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(54) **Double-layer infrared-sensitive imageable elements with polysiloxane toplayer**

(57) IR-sensitive imageable element comprising:

- (a) a substrate with a hydrophilic surface,
b) a bottom layer,
comprising at least one photothermal conversion material and at least one polymer A soluble or swellable in an aqueous alkaline developer and insoluble in organic solvents with low polarity,

(c) a top layer,

comprising at least one polysiloxane selected from aryl-polysiloxanes and arylalkylpolysiloxanes having a glass transition temperature T_g of more than 60°C and a hydroxyl content of at least 1 % by weight.

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Description

[0001] The present invention relates to infrared-sensitive imageable elements, in particular IR-sensitive precursors of lithographic printing plates comprising two layers on the substrate wherein the top layer comprises a polysiloxane. The invention furthermore relates to a process for producing such imageable elements as well as 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 (in this context 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 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 attack 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 have been characterized by the use of alkali-soluble phenolic resins and naphthoquinone diazide derivatives; imaging was carried out with 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 form precursors which can be addressed directly by lasers. The digital image-forming information can be used to convey an image onto a printing form 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-A-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 of the composition, which restores the alkali solubility by photolytic decomposition of the onium salt. The printing form precursor can be used as a precursor of a positive working printing form or as a precursor of a negative printing form, if additional process steps are added between exposure and developing, as described in detail in British patent no. 2,082,339. The printing form precursors described in US-A-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 form precursor that can be used as a positive working system is described in US-A-5,372,907 and US-A-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 form precursor described in US-A-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 form precursors per se are UV-sensitive due to the acid-forming materials used.

[0009] US 5,658,708 describes positive and negative working thermally imageable elements. In the case of the negative working elements, the coating, which is applied in one step, for example comprises a compound with at least two enolether groups and an alkali-soluble resin with acid groups capable of reacting with the enolether groups upon heating. Drying is carried out at a relatively low temperature. During the image-forming step, the coating is image-wise heated to a high

temperature resulting in cross-linking which in turn renders the coating insoluble in the developer. In the case of positive working elements, the coating for example additionally comprises an acid former; drying is carried out at relatively high temperatures so that cross-linking of the coating of the unimaged element takes place, which coating is then insoluble in the developer. Image-wise irradiation with IR radiation then renders the coating soluble in the developer. The use of acid formers has the disadvantage that it renders the plate sensitive to UV light and thus also daylight (also in the sense of normal room light).

[0010] The document DE 198 50 181 describes printing plate precursors whose radiation-sensitive layer comprises a polymeric binder, a compound that releases an acid when heated, a photothermal conversion material and a cross-linkable polyfunctional enolether, wherein the polymeric binder both comprises protective groups that can be cleaved off by acid or heat and functional groups that allow cross-linking with enolethers, and wherein the binder is insoluble in aqueous alkaline media with a $\text{pH} \leq 13.5$.

[0011] U.S. patents 6,358,669, 6,352,811, and 6,352,812 describe thermally imageable elements with a double-layer coating. However, these elements exhibit a certain sensitivity to scratching; furthermore, lithographic printing plates produced therefrom tend to abrade on the printing machine which in turn affects the number of prints that can be obtained.

[0012] A novolak is preferably used as polymeric component of the top layer of the printing plates described in US 6,358,669 B1. It would, however, be desirable to improve the developer resistance of the coating and to avoid formation of sludge in the processor.

[0013] EP-A-0 862 998 describes a heat sensitive element comprising on a lithographic base a heat abatable recording layer and a top layer comprising an inorganic-organic composite or hybrid material. The removal of the non-image areas takes place by ablation; however, ablation of materials from the plate may cause staining of the optical system of the laser used for imagewise applying radiation/heat to the precursor.

[0014] Further heat-sensitive elements comprising two layers on a substrate are disclosed in EP-A-1 249 341. The element of EP-A-1 249 341 comprises a first layer containing a phenolic resin (like novolaks and resols) and a second layer containing a polysiloxane compound; this element, however, suffers from poor solvent resistance.

[0015] It is the object of the present invention to provide positive working thermally imageable lithographic printing plate precursors, which after exposure are developable without sludge formation in the processor, show high sensitivity in combination with good bakeability as well as solvent resistance for UV ink applications and good shelflife.

[0016] This object is surprisingly achieved by a lithographic printing plate precursor comprising

- (a) a substrate with a hydrophilic surface,
- (b) a bottom layer, comprising at least one photothermal conversion material and at least one polymer A soluble or swellable in an aqueous alkaline developer and insoluble in organic solvents with low polarity and
- (c) a top layer, comprising at least one polysiloxane selected from arylpolysiloxanes and arylalkylpolysiloxanes having a glass transition temperature T_g of more than 60°C and a hydroxyl content of at least 1 % by weight.

[0017] The present invention also relates to a process for the production of an element as defined above; the process comprises:

- (a) applying a solution comprising polymer A as defined above and at least one photothermal converting material, to an untreated or pretreated substrate, and
- (b) after drying the applied solution, applying a second solution comprising at least one polysiloxane as defined above.

[0018] In addition, the present invention relates to a process for imaging the above-defined IR-sensitive imageable element; the process comprises:

- (a) imagewise exposing an IR-sensitive imageable element as defined above, and
- (b) contacting the exposed element with an aqueous alkaline developer to remove exposed areas.

[0019] 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".

[0020] 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.

[0021] Solvents of low polarity wherein polymer A is insoluble include for example butyl acetate, ethyl acetate, methyl isobutyl ketone, propylene glycol monomethylether acetate and propylene glycol monoethylether acetate.

[0022] 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 , NR^7_2 ,

C(O)OR⁷ and OR⁷ (R⁷ 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 alkaryl group. The definition also applies to alkenyl groups, except that they comprise a C-C double bond in the hydrocarbon group.

[0023] 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, NR⁷₂, COOR⁷ and OR⁷ (wherein each R⁷ is independently selected from hydrogen, alkyl and aryl). The above definition also applies to the aryl unit of an aralkyl group and alkaryl group. Preferred examples include a phenyl group and a naphthyl group which can optionally be substituted (e.g. resulting in a tolyl group).

