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(54) Heat-sensitive lithographic printing plate precursor

(57) Heat-sensitive element, comprising

(a) an optionally pretreated substrate
(b) a positive working heat-sensitive coating, comprising at least one phenolic resin and at least one inhibitor polymer selected from

(i) polymers comprising saturated (hetero)cyclic moieties with at least one carbonyl group, the carbon atom of which is part of the (hetero)cyclic moiety, said (hetero)cyclic moieties being bonded to a polymer chain directly
(ii) polymers comprising unsaturated heterocyclic moieties which are bonded to a polymer chain directly and which have a ring nitrogen atom, said ring nitrogen atom being bonded to the two adjacent ring carbon atoms via a single bond and a double bond and moreover having a free electron pair, and
(iii) copolymers comprising both saturated (hetero)cyclic moieties as defined in (i) and unsaturated heterocyclic moieties as defined in (ii).

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Description

[0001] The present invention relates to heat-sensitive positive working elements, in particular heat-sensitive printing plate precursors whose heat-sensitive coating comprises a phenolic resin whose solubility in alkaline developers has been reversibly reduced by the use of a second polymer; the invention furthermore relates to a process for their production as well as to a process for imaging such elements.

[0002] The technical field of 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. Alternatively, the plate can also be exposed digitally without a film, e.g. with a UV laser. 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 reach 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.

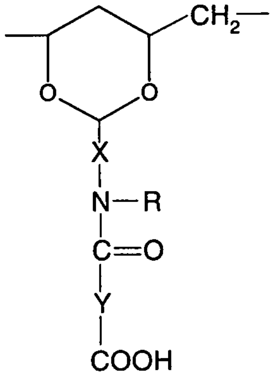
[0007] One example of a positive working, direct laser-addressable printing plate precursor is described in US-A-4,708,925. The patent describes a lithographic printing plate precursor whose imaging layer comprises a phenolic resin and a radiation-sensitive onium salt. As described in the patent, the interaction between the phenolic resin and the onium salt results in an alkali solvent resistance 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 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] EP-A-0 823 327 describes IR-sensitive printing plate precursors whose radiation-sensitive coating comprises, in addition to an IR absorber and a polymer such as for example novolak, a substance that decreases the solubility of the composition in an alkaline developer. Amongst others, sulfonic acid esters, phosphoric acid esters, aromatic carboxylic acid esters, carboxylic acid anhydrides, aromatic ketones and aldehydes, aromatic amines and aromatic ethers are mentioned as such "insolubilizers". These printing plate precursors show a high degree of IR sensitivity and do not require additional process steps between exposure and developing; moreover, they can be handled under normal lighting conditions (daylight with a certain portion of UV radiation), i.e. no yellow light is necessary. However, the resistance of the developed printing plates to printing chamber chemicals (fountain solutions, in particular fountain solution additives for alcohol-free or alcohol-reduced printing, organic solvents in printing inks, washing solutions etc.) is not completely satisfactory.

[0010] WO 99/21725 discloses IR-sensitive positive working printing plate precursors whose heat-sensitive layer comprises a substance that improves the resistance of the non-heated areas to an attack by the alkaline developer; this substance is selected from compounds with polyalkylene oxide units, siloxanes, as well as esters, ethers and amides of multivalent alcohols. These printing plate precursors as well are characterized by a high degree of IR sensitivity and can be used under normal daylight conditions. An improved resistance to printing chamber chemicals would be desirable in this case, too. For applications involving higher numbers of copies, a baking step is recommended.

[0011] EP-A-1 101 607 describes IR-sensitive elements whose IR-sensitive coatings additionally comprise a carboxylic acid derivative of a cellulose polymer. By using this acidic cellulose polymer, the resistance of the coating to organic solvents, which are e.g. used in some printing inks, fountain solutions and washing solutions, could be improved, which allows higher number of prints in the case of printing plates. In this application, carboxyl-group containing polymers of the methacrylic/acrylic acid type, copolymers of maleic acid, an acidic polyester, an acidic colophonium derivative as well as polyvinyl acetals with the following structural unit were tested as well



X = aliphatic, aromatic or araliphatic spacer

R = H, aliphatic, aromatic or araliphatic group

Y = saturated or unsaturated plate or ring-shaped spacer

[0012] However, the solvent resistance could not be improved with such polymers. Despite the improvement achieved with the acidic cellulose polymer, there is still a demand for coatings with superior resistance to pressroom chemicals, in particular in the field of lithographic printing plate precursors; the use of the acidic cellulose polymer resulted for example in a deterioration of the alkaline developer resistance.

