

SPECIFICATION

Light-sensitive printing plate precursors

- 5 This invention relates to a light-sensitive printing plate precursor and, more particularly, to a light-sensitive printing plate precursor having a polymer coating deposited onto the surface of the light-sensitive layer. 5
- Exposure of a light-sensitive printing plate precursor through an original has conventionally been conducted by disposing a light-sensitive printing plate precursor and an original in a superposed state between a rubber sheet and a pressure glass, and evacuating the interface between the rubber sheet and the
- 10 pressure glass to completely contact the original with the surface of the light-sensitive layer of the light-sensitive printing plate precursor. 10
- In order to shorten the vacuum-contacting time, there is known a light-sensitive printing plate precursor having micro-patterns consisting of coating portions and non-coating portions on the light-sensitive layer prepared according to the process described in, for example, U.S. Patent 4,216,289.
- 15 Recent requirements for saving resources have promoted the spread of double-coated light-sensitive printing plate precursors. However, in the case of providing micro-patterns on both light-sensitive layer surfaces of such type light-sensitive printing plate precursor according to the above-described process, the micro-patterns must be first coated on one side of the plate precursor and dried, then on the other side of the plate precursor, and thus considerably large-scale equipment is required. In addition, the coated portions of
- 20 the micro-patterns provided on the back side according to the above-described process are often delaminated or crushed before the step of being cut into a desired size due to rubbing by conveyor rollers, resulting in a longer vacuum-contacting time upon imagewise exposure of the light-sensitive layer on the back side as compared with the exposure on the surface. Also, in the exposure step, the coated portions of the micro-pattern on the back side to be exposed layer are sometimes pressed and crushed by a printer upon
- 25 vacuum exposure of the surface, resulting in a prolonged evacuation upon exposure of the back side. 25
- Japanese Patent Application (OPI) No. 98505/76 (the term "OPI" as used herein refers to a "published unexamined Japanese Patent Application") discloses a process for coating a dispersion of waxy or fine-powdered resin having release properties in a low-boiling organic solvent by air-spraying to thereby solve the problem that the coating for improving the vacuum contact properties stains a film original.
- 30 However, this spray-coated layer is liable to be delaminated due to weak adhesion force for the surface of the light-sensitive printing plate precursor, thus also causing the above-described problem. In addition, the use of an organic solvent is not favorable from the viewpoint of safety during production of the printing plate precursor. 30
- British Patent GB2,025,646A discloses a process of powdering solid powder and thermally fixing it on a
- 35 light-sensitive printing plate precursor. With double-coated light-sensitive printing plates precursors, however, the mat layer on one side is likely to be crushed during roller conveying before being cooled after the thermowelding. Conveying without using rollers involves handling difficulties. Further, preparation of powder requires pulverization and classification of a resin, leading to high production costs. 35
- Therefore, an object of the present invention is to provide a light-sensitive printing plate precursor resistant to rubbing or pressure, by which the vacuum-contacting time upon exposure can be shortened.
- 40 Another object of the present invention is to provide a light-sensitive printing plate precursor showing shortened vacuum-contacting time, which can be prepared according to a safe process using simple equipment. 40
- We have discovered that a light-sensitive printing plate precursor enabling the attainment of the
- 45 above-described objects can be obtained by spray-coating an aqueous liquid containing a dissolved or dispersed resin therein on the surface of the light-sensitive layer, and drying it. 45
- Thus, the present invention provides a light-sensitive printing plate precursor comprising a support having provided thereon a light-sensitive layer, said light-sensitive layer having spray-coated and dried thereon an aqueous liquid containing a resin in a dissolved or dispersed state; it also provides a process of providing
- 50 such a precursor. 50
- Although the reasons are not completely clear, it is believed that when the aqueous liquid is spray-coated and dried according to the invention, spray-atomized liquid droplets deposit on the surface of the light-sensitive layer, and the drying rate is so fast that, even when the deposited polymer is brought into contact with conveyor rollers within a comparatively short time, the polymer is not crushed or delaminated.
- 55 This is believed to be due to a sufficient degree of drying and fixation occurring, and due to strong adhesion to the surface of the light-sensitive layer. In addition, the sprayed and dried polymer has a strong resistance to rubbing by rollers and to pressure applied thereto upon vacuum-contacting for imagewise exposure, seemingly because the polymer is present as smaller size particles as compared with the coated portions formed by the process described in Japanese Patent Application (OPI) No. 96604/76. Further, the use of the
- 60 aqueous liquid removes the possibility of explosion encountered in spraying an organic solvent and eliminates the necessity of providing explosion-proof equipment. 60
- As the resin to be dissolved or dispersed in the above-mentioned aqueous liquid, the inventors have discovered that copolymers containing the following polymeric units (a), (b) and (c) are particularly excellent:
- 65 (a) polymeric units derived from, as monomer(s), at least one of alkyl acrylates having from 2 to 10 carbon 65