[0024] A dimensionally stable plate or foil-shaped material is preferably used as the substrate, especially in the production of printing plate precursors. Preferably, a material is used as dimensionally stable plate or foil-shaped material that has already been used as a substrate for printing forms. 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 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.

[0025] 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.

[0026] 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 phosphoric acid, the metal substrate can be subjected to a treatment with an aqueous solution of sodium silicate, calcium zirconium fluoride, polyvinylphosphonic acid or phosphoric acid. Within the framework of the present invention, the term "substrate" also encompasses an optionally pre-treated substrate exhibiting, for example, a so-called interlayer on its surface.

[0027] The details of the above-mentioned substrate pre-treatment are known to the person skilled in the art.

[0028] The first layer comprises at least one polymer A soluble or swellable in an aqueous alkaline developer but insoluble in organic solvents of low polarity.

[0029] Examples of polymer A include acrylic polymers and copolymers with carboxy 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.

[0030] 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 most preferred that all three monomers be contained in polymerized form. Preferred polymers of that type are copolymers of N-phenylmaleimide, (meth)acrylamide and (meth)acrylic acid, more preferred are 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 part 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.

[0031] Another group of suitable polymers A 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-% CH₂C(R)C(O)NHCH₂OR' (wherein R is C₁-C₁₂ alkyl, phenyl, substituted phenyl, aralkyl or Si(CH₃)₃ and R' represents H or CH₃). Such copolymers are described in detail for example in WO 2005/018934.

[0032] Copolymers comprising a monomer in polymerized form which contains a urea group in its side chain form another group of preferred polymers A; such copolymers are e.g. 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 formula (I) below:



wherein

- R is a hydrogen atom or a methyl group,
- X is a divalent spacer group,
- Y is a divalent substituted or unsubstituted aromatic group, and

Z is selected from OH, COOH and SO₂NH₂.

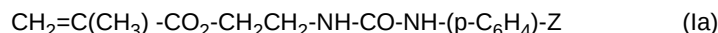
R is preferably a methyl group.

X is preferably a substituted or unsubstituted alkylene group, a substituted or unsubstituted phenylene group (C₆H₄) or a substituted or unsubstituted naphthalene group (C₁₀H₆), such as -(CH₂)_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 -(CH₂)_n- wherein n = 2 or 3, and most preferred, X represents -(CH₂CH₂)_n-.

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

Z is preferably OH.

[0033] A preferred monomer is



wherein Z is selected from OH, COOH and SO₂NH₂, and is preferably OH.

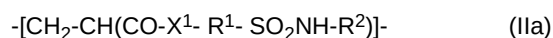
[0034] Monomers comprising one or more urea groups can be used in the synthesis of the copolymers. In polymerized form, the copolymers furthermore comprise 20 to 90 wt.-% of other polymerizable monomers such as maleimide, acrylic acid, methacrylic acid, acrylic acid esters, methacrylic acid esters, acrylonitrile, methacrylonitrile, acrylamides and methacrylamides. 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).

[0035] The polymers described above are soluble in aqueous alkaline developers; furthermore, they are soluble in polar solvents such as ethylene glycol monomethylether, which can be used as coating solvent for the first coating solution, or mixtures of methyl lactate, methanol and dioxolane. The polymers described above can be prepared by means of known processes of free-radical polymerization.

[0036] 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 polymer A 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.

[0037] Another group of polymers that can be used as polymer A are copolymers comprising 1 to 90 mole-% of a sulfonamide monomer unit, in particular N-(p-aminosulfonylphenyl)methacrylamide, N-(m-aminosulfonylphenyl)methacrylamide, N-(o-aminosulfonylphenyl)methacrylamide and/or corresponding acrylamides. Suitable polymers comprising a sulfonamide group in their pendant-group, processes for their production as well as 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 name PU-Copolymers.

[0038] Furthermore, polyacrylates comprising structural units of the following formulas (IIa) and/or (IIb) can be used as polymer A:



wherein

X¹ represents O or NR³;

R¹ represents a substituted or unsubstituted alkylene group (preferably C₁-C₁₂), cycloalkylene group (preferably C₆-C₁₂), arylene group (preferably C₆-C₁₂) or aralkylene group (preferably C₇-C₁₄);

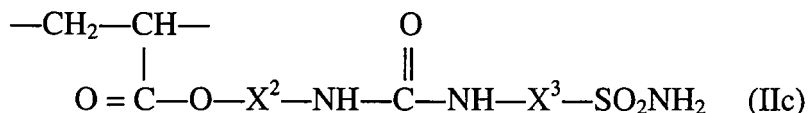
R² and R³ each independently represent a hydrogen atom or a substituted or unsubstituted alkyl group (preferably C₁-C₁₂); cycloalkyl group (preferably C₆-C₁₂), aryl group (preferably C₆-C₁₂) or aralkyl group (preferably C₇-C₁₄) and

R^{2a} represents a substituted or unsubstituted alkyl group (preferably C₁-C₁₂), cycloalkyl group (preferably C₆-C₁₂), aryl group (preferably C₆-C₁₂) or aralkyl group (preferably C₇-C₁₄).

[0039] Such polyacrylates and starting monomers and comonomers for their production are described in detail in EP-A-0 544 264 (pages 3 to 5).

[0040] Polymethacrylates analogous to the polyacrylates of the formulas (IIa) and (IIb) can also be used as polymer A according to the present invention.