[0013] WO 99/01795 describes heat-sensitive coatings which use polymers with specific functional groups Q as insolubilizers for novolaks, said polymers preferably do not comprise diazide groups or acid or acid-forming groups.

[0014] In WO 97/39894, the heat-sensitive coating comprises nitrogen-containing compounds as insolubilizers for novolak wherein at least one nitrogen atom is quaternized and forms part of a heterocyclic ring; examples include e. g. quinolinium compounds, benzothiazolium compounds and pyridinium compounds, and in particular cationic trimethylmethane dyes such as Victoria Blue (C I Basic Blue 7), crystal violet (C I Basic Violet 3) and ethyl violet (C I Basic Violet 4). Furthermore, compounds such as N-(4-bromobutyl)-phthalimide, benzophenone and phenanthrenequinone and compounds of the formula Q_1-S(O)$_n$-Q_2 (wherein Q_1 = optionally substituted phenyl or alkyl group; n = 0,1 or 2; Q_2 = halogen atom or alkoxy group), Acridine Orange Base and ferrocenium compounds are mentioned as insolubilizers for novolak.

[0015] WO 98/42507 and EP-A 0 823 327 describe xanthone, flavanone, flavone, 2,3-diphenyl-1-indenone, pyrone, thiopyrone and 1'-(2'-acetonaphthonyl)benzoate as insolubilizers for novolaks.

[0016] US-B-6,320,018 describes heat-sensitive elements whose coating comprises functionalized novolaks. These novolaks contain substituents which allow a two- or four-center hydrogen bond (preferably a four-center hydrogen bond) between the polymer molecules. This also decreases the aqueous alkaline developer solubility of the underlying novolak. It is assumed that such hydrogen bonds are broken by heating and that thus the original solubility of the novolak is restored.

[0017] It is the object of the present invention to provide heat-sensitive elements such as lithographic printing plate precursors that are characterized by excellent resistance to chemicals without affecting their IR sensitivity and developability and which allow large numbers of prints.

[0018] It is furthermore an object of the present invention to provide a process for producing such elements as well as a process for imaging these elements.

[0019] The first object is surprisingly achieved by an element comprising:

(a) an optionally pretreated substrate

(b) a positive working heat-sensitive coating, comprising at least one phenolic resin and at least one inhibitor polymer selected from

  (i) polymers comprising saturated (hetero)cyclic moieties with at least one carbonyl group, the carbon atom of which is part of the (hetero)cyclic moiety, said (hetero)cyclic moieties being bonded to a polymer chain directly,

  (ii) polymers comprising unsaturated heterocyclic moieties which are bonded to a polymer chain directly and which have a ring nitrogen atom, said ring nitrogen atom being bonded to the two adjacent ring carbon atoms via a single bond and a double bond and moreover having a free electron pair, and

  (iii) copolymers comprising both saturated (hetero)cyclic moieties as defined in (i) and unsaturated heterocyclic moieties as defined in (ii).

[0020] The inventive process for imaging these elements comprises the following steps:

(a) providing a heat-sensitive element as defined above

(b) image-wise exposure of said element with IR radiation or image-wise direct heating and

(c) removing the exposed or directly heated areas of the coating with an aqueous alkaline developer.

[0021] The heat-sensitive elements according to the present invention can e.g. be printing plate precursors (in particular precursors of lithographic printing plates), printed circuit boards for integrated circuits or photomasks.

[0022] A dimensionally stable plate or foil-shaped material is preferably used as a substrate 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 matters. 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 acetate-butyrate, 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.

[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] 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 an aftertreatment with an aqueous solution of e.g. sodium silicate, calcium zirconium fluoride, polyvinylphosphonic acid or phosphoric acid. Within the framework of the present invention, the term "substrate" also encompasses an optionally pretreated substrate exhibiting, for example, a hydrophilizing layer on its surface.

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

[0026] The heat-sensitive coating comprises at least one polymer that reduces the aqueous alkaline developer solubility of a phenolic resin, whereby this reduction in solubility is reversed by the application of heat. In the following, this polymer is briefly referred to as "insolubilizer" or "inhibitor polymer".

