show a much better resistance against solvents like UV Wash and Butylcellosolve than the top layers of the comparative examples.

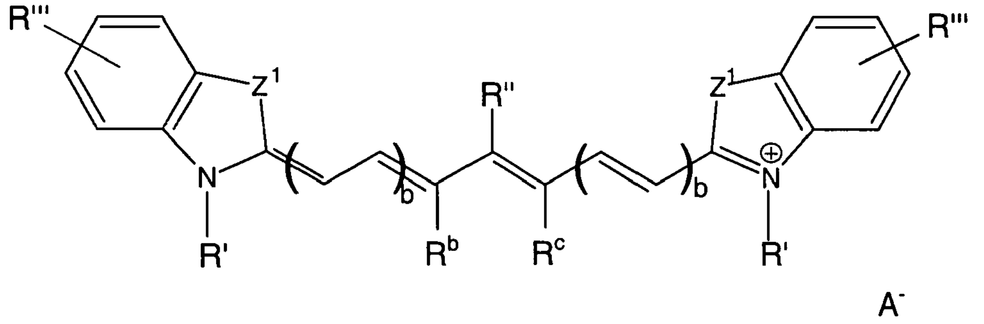
Claims

1. Heat-sensitive positive working element comprising:

a) a substrate;
b) a bottom layer, which is soluble or swellable in aqueous alkaline developers and comprises at least one first polymeric material soluble or swellable in aqueous alkaline developers and insoluble in organic solvents of low polarity; and
c) an ink-accepting top layer which is not soluble or dispersible in and not penetrable by an aqueous alkaline developer but is rendered soluble or dispersible in or penetrable by the developer upon exposure to heat and/or IR radiation, and which comprises a second polymeric material which is different from the first polymeric material, comprises a polymer backbone and pendant phosphonic acid groups and/or phosphate groups and has an acid number of up to 60 mg KOH/g polymer.

2. Element according to claim 1, further comprising a photothermal conversion material present either in the bottom layer or a separate absorber layer adjacent to the bottom layer.

3. Element according to claim 2, wherein the photothermal conversion material is represented by formula (III)



(III)

wherein

each Z^1 independently represents S, O, NR^a or $C(alkyl)_2$;
each R' independently represents an alkyl group, an alkylsulfonate group or an alkylammonium group;
R" represents a halogen atom, SR^a, OR^a, SO_2R^a or NR^a_2;
each R"' independently represents a hydrogen atom, an alkyl group, $-COOR^a$, $-OR^a$, $-SR^a$, $-NR^a_2$ or a halogen atom, or a benzofused ring;
R^b and R^c either both represent hydrogen atoms or, together with the carbon atoms to which they are bonded, form a five- or six-membered carbocylic ring;
A^- represents an anion;
R^a represents a hydrogen atom, an alkyl or aryl group;
each b is independently 0, 1, 2 or 3.

4. Element according to any one of claims 1 to 3 wherein said second polymeric material is represented by the following structure (I):

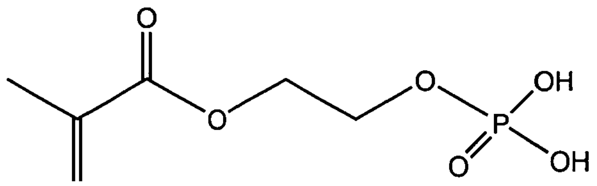
$$-(A)_x-(B)_y- \qquad (I)$$

wherein A and B together represent said polymer backbone in which A represents recurring units comprising pendant phosphonic acid groups and/or phosphate groups, and B represents different recurring units, x represents 3 to 15 mole%, and y represents 85 to 97 mole%.