[0041] Polyacrylates with sulfonamide pendant groups which additionally comprise a urea group in the side chain can be used as polymer A as well. Such polyacrylates are for example described in EP-A-0 737 896 and exhibit the following structural unit (IIc):

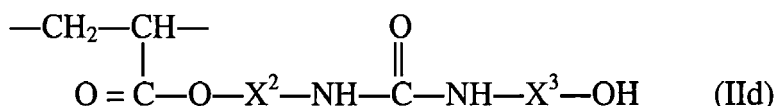


wherein

X^2 is a substituted or unsubstituted alkylene group (preferably $\text{C}_1\text{--C}_{12}$), cycloalkylene group (preferably $\text{C}_6\text{--C}_{12}$), arylene group (preferably $\text{C}_6\text{--C}_{12}$) or aralkylene group (preferably $\text{C}_7\text{--C}_{14}$), and X^3 is a substituted or unsubstituted arylene group (preferably $\text{C}_6\text{--C}_{12}$).

[0042] Polymethacrylates analogous to the polyacrylates of formula (IIc) can also be used as polymer A according to the present invention.

[0043] The polyacrylates of formula (IId) with urea groups and phenolic OH mentioned in EP-A-0 737 896 can also be used as polymer A:



wherein

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

[0044] Polymethacrylates analogous to the polyacrylates of formula (IId) can also be used as polymer A according to the present invention.

[0045] The weight-average molecular weight of suitable poly(meth)acrylates with sulfonamide pendant groups and/or phenolic pendant groups is preferably 2,000 to 300,000.

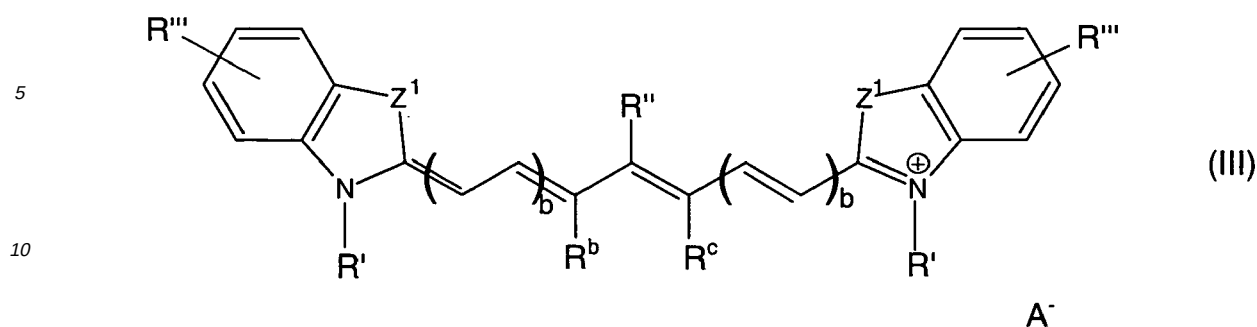
[0046] Of course, mixtures of different polymers A soluble in alkaline developer and insoluble in organic solvents with low polarity can be used as well.

[0047] Preferably, polymer A is present in the first coating in an amount of at least 50 wt.-%, more preferably at least 60 wt.-%, even more preferred at least 70 wt.-% and most preferred at least 80 wt.-% based on the dry layer weight. Usually, the amount does not exceed 99 wt.-%, more preferably 95 wt.-%, most preferred 85 wt.-%.

[0048] The first layer furthermore comprises at least one photothermal conversion material (in the following also referred to as "IR absorber").

[0049] 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 does not or does 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. The compounds mentioned in Table 1 of US-A-6,326,122 for example are suitable IR absorbers. Further examples can be found in US-A-4,327,169, US-A-4,756,993, US-A-5,156,938, WO 00/29214, US-B-6,410,207 and EP-A-1 176 007.

[0050] According to one embodiment, a cyanine dye of the formula (III)



15 is used, wherein

- each Z¹ 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, SO₂R^a or NR^a₂;
 20 each R''' independently represents a hydrogen atom, an alkyl group, -COOR^a, -OR^a, -SR^a, -NR^a₂ or a halogen atom; R''' can also be 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;
 25 R^a represents a hydrogen atom, an alkyl or aryl group;
 each b is independently 0, 1, 2 or 3.

[0051] If R' represents an alkylsulfonate group, an inner 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⁻.

- 30 Z¹ 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.
 35 R^a is preferably an optionally substituted phenyl group or an optionally substituted heteroaromatic group.

[0052] Preferably, R^b and R^c, together with the carbon atoms to which they are bonded, form a 5- or 6-membered carbocyclic ring.

[0053] The counterion A⁻ is preferably a chloride ion, trifluoromethylsulfonate or a tosylate anion.

40 [0054] Of the IR dyes of formula (II), 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,

45 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,

50 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,

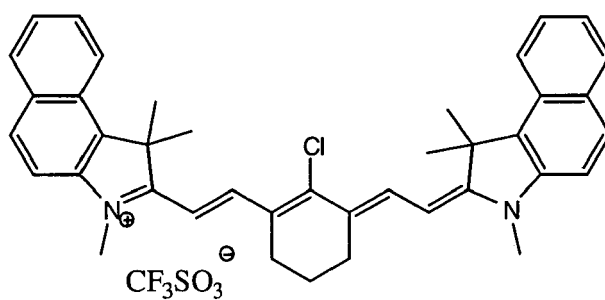
2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-benzo[e]-indole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,3,3-trimethyl-1H-benzo[e]-indolium-tosylate and

55 2-[2-[2-chloro-3-[2-ethyl-(3H-benzthiazol-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-3-ethyl-benzthiazolium-tosylate.