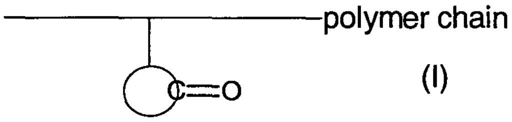
[0027] The inhibitor polymer is selected from

(i) polymers comprising saturated (hetero)cyclic moieties with at least one carbonyl group, the carbon atom of which is part of the (hetero)cyclic moiety, said (hetero)cyclic moieties being bonded to a polymer chain directly without spacer,

(ii) polymers comprising unsaturated heterocyclic moieties which are bonded to a polymer chain directly without spacer and which have a ring nitrogen atom, said ring nitrogen atom being bonded to the two adjacent ring carbon atoms via a single bond and a double bond and moreover having a free electron pair, and

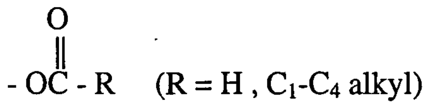
(iii) copolymers comprising both saturated (hetero)cyclic moieties as defined in (i) and unsaturated heterocyclic moieties as defined in (ii).

[0028] The inhibitor polymer (i) can be depicted as follows:



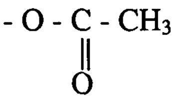
(I)

[0029] In addition to the (hetero)cyclic moiety shown above, the polymer chain can comprise further substituents, such as e.g. C_1-C_4 alkyl groups, OH, and



$$-O\overset{\overset{O}{\|}}{C}-R \quad (R = H, C_1\text{-}C_4 \text{ alkyl})$$

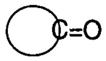
[0030] Preferably, it is a polyolefin skeleton, which in addition to the (hetero)cyclic moiety comprises



$$-O-\underset{\underset{O}{\|}}{C}-CH_3$$

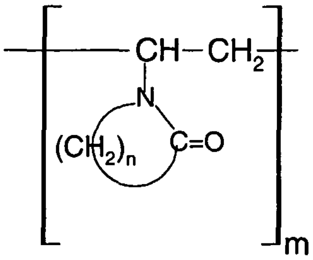
and optionally OH as substituents.

[0031] The symbol



represents a saturated cyclic or heterocyclic moiety, wherein the heteroatom - if present - is selected from N, O and S (preferably N). In the case of a heterocyclic moiety, 2 heteroatoms can be present as well. The (hetero)cyclic moiety can comprise 4 to 8 (especially preferred 5 to 7) ring atoms. It is preferably a heterocyclic moiety wherein one of the ring atoms is a nitrogen atom; it is especially preferred that the nitrogen atom is adjacent to the carbonyl function.

[0032] Especially preferred inhibitor polymers (i) comprise a lactam substituent and are represented by formula (II):

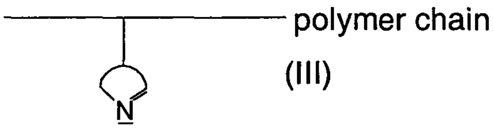


(II)

wherein n is 3, 4 or 5, preferably 3.

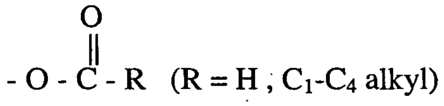
[0033] Of the inhibitor polymers of formula (II), polyvinylpyrrolidone as well as copolymers derived from vinylpyrrolidone and vinylacetate are especially preferred; in the case of the copolymers, the amount of parts derived from vinylacetate is preferably 10-85 mole-% and the amount of parts derived from vinylpyrrolidone is preferably 15-90 mole-%.

[0034] The inhibitor polymer (ii) can be depicted as follows:



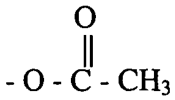
(III)

[0035] In addition to the unsaturated heterocyclic moiety shown above, the polymer chain can comprise further substituents, such as e.g. C_1-C_4 alkyl groups, OH, and



$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad (R = H\,;\, C_1\text{-}C_4 \text{ alkyl})$$

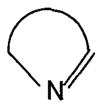
[0036] Preferably, it is a skeleton without any additional substituents or with



$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

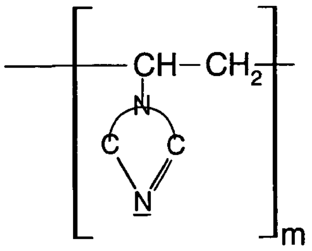
as further substituent.