atoms in the alkyl moiety and alkyl methacrylates having from 4 to 10 carbon atoms in the alkyl moiety;

(b) polymeric units derived from, as monomer(s), at least one of styrenes, acrylonitriles, methyl methacrylate and ethyl methacrylate; and

(c) polymeric units derived from, as monomer(s), at least one of acrylic acid, methacrylic acid, maleic acid, itaconic acid, alkali metal salts thereof and ammonium salts thereof.

Polymeric unit (a) is a component imparting adhesiveness for the surface of the light-sensitive layer.

Specific examples of monomers useful therefore include ethyl acrylate, *n*-propyl acrylate, isopropyl acrylate, *n*-butyl acrylate, isobutyl acrylate, *n*-amyl acrylate, isoamyl acrylate, *n*-hexyl acrylate, 2-ethylhexyl acrylate, *n*-octyl acrylate, *n*-decyl acrylate, *n*-butyl methacrylate, isobutyl methacrylate, *n*-amyl methacrylate, 2-ethylhexyl methacrylate, *n*-octyl methacrylate, and *n*-decyl methacrylate.

Polymeric unit (b) is a component imparting resistance against pressure. Specific examples of monomers useful therefor include styrene, *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, 3,4-dimethylstyrene, 3,5-dimethylstyrene, 2,4,5-trimethylstyrene, 2,4,6-trimethylstyrene, *o*-ethylstyrene, *m*-ethylstyrene, *p*-ethylstyrene, 3,5-diethylstyrene, 2,4,5-triethylstyrene,

p-*n*-butylstyrene, *m*-sec-butylstyrene, *m*-tert-butylstyrene, *p*-hexylstyrene, *p*-*n*-heptylstyrene, *p*-2-ethylhexylstyrene, *o*-fluorostyrene, *m*-fluorostyrene, *p*-fluorostyrene, *o*-chlorostyrene, *m*-chlorostyrene, *p*-chlorostyrene, 2,3-dichlorostyrene, 2,4-dichlorostyrene, 2,5-dichlorostyrene, 2,6-dichlorostyrene, 3,4-dichlorostyrene, 3,5-dichlorostyrene, 2,3,4,5,6-pentachloro-styrene, *m*-trifluoromethylstyrene, *o*-cyanostyrene, *m*-cyanostyrene, *m*-nitrostyrene, *p*-nitrostyrene, *p*-dimethylaminostyrene, acrylonitrile, α -chloroacrylonitrile, α -bromoacrylonitrile, α -trifluoromethylacrylonitrile, α -trifluoromethylcarboxy-acrylonitrile, methyl methacrylate, and ethyl methacrylate.

Polymeric unit (c) is a component improving solubility in a developing solution. The polymer is preferably soluble in such solution. Specific examples of unit (c) include acrylic acid, sodium acrylate, potassium acrylate, ammonium acrylate, methacrylate acids, sodium methacrylate, potassium methacrylate, ammonium methacrylate, maleic acid, sodium maleate, potassium maleate, ammonium maleate, itaconic acid, sodium itaconate, potassium itaconate and ammonium itaconate.