[0055] The following compounds are also IR absorbers suitable for use in the present invention:

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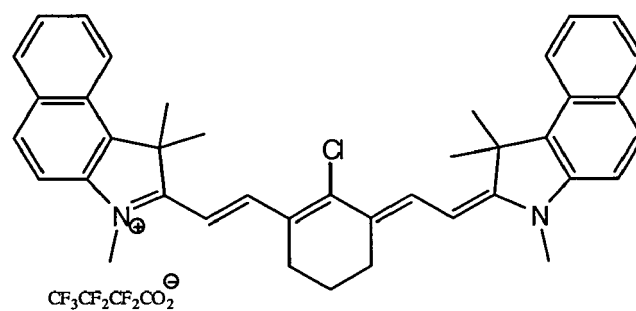
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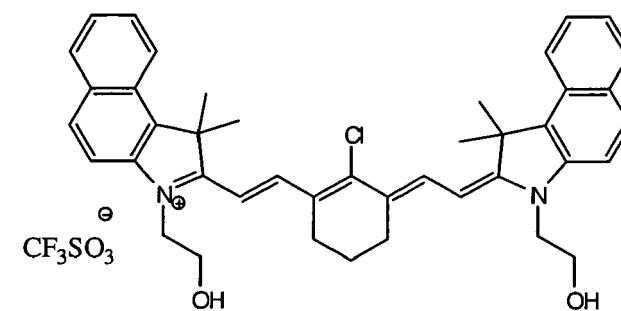
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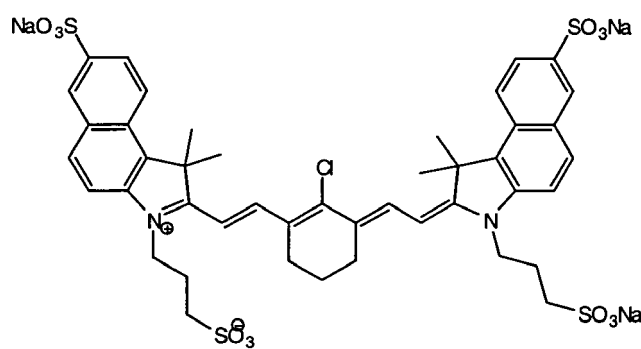
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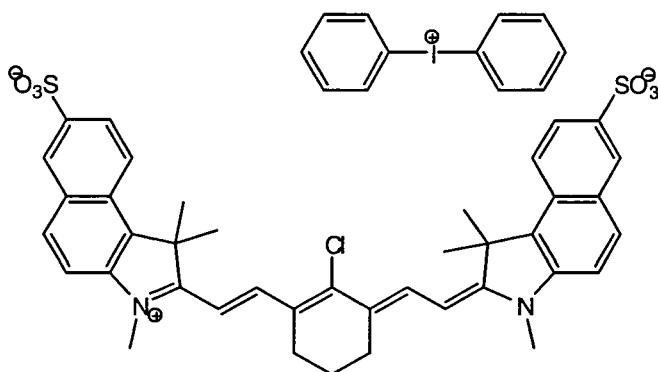
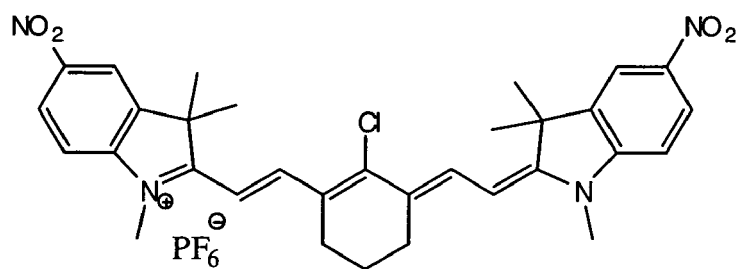
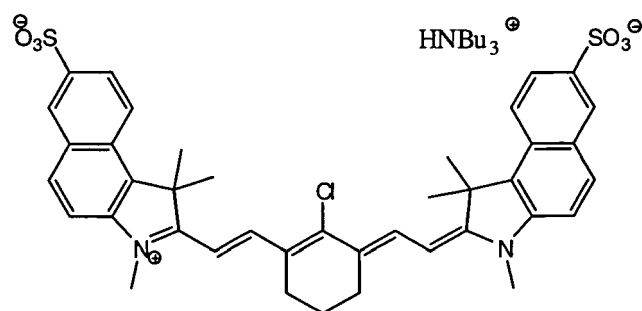
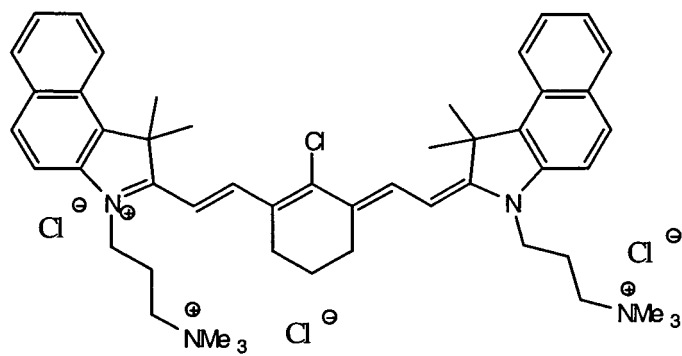