[0037] The symbol



represents an unsaturated heterocyclic moiety, wherein further heteroatoms selected from N, O and S (preferably N) can be present in the ring in addition to the nitrogen atom shown above, which is bonded to the two adjacent carbon atoms via a single bond and a double bond, and furthermore comprises a free electron pair. Including the nitrogen atom shown above, the heterocyclic moiety can comprise 4 to 8 (especially preferred 5 to 7) ring atoms. Preferably, in addition to the nitrogen atom shown above, the heterocyclic moiety comprises another nitrogen atom which is bonded to the two adjacent carbon atoms via a single bond.

[0038] Especially preferred inhibitor polymers (ii) are represented by formula (IV):



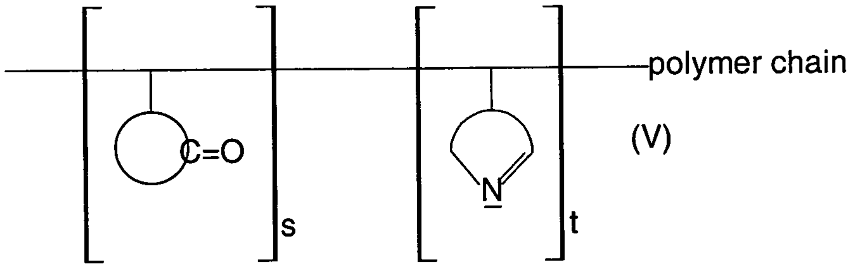
(IV)

wherein further double bonds can be present in addition to the double bond shown in formula (IV);

means that the nitrogen atom depicted in the formula is bonded to the carbon atom directly or via a spacer, resulting in a mono- or polyunsaturated heterocyclic moiety as defined above.

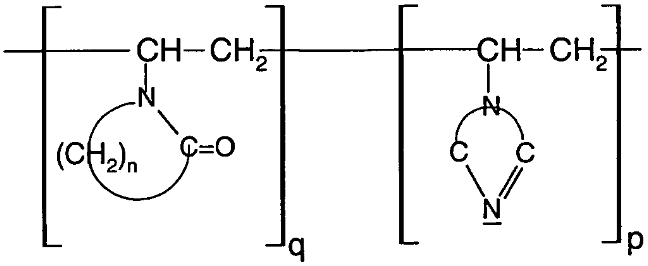
[0039] Of the inhibitor polymers of formula (IV), polyvinyl imidazole is especially preferred.

[0040] According to another embodiment, a copolymer (iii) is used as inhibitor polymer, which comprises both the side chain shown in formula (I) (preferably formula (II)) and the side chain shown in formula (III) (preferably formula (IV)). Such a copolymer can be depicted as follows:



(V)

[0041] Formula (V) is to be understood such that both block copolymers and copolymers with (statistically or regularly) alternating functional side chains are to be encompassed. The same applies to formula (VI), which represents a preferred copolymer.



(VI)

[0042] The total amount of the inhibitor polymer(s) in the heat-sensitive coating is preferably 0.1 to 60 wt.-%, more preferred 10 to 40 wt.-% and especially preferred 10 to 20 wt.-%, based on the dry layer weight.

[0043] With respect to its molecular weight, the inhibitor polymer is not particularly restricted. However, the molecular weight is preferably in the range of 10,000 to 500,000.

[0044] Novolak resins, a polyvinylphenol polymer, a vinylphenol/hydrocarbylacrylate copolymer, a pyrogallol/acetone polymer or mixtures thereof can for example be used as phenolic resins in the present invention. Novolak resins are preferably used in the present invention, i.e. condensation products of suitable phenols, e.g. phenol itself, C-alkyl-substituted phenols (including cresols, xylenols, p-tert-butylphenol, p-phenylphenol and nonylphenols), and of diphenols (e.g. bisphenol-A), with suitable aldehydes such as formaldehyde, acetaldehyde, propionaldehyde and furfuraldehyde. The type of catalyst and the molar ratio of the reactants determine the molecular structure and thus the physical properties of the resin. 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" which have a thermoplastic character. As used in the present application, however, the term "novolak resin" should also encompass the phenolic resins known as "resols" which are obtained at higher aldehyde/phenol ratios (e.g. 1:1 to 3:1) and in the presence of alkaline catalysts. Mixtures of different phenolic resins, e.g. mixtures of novolak in the narrow sense and a resol, can be used as well.