In such copolymers, the contents of polymeric units (a), (b) and (c) are preferably from 10 to 70 wt.%, from 20 to 80 wt.% and from 6 to 50 wt.%, respectively. As the content of polymeric unit (a) is decreased to less than 10%, the adhesion force of the copolymer to the surface of the light-sensitive layer is reduced; on the other hand, as the content is increased to more than 70 wt.%, the pressure-resistance of the copolymer is reduced. As the content of polymeric unit (b) is decreased to less than 20 wt.%, the hardness and pressure resistance of the copolymer are reduced; on the other hand, as the content is increased to more than 80 wt.%, the solubility of the copolymer in a developer and adhesion force to the light sensitive layer are reduced. Further, as the content of polymeric unit (c) is decreased to less than 6 wt.%, the solubility of the copolymer in a developer becomes poorer, but as the content increases to more than 50 wt.%, the copolymer becomes more fragile and its adhesion force to the surface of the light-sensitive layer is reduced. Thus, particularly preferably contents of the polymeric units (a), (b), and (c) are from 15 to 50 wt.%, from 40 to 70 wt.%, and from 10 to 30 wt.%, respectively.

In case of using the polymer unit (c) wherein 50 to 100 mol.%, preferably 80 to 100 mol.%, of the acid residue are ammonium salt, the spray-coated copolymer shows particularly excellent adhesiveness and such is preferred.

The above-described copolymer may be obtained in the same manner as in synthesizing an ordinary latex, by emulsifying the starting monomers in water with the aid of a surfactant and conducting emulsion polymerization using a polymerization initiator, such as potassium persulfate, to obtain an aqueous dispersion. Detailed synthesis methods are described in U.S. Patents, 1,933,052, 2,117,321, 2,118,863, 2,144,233 and 3,057,812. It is also possible to obtain an aqueous solution of the copolymer using a sodium salt, potassium salt or ammonium salt of acrylic or methacrylic acid as the polymeric unit (c).

The concentration of the polymer in the aqueous solution or dispersion thereof to be sprayed over the surface of the light-sensitive layer preferably is from 10 to 30 wt.%, based on the weight of the aqueous solution or dispersion.

The aqueous liquid to be sprayed may contain other fillers which do not themselves adhere to the light-sensitive layer. As such fillers, there are, for example, silicon dioxide, zinc dioxide, titanium oxide, zirconium oxide, glass particles, alumina and polymer particles (for example, particles of polymethyl methacrylate, polystyrene or a phenolic resin). These can be used in combinations of two or more.

For spraying such aqueous solution or dispersion over the surface of the light-sensitive layer, there may be employed known methods such as an air-spraying method, an airless spraying method, an electrostatic air-spraying method, an electrostatic airless spraying method, and an electrostatic spray electrostatic coating method.

The term "spray" means a method comprising spraying an aqueous solution or dispersion of a the polymer (coating solution) by a spraying device to atomize the coating solution and to coat the coating solution onto the light-sensitive surface of a printing plate precursor.

The air-spraying method comprises using a compressed air as spraying medium. The airless spraying method (liquid pressure spraying method) comprises spraying the coating solution by applying high pressure to the coating solution. The electrostatic spraying method comprises spraying the coating solution by electrostatic force. The electrostatic coating method is advantageous to increase adhesion efficiency of

the polymer in the coating solution and comprises employing an earthed article to be coated as an anode and a coating solution spraying device as a cathode, forming an electrostatic field between the anode and the cathode by applying high negative voltage, negatively charging the resin particles and adsorbing the polymer particles on the article to be coated with good efficiency.

- 5 The aqueous solution or dispersion of the polymer spray-coated on the surface of the light-sensitive layer is then dried. Drying may be conducted in a conventional manner by, for example, blowing warm air over the layer.

The particles thus deposited on the surface of the light-sensitive layer have nearly a hemisphere shape and are from 1 to 20 μ in height, from 20 to 200 μ in width (diameter), and are present in a coverage of from 1 to 1000 particles per mm^2 , and preferably 5 to 500 particles per mm^2 .