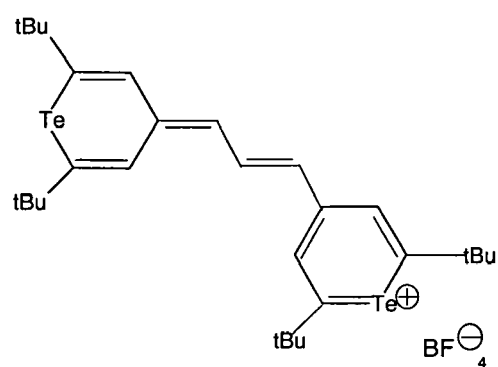
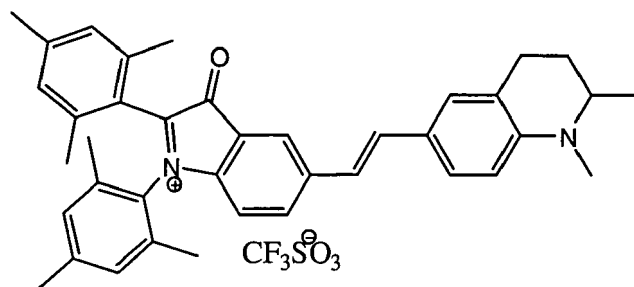
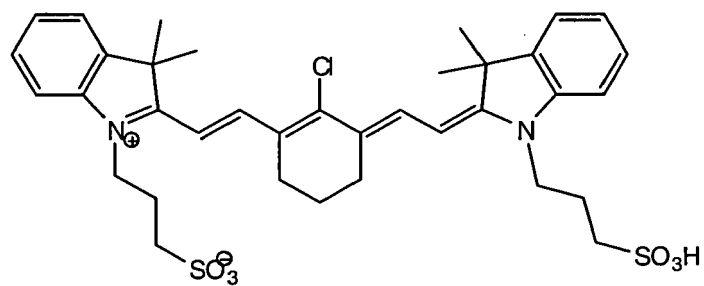
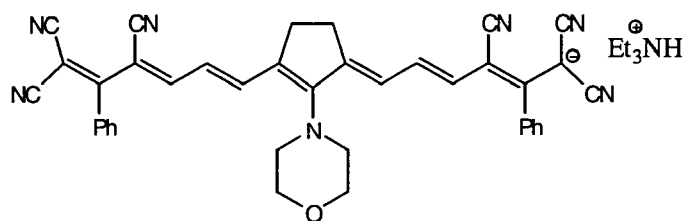
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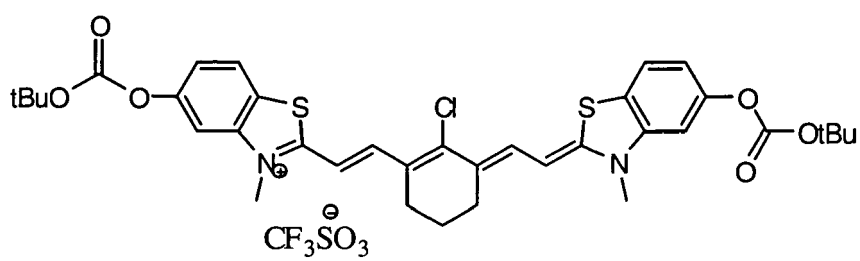
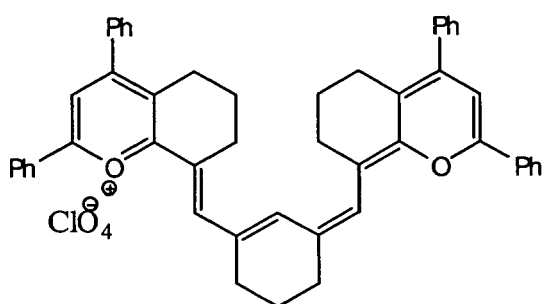
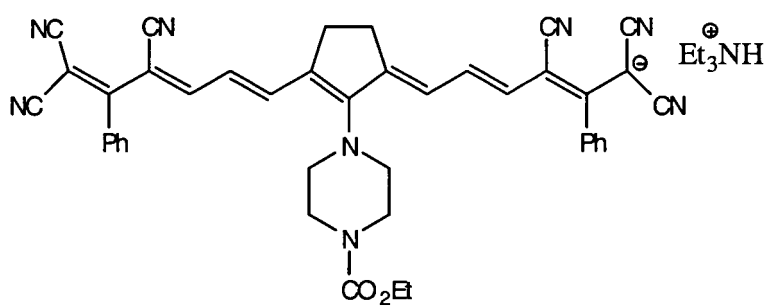
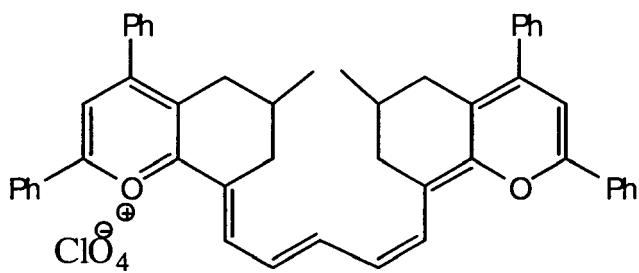
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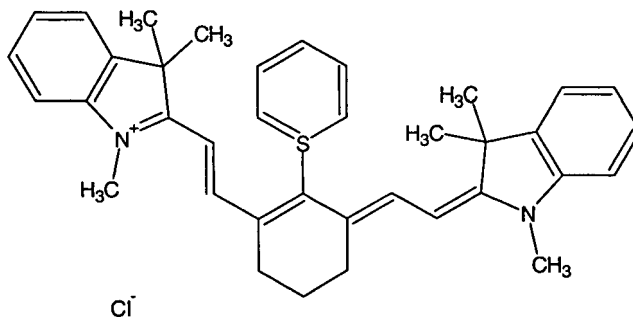
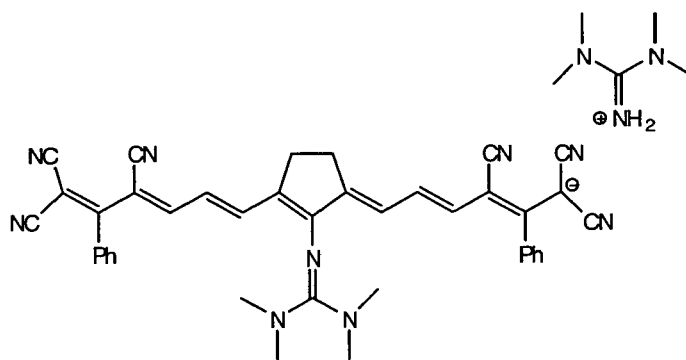
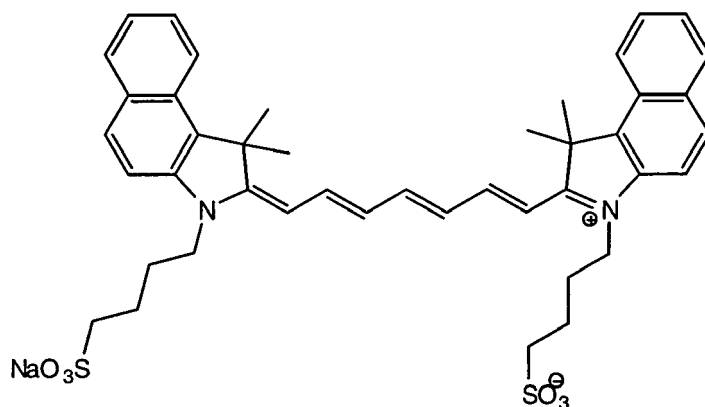
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[0056] The IR absorber is preferably present in an amount of at least 1 wt.-%, based on the dry layer weight, more preferred at least 3 wt.-%, still more preferred at least 5 wt.-%. Usually, the amount of IR absorber does not exceed 50 wt.-%, more preferred 30 wt.-% and most preferred 20 wt.-%. If carbon black is used as IR absorber, it is preferably used in an amount of no less than 40 wt.-%. 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.