[0045] The total amount of the phenolic resin(s) in the heat-sensitive coating is preferably larger than the amount of inhibitor polymer. Based on the dry layer weight, the amount of novolak resin is preferably at least 40 wt.-%, more preferred at least 50 wt.-%, still more preferred at least 70 wt.-% and especially preferred at least 80 wt.-%. Usually, the amount does not exceed 95 wt.-%, preferably 85 wt.-%.

[0046] Imaging of the heat-sensitive elements can be carried out either by direct application of heat or by IR radiation, which is absorbed and converted into heat by photothermal conversion material (in the following also simply referred to as IR absorber).

[0047] 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. It is furthermore preferred that the IR absorber does not or not essentially absorb radiation in the UV range of 300 to 420 nm. The absorbers are for example selected from carbon black, phthalocyanine pigments/dyes and pigments/dyes of the squarylium, 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-B-6,410,207 and EP-A-1 176 007.

[0048] If an IR absorber is present in the heat-sensitive coating, it is preferably present in an amount of at least 0.1 wt.-%, based on the dry layer weight, more preferred at least 1 wt.-%, still more preferred at least 2 wt.-%. Usually, the amount of IR absorber does not exceed 25 wt.-%, more preferred 20 wt.-% and most preferred 15 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.

[0049] Furthermore, the radiation-sensitive coating of the present invention can comprise dyes or pigments for coloring the layer. Examples of colorants include e.g. phthalocyanine pigments, azo pigments, carbon black and titanium dioxide, ethyl violet, crystal violet, azo dyes, anthraquinone dyes and cyanine dyes. The amount of colorant is preferably 0 to 20 wt.-%, based on the dry layer weight, especially preferred 0.5 to 10 wt.-%.

[0050] For improving the physical properties of the hardened coating, the inventive radiation-sensitive coating can additionally comprise further additives such as plasticizers or inorganic fillers. Suitable plasticizers include e.g. dibutyl phthalate, dioctyl phthalate, didodecyl phthalate, dibutyl sebacate, triacetyl glycerin and triaryl phosphates. The amount of plasticizer is not particularly restricted, however, it is preferably 0 to 10 wt.-%, based on the dry layer weight, especially preferred 0.25 to 5 wt.-%.

[0051] Developing aids (so-called "accelerators") such as e.g. polyvinyl phenols, tetrahydrophthalic acid or anhydride, pyromellitic acid etc. should be mentioned as another optional component. Their amount is not particularly restricted, however, it is preferably 0 to 20 wt.-%, based on the dry layer weight, especially preferred 0.5 to 10 wt.-%.

[0052] Additionally, the radiation-sensitive coating can comprise surfactants (e.g. anionic, cationic or neutral tensides or mixtures thereof). Suitable surfactants include siloxane-containing polymers, fluorine-containing polymers and polymers with ethylene oxide and/or propylene oxide groups. 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.-%.

[0053] The heat-sensitive layer is produced by applying a solution of all components onto an optionally pretreated substrate and drying. All solvents and solvent mixtures can be used in which the phenolic resin and the inhibitor polymer are both soluble. If the phenolic resin and the inhibitor polymer have very different solubility characteristics, a solvent mixture of 2 or more components is usually required, with one component commonly being water. In particular in the case of inhibitor polymers (i) and in particular those of formula (II), a mixture of water, tetrahydrofuran (THF), optionally propylene glycol monomethylether (PGME) and optionally methyl lactate (ML) has proven to be convenient. The water content in such a solvent mixture is preferably 0.5 to 20 vol.-%, based on the entire solvent mixture, especially preferred 5 to 15 vol.-%. The amount of PGME is preferably 0 to 30 vol.-%, especially preferred 10 to 20 vol.-%. The amount of THF is preferably 30 to 90 vol.-%, especially preferred 50 to 75 vol.-%, and the amount of ML is preferably 0 to 30 vol.-%, especially preferred 10 to 20 vol.-%. The following rule of thumb applies: The more novolak is used, the less water is used; the more inhibitor polymer is used, the more water is used.

[0054] The coating can be carried out by means of common coating processes, e.g. coating by means of doctor blades, spin coating, coating with a slot coater etc.

[0055] The dry layer weight of the heat-sensitive layer in lithographic printing plate precursors is preferably 0.5 to 4.0 g/m^2, especially preferred 1 to 2 g/m^2.

[0056] Imaging can be carried out by the application of direct heat or by means of IR radiation. If IR radiation is used, e.g. in the form of IR lasers or IR laser diodes that emit in the range of 750 to 1,120 nm, the heat-sensitive coating should contain an IR absorber. All image-setters with IR lasers known to the person skilled in the art can be used.