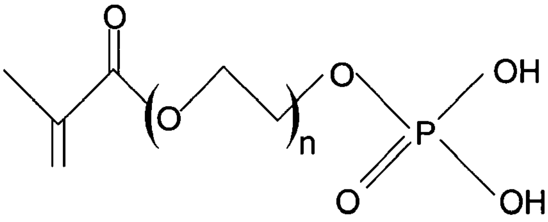
5. Element according to claim 4 wherein B represents recurring units derived from a styrenic monomer, (meth)acrylamide, (meth)acrylic acid or esters thereof, (meth)acrylonitrile, vinyl acetate, maleic anhydride, N-substituted maleimide, or mixtures thereof.

6. Element according to any one of claims 4 or 5 wherein x is from about 5 to about 10 mole%.

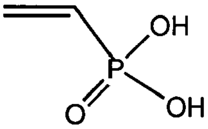
7. Element according to any one of claims 1 to 6 wherein said solvent-resistant polymer has recurring units A derived from one or more of the following compounds represented by the following Structures A1 through A5:



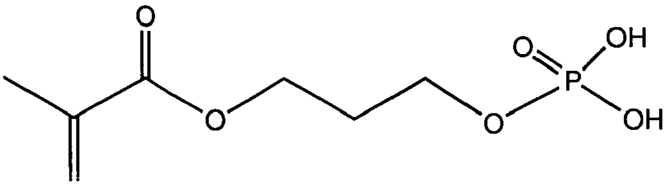
Ethylene glycol methacrylate phosphate (A1)



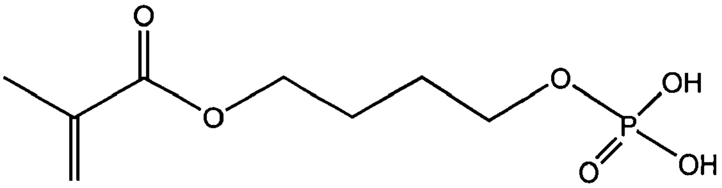
Polyethylenglycol methacrylate phosphate (A2)



Vinyl phosphonic acid (A3)



1,3-Propylene glycol methacrylate phosphate (A4)



1,4-n-Butylene glycol methacrylate phosphate (A5)

8. Element according to any of claims 1 to 7, wherein the second polymeric material has an acid number of 10 to 60 mg KOH/g copolymer.

9. Element according to any of claims 1 to 8, wherein the first polymeric material is selected from copolymers derived from N-substituted maleimides and comonomers copolymerizable therewith, copolymers having a urea group in their side chain and copolymers having a sulfonamide group in their side chain, and mixtures thereof.

10. Element according to any one of claims 1 to 9, wherein the element is a lithographic printing plate precursor.

11. Element according to any one of claims 1 to 10, wherein the dry coating weight of the bottom layer is from about 0.1 to about 5 g/m^2 and the dry coating weight of the top layer is from about 0.1 to about 5 g/m^2.

12. Process for the production of an element as defined in any of claims 1 to 11 comprising:

(a) applying a first solution comprising at least one first polymeric material as defined in claim 1 onto the substrate,
(b) applying a second solution comprising at least one second polymeric material as defined in claim 1, and
(c) drying.

13. Process for imaging a heat-sensitive element comprising:

(a) image-wise exposure of an element as defined in claim 2 to IR radiation or image-wise exposure of an element as defined in claim 1 and not comprising a photothermal conversion material to heat, and
(b) removing the exposed areas of the coating with an aqueous alkaline developer, revealing the substrate in these areas.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 01 6333

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2004/020484 A (KODAK POLYCHROME GRAPHICS GMBH [DE]; TIMPE HANS-JOACHIM [DE]; MUELLER) 11 March 2004 (2004-03-11) * page 4 - page 6, line 17 * * page 8 * * page 13, paragraph 4 - page 14 * * examples * -----	1,12,13	INV. B41C1/10 B41M5/36
A,D	EP 1 433 594 A2 (FUJI PHOTO FILM CO LTD [JP]) 30 June 2004 (2004-06-30) * paragraph [0015] - paragraph [0090] * * examples * -----	1,12,13	

TECHNICAL FIELDS SEARCHED (IPC)

B41C
B41M

The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
The Hague	4 December 2006	Markham, Richard

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