[0057] In addition to low-molecular IR absorbers, IR dyes covalently bonded to a polymer can be used as well whereby the polymer used is soluble in aqueous alkaline solutions (see e.g. DE 10 2004 029 503.4). In such a case, no additional polymer A is required in the first layer.

[0058] In addition to IR dyes covalently bonded to a polymer, IR dye cations can be used as well (i.e. the cation is the IR absorbing portion of the dye salt) which ionically interact with a polymer comprising -COOH, -SO₃H, -PO₄H₂ and/or -PO₄H₂ groups in its side chains (see e.g. DE 10 2004 029 501.8).

[0059] The first 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 dyes are preferably present in the first layer in an amount of from 0 to 15 wt.-%, more preferred 0.5 to 10 wt.-%, especially preferred in an amount of from 1.5 to 7 wt.-%, based on the dry layer weight of the first layer.

[0060] Furthermore, the first 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.-%.

[0061] The first 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.-%.

[0062] Also, flow improvers can be present in the first 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.

[0063] The first layer can furthermore comprise anti-oxidants 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.-%.

[0064] Other coating additives can of course be present as well.

[0065] A phenolic resin (e.g. novolaks, resol) can optionally be present in the first layer. If the first layer comprises a phenolic resin as optional component, it is preferably present in an amount of no more than 10 wt.-%, based on the dry layer weight; it is especially preferred that the first layer does not comprise a phenolic resin like a novolak.

[0066] Novolak resins suitable as optional component of the first layer of the present invention are condensation products of one or more suitable phenols, e.g. phenol itself, m-cresol, o-cresol, p-cresol, 2,5-xyleneol, 3,5-xyleneol, 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, xyleneols resorcinol and pyrogallol are preferably not used as single phenol for the 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 obtained at higher aldehyde/phenol ratios and in the presence of alkaline catalysts are known as "resols".

[0067] Suitable novolaks and resols 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.

[0068] The top layer comprises at least one polysiloxane selected from arylpolysiloxanes and arylalkylpolysiloxanes, preferably at least 10 wt.-% based on the dry layer weight. According to one embodiment the top layer consists of a polysiloxane or a mixture thereof.

[0069] The arylpolysiloxanes or arylalkylpolysiloxanes used in the present invention have a glass transition temperature T_g of more than 60°C and a hydroxyl content of at least 1 % by weight. The molecular weight is preferably from 500 to 10,000 g/mol with particular preference from 500 to 6,000 g/mol. Their hydroxyl content is preferably up to about 8 wt.-% based on the weight of the arylpolysiloxane, more preferably up to 6 wt.-%; it is preferred that at least 3 wt.-% hydroxy groups are present; in the framework of the present invention the hydroxyl content relates to OH groups present as silanol groups. Their T_g is preferably at least 65°C (more preferably at least 70°C) and up to 200°C.

[0070] The polysiloxanes can be prepared by reacting identical or different alkoxysilanes of the general formula (I)



with each R being independently selected from a hydrogen atom, an aryl and an alkyl, with the proviso that at least one R is an aryl group, each R' being independently H or an alkyl group, x being from 0 to 3 and y being from 4 to 1, with $x + y = 4$, in the presence of acid, water and an organic solvent having a boiling point above that of water, the acid used being removed by distillation at the end.

[0071] R is preferably an optionally substituted linear C_1 - C_{18} alkyl or aryl, in particular, a radical selected from methyl, ethyl, propyl and phenyl, with the proviso that at least one R is an aryl group like phenyl.

[0072] R' is preferably H, methyl or ethyl.

[0073] The polysiloxanes used in the present invention are described for instance in US 6,552,151 B1, DE 198 57 348 and WO 00/35994 which are incorporated herein by reference. Processes for their production are also described in detail in said documents. Suitable products are commercially available under the tradename Silres® from Wacker

Chemie GmbH, Germany.

[0074] The above described polysiloxanes are characterized by a relatively high content of OH groups compared to other siloxanes. This is believed to allow crosslinking of the siloxanes at a temperature of 230°C or above which means that crosslinking occurs at the imaged precursor when it is baked resulting in an improved print run length. On the other hand the high content of OH groups seems to result in better solubility of the unbaked coating in aqueous alkaline developers so that sludge formation in the processor can be avoided.

[0075] No IR absorber is present in the top layer.

[0076] Additionally, the top layer can comprise dyes or pigments having a high absorption in the visible spectral range. Suitable dyes and pigments include e.g. those described above in connection with the first layer. 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.

[0077] The surfactants mentioned in connection with the first layer can also be present in the second coating solution. 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.

[0078] Furthermore, the top layer can comprise flow control agents such as poly(glycol)ether-modified starch. They are preferably present in an amount of 0 to 1 wt.-%, based on the dry layer weight of the top layer.

[0079] Usually, the polymers A are soluble in polar solvents but insoluble in organic solvents with low polarity. Suitable solvents for applying the first layer are therefore e.g. protic, watersoluble solvents, in particular ethylene glycol monomethyl ether, methyl lactate, methanol and mixtures thereof; these solvents can also be combined with 1,3-dioxolane, ketones, such as acetone and methyl ethyl ketone, and mixtures thereof.

[0080] Commonly used coating devices can be used for applying the coating solutions; the coating solutions can for example be applied by means of spin coating, coating with doctor blades, roll coating, gravure coating, or coating with a slot nozzle (also referred to slot coater, Hopper coater).

[0081] The dry layer weight of the first layer is preferably 0.1 to 5 g/m², more preferred 0.2 to 3.0 g/m².