[0057] The image-wise exposed/heated elements, such as e.g. printing plate precursors, are developed with an aqueous alkaline developer which usually has a pH value in the range of 10 to 14. Commercially available developers can be used for this purpose.

[0058] Developed printing plates can furthermore be subjected to a "baking" step in order to increase the abrasion resistance of the printing areas; however, this is not necessarily required for the printing plates according to the present invention since due to their excellent solvent resistance, high numbers of copies can be printed without any loss in quality.

[0059] The printing plates according to the present invention are characterized by an excellent chemical resistance to organic solvents e.g. contained in fountain solutions, washing solutions and some printing inks (e.g. petrol ethers, glycols and glycol ethers, as well as straight-chain, branched and cyclic alkanols), while their developability and IR sensitivity are maintained at a high level.

[0060] Preferably, the heat-sensitive elements of 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. do not require yellow light conditions.

[0061] The invention will be explained in more detail in the following examples; however, they shall not restrict the invention in any way.

Examples

Example 1

(Confirmation of improved washing agent resistance and higher number of copies)

[0062] A solution (9 wt.-%) was prepared by dissolving 79 wt.-% PD 140 A (m/p-cresol novolak, available from Borden Chemicals), 20 wt.-% PVP/VA-W 635 (vinylpyrrolidone/vinylacetate copolymer; aqueous solution; 60% polyvinylpyrrolidone, 40% vinylacetate; 50% solids content) and 1 wt.-% Trump dye (IR dye absorbing at 830 nm) in a solvent mixture of acetone, methyl lactate, THF, propylene glycol methylether (PGME) and water (weight ratio: 37:10:37:10:6). This solution was applied onto a substrate by means of a wire-wound blade, resulting in a dry layer weight of 1.5 g/m^2. The substrate was an electrochemically grained and anodized aluminum plate sealed with polyvinylphosphonic acid. The coating was dried at 100°C for 10 minutes.

[0063] The resistance of this plate to roller washing agents (in the following simply "washing agents") (simulated with a mixture of gasoline 135/180, isopropanol and water in a weight ratio of 80:19:1) was examined by dipping the plate into this washing solution and rubbing it several times. Up until 4 minutes, no attack on the coating was observed. In comparison, the coating of the commercially available ElectraExcel plate (positive working thermoplate) from Kodak Polychrome Graphics had dissolved after only 30 seconds, and the coating of the commercially available Easy Print plate (analogous positive working plate) from Kodak Polychrome Graphics was attacked after 30 seconds.

[0064] The plate was exposed in a Creo Trendsetter image-setter (830 nm) with 400 mJ/cm^2 in a checkerboard pattern with different point sizes, developed at 25°C with the developer 9005, commercially available from Kodak Polychrome Graphics, rinsed, gummed with a gumming solution 850 S, available from Kodak Polychrome Graphics, which had been diluted with water in a ratio of 1:1, and dried. The plate showed a good image with a high resolution, i.e. the checkerboard pattern of 1 x 1 pixels (10 μm) was visible.

[0065] Another printing plate was prepared by carrying out exposure, developing and gumming as described above, however, a solid area and a digital gray scale of FOGRA and GATF as well as different screen values with 80 lines/cm were used for exposure and the printing plate was used on a MAN-Roland 200 printing press. 10% isopropanol to which 4% Combifix (fountain solution additive, available from Hostmann-Steinberg) had been added was used as fountain solution; Hartmann Schwarz Offset S 8900 Cora was used as printing ink. The number of copies yielded by the non-conditioned plate was 65,000; the ElectraExcel plate (same substrate and conditioned for 3 days at 55°C) only yielded 50,000 copies.

Example 2

(Use of different types of PVP/VA and different novolaks)

[0066] As in Example 1, a 9 wt.-% solution was prepared by dissolving 38.5 wt.-% 6564 LB (phenol/m-cresol novolak from Bakelite), 38.5 wt.-% PD 140 A, 20 wt.-% PVP/VA, 1 wt.-% Trump dye and 2 wt.-% crystal violet in a solvent mixture of 31 % methyl lactate, 56% THF and 13% water.