- 10 The light-sensitive printing plate precursor on which the resin is to be deposited as described above fundamentally comprises a support having provided thereon a light-sensitive layer. Particularly remarkable effects of the present invention can be obtained with light-sensitive printing plate precursors to be used for preparing lithographic printing plates. As the support for such light-sensitive lithographic printing plate precursors, various plates are known which are described in detail in British Patent Specification No. 2030309A. The light-sensitive layer can comprise a diazo resin, an *o*-quinonediazide compound, a light-sensitive azide compound, a photopolymerizable composition or a light-sensitive resin. These are also described in detail in British Patent Specification No. 2030309A.

- 15 Coverage of the light-sensitive layer is generally from 0.1 to 7 g/m^2 , and preferably from 0.5 to 3 g/m^2 , in terms of dry weight per side of the plate.

The present invention enables the obtainment of a double-coated light-sensitive printing plate precursor having less differences between the surface and the back side, and having excellent vacuum-contact properties, and raises the efficiency of plate-making steps. Furthermore, in the production steps, coating can be conducted safely using simple equipment.

- 20 The present invention will now be described in more detail by reference to examples of preferred embodiments of the present invention, which, however, are not limitative.

Example 1

- Both sides of a 0.24-mm thick aluminum plate were grained using a nylon brush and a 400-mesh pumice stone suspension in water, and then washed well with water. This plate was dipped for 3 minutes in a 70°C sodium tertiary phosphate aqueous solution (5%), washed with water, and dried.

- A light-sensitive solution was prepared by dissolving 1 part by weight of naphthoquinone-1,2-diazido-5-sulfonic acid ester of polyhydroxyphenyl obtained by condensation polymerization between acetone and pyrogallol, as described in Japanese Patent Publication No. 28403/68 (corresponding to U.S. Patent 3,635,709, Example 1), and 2 parts by weight of a novolak type phenolformaldehyde resin in 20 parts by weight of 2-methoxyethyl acetate and 20 parts by weight of methyl ethyl ketone, and coated in sequence on the both sides of the support and dried to obtain a double-coated light-sensitive lithographic printing plate precursor.

- Copolymer aqueous liquids A to D having the following compositions and having a solid concentration of 20% were respectively coated on both sides of this light-sensitive lithographic printing plate precursor by electrostatic air-type spraying (amount of liquid fed: 28 cc/min, spraying air pressure: 3 kg/cm^2 , electrostatic voltage: -80 V, distance between coating material and plate: 350 mm, plate transfer speed: 39 m/sec) followed by drying for 5 seconds at 60°C.

		A	B	C	D
(b)	Methyl methacrylate	68 wt. %	68	80	15
(a)	Ethyl acrylate	20	28	8	70
(c)	Sodium acrylate	12	4	12	15

- In every coating, the amount of coated resin was 0.1 g/m^2 , the number of liquid droplets was 50 to 100 droplets per mm^2 , and the height and width of the resin after drying were from 2 to 6 μ , and from 20 to 150 μ , respectively. Time required for the vacuum contact was measured first with the surface of 550 $\times$ 650 mm film, then with the back side thereof, using a 1003 $\times$ 800 mm precursor. After imagewise exposure, the samples were processed in a developer, an aqueous 5 wt. % sodium silicate (molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$: 1.74) solution, and printing was conducted using the resulting lithographic printing plate precursors. Results thus obtained are tabulated in the following table.

		A	B	C	D	
	Vacuum-contact time:					
5	Surface	13 sec	13 sec	15 sec	20 sec	5
	Back side	13 sec	13 sec	20 sec	35 sec	
	Printing stain	o*	x**	o	o	
10	Inking properties	o	o	o	o	10

Symbols: o* = good, x** = bad.