[0082] The dry layer weight of the top layer is preferably 0.1 to 5 g/m², more preferred 0.2 to 3.0 g/m².

[0083] The imageable elements produced according to the present invention can be imaged with IR radiation. Semiconductor lasers or laser diodes which emit in the range of 650 to 1,300 nm, preferably 750 to 1,120 nm, can for example be used as a radiation source. 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 digitalized information in the computer which results in so-called computer-to-plate (ctp) printing plates. All image-setters with IR lasers known to the person skilled in the art can be used for this purpose.

[0084] The image-wise irradiated/heated elements such as printing plate precursors are developed with an aqueous alkaline developer, which usually has a pH value in the range of 10 to 14. For this purpose, commercially available developers can be used.

[0085] The developed printing plates can additionally be subjected to a "baking" step in order to increase the abrasion resistance of the printing areas.

[0086] Preferably, the heat-sensitive elements produced according to the present invention are not sensitive to visible light and the UV portion of daylight under common processing conditions for printing plates so that they can be processed under white light, i.e. they do not require yellow light conditions.

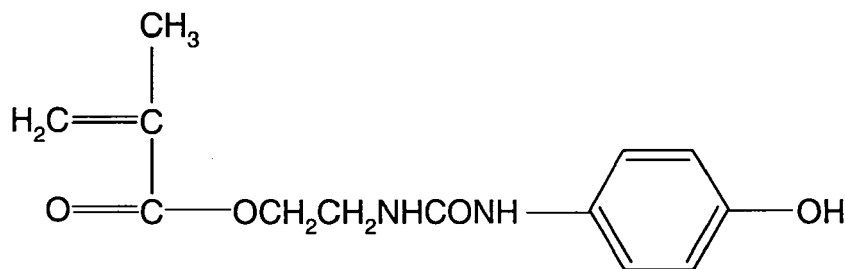
[0087] The invention will be explained in more detail in the following examples; however, they shall not restrict the invention in any way.

Examples

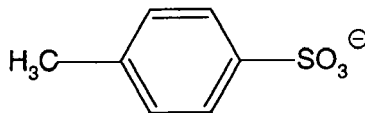
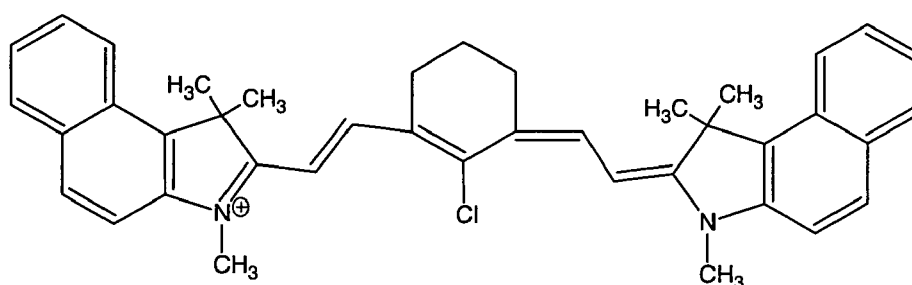
Example

[0088] The following coating composition was applied to an aluminum substrate (electrochemically grained to Ra = 0,5 µm, anodized and treated with polyvinylphosphonic acid):

5,80 g	terpolymer of methacrylic acid, methacrylamide and N-phenylmaleimide (mol ratio 20:35:45),
1,50 g	copolymer of N-phenylmaleimide (5 wt.-%), methacrylamide (10 wt.-%), acrylonitrile (45 wt.-%) and the following Monomer (40 wt.-%)



- 4,16 g GP649D99 which is a resole resin as supplied by Georgia-Pacific, Atlanta, GA,
 1,50 g Trump IR dye,
 0,15 g colorant D11 supplied by PCAS, France,
 0,15 g Byk 307 (a polyethoxylated dimethylpolysiloxane copolymer as supplied by BYK Chemie of Wallingford, CT),
 130 g solvent mixture of γ -butyrolatone, Dowanol PM, methyl ethyl ketone, and water (ratio 10:50:30:10 wt.-%)



Trump Dye

[0089] A dry coating weight of 1,3 g/m² was obtained.

[0090] A 10 wt./wt.-% solution of Silres® IC836 (phenylethoxysiloxane with 3 to 4.5 wt.-% silanol groups, softening point = 65-85°C, available from Wacker-Chemie GmbH) in diethylketone was coated by means of a wire bar on top of the bottom layer, followed by drying with hot air and then through an oven at 130°C for 30 seconds. The dry coating weight was 1,3 g/m². The resulting plate was exposed in a Creo Trendsetter (830 nm; 150 mJ); for exposure an UGRA control strip containing fine lines and gaps (10, 20 and 30 μ m) was used.

[0091] The exposed plate was developed through a Mercury processor filled with Goldstar Plus developer (available from Kodak Polychrome Graphics) at a speed of 1200 mm/min and gummed with 850S® (commercially available gumming solution, 1:1 diluted with water).

[0092] Result: The resolution looked good, i.e. all lines and gaps were reproduced. The plate was put on a press using the standard fountain solution (10 % isopropanol, 4 % Combifix from Hostmann-Steinberg). The ink acceptance of the image was as good as that of a standard positive plate (Virage®, commercially available from Kodak Polychrome Graphics), and the non image areas cleared even as fast.

Comparative Example

[0093] The Example was repeated, however, instead of Silres® IC836 Silikophen® P50/X (phenylmethylsiloxane from Tego Chemie, containing methoxy and butoxy groups and 2 % methylol groups but no silanol groups) was used.

[0094] Exposure and development was carried out as described in the Example. An image was obtained but resolution was poor, i.e. 30 μ m gaps were closed.