[0067] When PVP/VA-I-235 (vinylpyrrolidone/vinylacetate copolymer; solution in isopropanol; 20% polyvinylpyrrolidone, 80% vinylacetate; 50% solids content) was used, the resistance to Goldstar developer (available from Kodak Polychrome Graphics) was 30 seconds (i.e. after more than 30 seconds, a first attack could be observed), while a first attack was observed after only 90 seconds when PVP/VA-W-735 (aqueous solution; 70% PVP, 30% VA) was used. It can be concluded that the developer resistance can be further increased by increasing the amount of PVP in the copolymer.

[0068] The resistance to "washing agents" also increased in combination with a higher content of PVP. When PVP/VA-357 (30% PVP, 70% VA) was used, a first attack by the washing agent was observed after 1 minute, while such an attack was only observed after 4 minutes when PVP/VA-535 (50% PVP, 50% VA) was used.

Example 3

(Use of polyvinylimidazol instead of polyvinylpyrrolidone etc.)

[0069] A coating solution was prepared by dissolving the following solids:

43.3 wt.-% LB6564 (phenol/m-cresol novolak from Bakelite)
43.3 wt.-% PD140 A
1 wt.-% Trump dye
2 wt.-% crystal violet and
10 wt.-% PVI-W (polyvinylimidazole of the company Panchim)

in the following solvent mixture:

40 wt.-% THF
15 wt.-% water
25 wt.-% Dowanol PM
20 wt.-% methanol

and applied onto a substrate with a wire-wound blade, resulting in a dry layer weight of about 1.5 g/m^2. The substrate was an electrochemically grained and anodized aluminum plate sealed with polyvinylphosphonic acid. After coating, drying was first carried out in an air stream and then for 10 minutes in a 100°C oven. Then the plate was "conditioned" for 1 day at 50°C.

[0070] The resistance of this plate to roller washing agents (simulated with a mixture of gasoline 135/180, isopropanol and water in a weight ratio of 90:19:1) was examined by dipping the plate into this washing solution and rubbing it with a cloth after different time periods. Up until 5 minutes, no abrasion was observed. In comparison, the coating of a comparison plate which differed in that no PVI-W had been added showed a loss of layer material after only 30 seconds.

[0071] The resistance of this plate to the developer Goldstar was examined as well: The coating was first attacked after 45 seconds; loss of layer material was observed after 3 minutes. In comparison, the coating of a comparison plate which differed in that no PVI-W had been added showed a loss of layer material after only 45 seconds.

[0072] The plate was exposed in a Creo Trendsetter image-setter with 400 mJ/cm^2 in a checkerboard pattern with different point sizes and developed at 20°C for 30 seconds with the developer Goldstar from KPG. The plate showed a good image with a high resolution. The above-mentioned comparison plate, however, yielded no image.

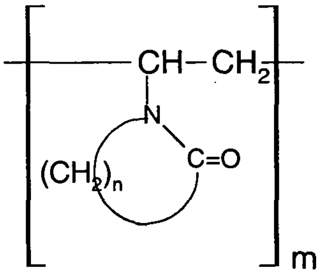
Claims

1. Heat-sensitive element, comprising

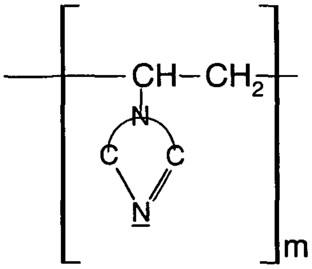
    (a) an optionally pretreated substrate
    (b) a positive working heat-sensitive coating, comprising at least one phenolic resin and at least one inhibitor polymer selected from

        (i) polymers comprising saturated (hetero)cyclic moieties with at least one carbonyl group, the carbon atom of which is part of the (hetero)cyclic moiety, said (hetero)cyclic moieties being bonded to a polymer chain directly
        (ii) polymers comprising unsaturated heterocyclic moieties which are bonded to a polymer chain directly and which have a ring nitrogen atom, said ring nitrogen atom being bonded to the two adjacent ring carbon atoms via a single bond and a double bond and moreover having a free electron pair, and
        (iii) copolymers comprising both saturated (hetero)cyclic moieties as defined in (i) and unsaturated heterocyclic moieties as defined in (ii).

2. Heat-sensitive element according to claim 1, wherein the inhibitor polymer is selected from polymers of formulas (II) and (IV)



(II)



(IV)

wherein n is 3, 4 or 5,
or copolymers thereof.

3. Heat-sensitive element according to claim 1 or 2, wherein the phenolic resin is present in an amount of 40 to 95 wt.-%, based on the dry layer weight.