15	Sample B can be a useful material, without printing stain, with other developers.	15
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Example 2

20	In the same manner as in Example 1, except for using as the resin layer to be coated on the light-sensitive lithographic printing plate precursor a copolymer aqueous dispersion having the following composition (mean particle size: 0.05 μ):	20
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25	(b) methyl methacrylate	27.5 wt. %	25
	(a) butyl methacrylate	60 wt. %	
	(c) methacrylic acid	12.5 wt. %	

30		30
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and coating it by electrostatic spraying (amount of liquid bed: 15 cc/min, spraying air pressure: 2 kg/cm², electrostatic voltage: -70V, distance between coating material and plate: 300 mm, plate transfer speed: 25 m/min), there was prepared a sample, which showed the same good vacuum-contact properties as Sample

35	A in Example 1, and caused no problems as to performance characteristics.	35
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Example 3

40	In the same manner as in Example 1 except for changing the composition of the coating solution of the light-sensitive layer to that described below, there was obtained a light-sensitive lithographic printing plate precursor.	40
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Light sensitive layer coating solution

45	2-Hydroxyethyl methacrylate copolymer (1) (Note 1)	... 0.87 g	45
	2-Methoxy-4-hydroxy-5-benzoylbenzene- sulfonic acid salt of a condensate between <i>p</i> -diazodiphenylamine and paraformaldehyde	... 0.1 g	
50	C.I. 42595	... 0.03 g	50
	Methanol	... 6 g	
55	2-Methoxyethanol	... 6 g	55
	(Note 1): described in Example 1 of U.S. Patent 4,123,276		
60			60

Coating was conducted so that the dry coated amount was 2 g/m² on each side.

65	An aqueous colloidal dispersion (solids: 20 wt. %) of a copolymer of the following formulation was coated on the above-described light-sensitive plate precursor by electrostatic spraying under the same conditions	65
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as in Example 2 and dried at 50°C for 5 seconds.

5	(b) Methyl methacrylate	50 wt. %	5
	(b) Styrene	10 "	
	(a) Ethyl acrylate	31 "	
10	(c) Ammonium methacrylate	9 "	10

As is described in U.S. Patent 3,740,367, this aqueous colloidal dispersion was prepared by adding aqueous ammonia to an aqueous dispersion of methyl methacrylate/styrene/ethyl acrylate/methacrylic acid copolymer to convert methacrylic acid to ammonium salt. The coated amount of the resin was 0.08 g/m², the number of liquid droplets 80 to 150 per mm², the width 20 to 150 μ , and the height about 2.5 to 6 μ .

Differences between the surface and the back side were examined as to vacuum-contact properties and prolongation or shortening of the vacuum-contacting time after rubbing the coating by a cloth pad. Thus, it was found that the difference in vacuum-contacting time between the surface and the back side was only about 10% after rubbing, and the plate obtained had good vacuum-contact properties. The resulting plate also showed good development properties, no stains, and good inking properties after exposure and development processing.