Test concerning formation of sludge in the processor:**[0095]**

(A) A 10 wt/wt.-% solution of 30 % Silres® IC836, 70 % cresol-phenol novolak in Dowanol PM was coated by means of a wire bar and first dried by hot air and then in an oven at 105°C for 90 sec to give a coating weight of 1,5 g/m². The substrate was an aluminum substrate as used in the Example. 0,12 m² of above plate was immersed for 40 sec in 30 ml of developer. The resulting loaded developer - loading degree corresponds to about 1,5 m² per liter of the Example coating was left overnight and then checked for precipitates. A clear solution was obtained.

(B) The same test as described above was done with a coating which differs from that of (A) in that Silikophen® P50/X was used instead of Silres® IC836.

Result: The loaded developer looked very turbid and a flaky precipitate had collected at the bottom of the vessel over night.

Solvent resistance:

[0096] 0.3 ml butylglycol/water (80:20) were placed on an unexposed coating prepared according to the example and comparative example, respectively; when doing so, the plate was kept at 25°C. After a predetermined dwell time the plate was rinsed with water.

[0097] Then the color of the coating of the solvent-treated area was compared with the color of the coating in the untreated area. A visually determined brightening was interpreted as coating loss.

[0098] The coating of the comparative example showed brightening already after a dwell time of 30s; the coating was therefore not solvent resistant.

[0099] In comparison, the coating of the example did not show brightening even after a dwell time of 1 minute; the coating therefore showed excellent solvent resistance.

Claims**1.** IR-sensitive imageable element comprising:

(a) a substrate with a hydrophilic surface,

b) a bottom layer,

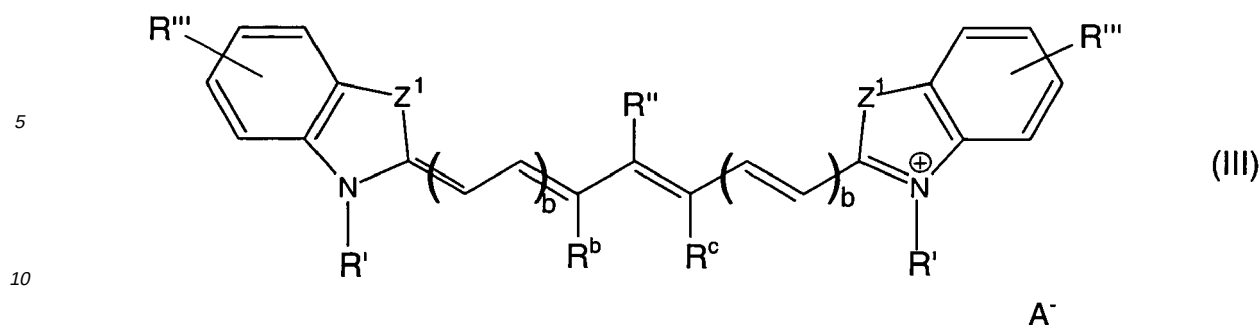
comprising at least one photothermal conversion material and at least one polymer A soluble or swellable in an aqueous alkaline developer and insoluble in organic solvents with low polarity and

(c) a top layer comprising at least one polysiloxane selected from arylpolysiloxanes and arylalkylpolysiloxanes having a glass transition temperature T_g of more than 60°C and a hydroxyl content of at least 1 % by weight.

2. Element according to claim 1, wherein the polymer A of the first coating solution is selected from copolymers derived from N-substituted maleimides and comonomers copolymerizable therewith, copolymers comprising a urea group in the side chain, and copolymers with a sulfonamide group in the side chain, and mixtures thereof.

3. Element according to claim 1 or 2, wherein polymer A is a terpolymer of methacrylic acid, methacrylamide and N-phenylmaleimide.

4. Element according to any of claims 1 to 3, wherein the photothermal conversion material has the formula



15 wherein

- 15 each Z¹ 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, SO₂R^a or NR^a₂;
 each R''' independently represents a hydrogen atom, an alkyl group, -COOR^a, -OR^a, -SR^a, -NR^a₂ or a halogen atom;
 R''' can also be a benzofused ring;
 A⁻ represents an anion;
 R^b and R^c both represent hydrogen 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;
 25 each b is independently 0, 1, 2 or 3.

5. Element according to any of claims 1 to 4, wherein the first layer furthermore comprises at least one additive selected from contrast dyes and pigments, surfactants, print-out dyes, flow control agents and antioxidants.
- 30 6. Element according to any of claims 1 to 5, wherein the polysiloxane has a molecular weight of 500 to 10.000 g/mol.
7. Element according to any of claims 1 to 6, wherein the hydroxyl content of the polysiloxane is at least 3 wt.-%.
8. Element according to any of claims 1 to 7, wherein the Tg of the polysiloxane is at least 65°C.
- 35 9. Element according to any of claims 1 to 8, wherein the top layer furthermore comprises at least one additive selected from contrast dyes and pigments, surfactants, print-out dyes, flow control agents and antioxidants.
10. Element according to any of claims 1 to 8, wherein the top layer consists of a polysiloxane or a mixture thereof.
- 40 11. Element according to any of claims 1 to 11, wherein the substrate is an aluminum plate or foil.
12. Element according to claim 11, wherein prior to the application of the bottom layer, the substrate is subjected to at least one treatment selected from graining, anodizing and hydrophilizing.
- 45 13. Process for the production of an element as defined in any of claims 1 to 12 comprising:

- (a) applying a solution comprising polymer A as defined in claim 1 and at least one photothermal converting material to an untreated or pretreated substrate, and
 50 (b) after drying the applied solution, applying a second solution comprising at least one polysiloxane as defined in claim 1.

14. Process for imaging an IR-sensitive imageable element comprising:

- 55 (a) imagewise exposure of an IR-sensitive imageable element as defined in any of claims 1 to 12, and
 (b) contacting the exposed element with an aqueous alkaline developer to remove the exposed areas.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 01 6408

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,D	EP 1 249 341 A (AGFA-GEVAERT AG) 16 October 2002 (2002-10-16) * claims 1,6,11,16 * * paragraph [0010]; example 1 * -----	1-14	B41M5/36 B41C1/10
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			TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 1 December 2005	Examiner Bacon, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 01 6408

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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01-12-2005

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