4. Heat-sensitive element according to any of claims 1 to 3, wherein the inhibitor polymer is present in an amount of 0.1 to 60 wt.-%, based on the dry layer weight.

5. Heat-sensitive element according to any of claims 1 to 4, wherein the phenolic resin is a novolak resin.

6. Heat-sensitive element according to any of claims 1 to 5, wherein the inhibitor polymer is polyvinylpyrrolidone, a vinylpyrrolidone/vinylacetate copolymer, polyvinylimidazole or a mixture thereof.

7. Heat-sensitive element according to any of claims 1 to 6, wherein the heat-sensitive coating comprises at least one substance capable of absorbing radiation of a wavelength in the range of 650 to 1,300 nm and converting it into heat.

8. Heat-sensitive element according to any of claims 1 to 7, wherein the heat-sensitive layer furthermore comprises at least one additive selected from surfactants, contrast dyes and pigments, plasticizers and developing aids.

9. Heat-sensitive element according to any of claims 1 to 8, wherein said element is a lithographic printing plate precursor.

10. Heat-sensitive element according to claim 9, wherein the substrate is an aluminum substrate which prior to coating with the heat-sensitive coating was subjected to at least one treatment selected from (a) mechanical and/or chemical graining, (b) anodizing and (c) hydrophilizing.

11. Heat-sensitive element according to claim 9 or 10, wherein the dry layer weight of the heat-sensitive layer is 0.5 to 4.0 g/m^2.

12. Process for producing a heat-sensitive element as defined in any of claims 1 to 11, comprising:

(a) providing an optionally pretreated substrate,
(b) applying a solution comprising
at least one phenolic resin,
at least one inhibitor polymer selected from

(i) polymers comprising saturated (hetero)cyclic moieties with at least one carbonyl group, the carbon atom of which is part of the (hetero)cyclic moiety, said (hetero)cyclic moieties being bonded to a polymer chain directly
(ii) polymers comprising unsaturated heterocyclic moieties which are bonded to a polymer chain directly and which have a ring nitrogen atom, said ring nitrogen atom being bonded to the two adjacent ring carbon atoms via a single bond and a double bond and moreover having a free electron pair, and
(iii) copolymers comprising both saturated (hetero)cyclic moieties as defined in (i) and unsaturated heterocyclic moieties as defined in (ii),

optionally one or more additives selected from surfactants, contrast dyes and pigments, and plasticizers and optionally at least one substance capable of absorbing radiation of a wavelength in the range of 650 to 1,300 nm and converting it into heat,
and
(c) drying.

13. Process according to claim 12, wherein a mixture of water, tetrahydrofuran, methyl lactate and propylene glycol monomethylether is used as a solvent for the solution used in step (b).

14. Process for imaging a heat-sensitive element, comprising:

(a) providing a heat-sensitive element as defined in any of claims 1 to 11,
(b) image-wise exposure of said element with IR radiation or image-wise direct heating and
(c) removing the exposed or directly heated areas of the coating with an aqueous alkaline developer.

15. Heat-sensitive composition, comprising

(a) one or more organic solvents,
(b) at least one phenolic resin,
(c) at least one inhibitor polymer selected from

(i) polymers comprising saturated (hetero)cyclic moieties with at least one carbonyl group, the carbon atom of which is part of the (hetero)cyclic moiety, said (hetero)cyclic moieties being bonded to a polymer chain directly
(ii) polymers comprising unsaturated heterocyclic moieties which are bonded to a polymer chain directly and which have a ring nitrogen atom, said ring nitrogen atom being bonded to the two adjacent ring carbon atoms via a single bond and a double bond and moreover having a free electron pair, and
(iii) copolymers comprising both saturated (hetero)cyclic moieties as defined in (i) and unsaturated heterocyclic moieties as defined in (ii),

(d) optionally at least one additive selected from surfactants, contrast dyes and pigments, and plasticizers.

16. Heat-sensitive composition according to claim 15, wherein the composition furthermore comprises at least one substance capable of absorbing radiation of a wavelength in the range of 650 to 1,300 nm and converting it into heat.

17. Heat-sensitive composition according to claim 15 or 16, wherein the solvent is a mixture of water, tetrahydrofuran, methyl lactate and propylene glycol monomethylether.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 00 3616

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	GB 1 195 842 A (AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP) 24 June 1970 (1970-06-24) * claims 1-4; example 20 * ---	1-17	B41M5/36 B41C1/10
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 May 2004	Bacon, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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