CLAIMS

1. A light-sensitive printing plate precursor comprising a support having thereon a light-sensitive layer, said light-sensitive layer having deposited thereon a layer of particles of a synthetic polymer which is soluble in a developer for the light-sensitive layer and which was deposited by spray-coating an aqueous dispersion or solution of the polymer and drying to remove water.
2. A light-sensitive printing plate precursor as claimed in Claim 1, wherein said resin is a copolymer of three monomer units selected from:
 - (a) alkyl acrylates having from 2 to 10 carbon atoms in the alkyl moiety and alkyl methacrylates having from 4 to 10 carbon atoms in the alkyl moiety;
 - (b) styrenes, acrylonitriles, methyl methacrylate and ethyl methacrylate; and
 - (c) acrylic acid, methacrylic acid, maleic acid, itaconic acid, alkali metal salts thereof and ammonium salts thereof.
3. A light-sensitive printing plate precursor as claimed in Claim 2, wherein said copolymer comprises from 10 to 70 wt. % of said units (a), from 20 to 80 wt. % of said units (b) and from 6 to 50 wt. % of said units (c).
4. A light-sensitive printing plate precursor as claimed in Claim 3, wherein said copolymer comprises from 15 to 50 wt. % of said units (a), from 40 to 70 wt. % of said units (b) and from 10 to 30 wt. % of said units (c).
5. A light-sensitive printing plate precursor as claimed in Claim 1, 2, 3 or 4, wherein the particles deposited on the surface of the light-sensitive layer are hemispheres from 1 to 20 microns in height, from 20 to 200 microns in width, and are present in a coverage of from 1 to 1,000 particles per square millimetre.
6. A light-sensitive printing plate precursor as claimed in Claim 5, wherein said particles are present in a coverage of from 5 to 500 particles per mm².
7. A light-sensitive printing plate precursor as claimed in Claim 2, substantially as hereinbefore described with reference to any of the Samples of the Examples.
8. A process of producing a light-sensitive printing plate precursor as claimed in any preceding claim, which comprises spray-coating an aqueous solution or liquid dispersion containing said polymer onto the light-sensitive layer of the precursor, and drying the aqueous liquid.
9. A process for producing a precursor as claimed in Claim 8, wherein said polymer comprises from 10 to 30 wt. % of said aqueous liquid.
10. A process of producing a light-sensitive printing plate precursor as claimed in Claim 8, substantially as hereinbefore described with reference to any of the Examples.
11. A process of preparing a printing plate which comprises imagewise exposing by vacuum contact a precursor as claimed in any of Claims 1 to 7 or made by a process as claimed in Claim 8, 9 or 10 and developing the exposed light-sensitive layer.

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as in Example 2 and dried at 50°C for 5 seconds.

5	(b) Methyl methacrylate	50 wt. %	5
	(b) Styrene	10 "	
	(a) Ethyl acrylate	31 "	
10	(c) Ammonium methacrylate	9 "	10

As is described in U.S. Patent 3,740,367, this aqueous colloidal dispersion was prepared by adding aqueous ammonia to an aqueous dispersion of methyl methacrylate/styrene/ethyl acrylate/methacrylic acid copolymer to convert methacrylic acid to ammonium salt. The coated amount of the resin was 0.08 g/m², the number of liquid droplets 80 to 150 per mm², the width 20 to 150 μ, and the height about 2.5 to 6 μ.

Differences between the surface and the back side were examined as to vacuum-contact properties and prolongation or shortening of the vacuum-contacting time after rubbing the coating by a cloth pad. Thus, it was found that the difference in vacuum-contacting time between the surface and the back side was only about 10% after rubbing, and the plate obtained had good vacuum-contact properties. The resulting plate also showed good development properties, no stains, and good inking properties after exposure and development processing.

CLAIMS

1. A light-sensitive printing plate precursor comprising a support having thereon a light-sensitive layer, said light-sensitive layer having deposited thereon a layer of particles of a synthetic polymer which is soluble in a developer for the light-sensitive layer and which was deposited by spray-coating an aqueous dispersion or solution of the polymer and drying to remove water.
2. A light-sensitive printing plate precursor as claimed in Claim 1, wherein said resin is a copolymer of three monomer units selected from:
 - (a) alkyl acrylates having from 2 to 10 carbon atoms in the alkyl moiety and alkyl methacrylates having from 4 to 10 carbon atoms in the alkyl moiety;
 - (b) styrenes, acrylonitriles, methyl methacrylate and ethyl methacrylate; and
 - (c) acrylic acid, methacrylic acid, maleic acid, itaconic acid, alkali metal salts thereof and ammonium salts thereof.
3. A light-sensitive printing plate precursor as claimed in Claim 2, wherein said copolymer comprises from 10 to 70 wt. % of said units (a), from 20 to 80 wt. % of said units (b) and from 6 to 50 wt. % of said units (c).
4. A light-sensitive printing plate precursor as claimed in Claim 3, wherein said copolymer comprises from 15 to 50 wt. % of said units (a), from 40 to 70 wt. % of said units (b) and from 10 to 30 wt. % of said units (c).
5. A light-sensitive printing plate precursor as claimed in Claim 1, 2, 3 or 4, wherein the particles deposited on the surface of the light-sensitive layer are hemispheres from 1 to 20 microns in height, from 20 to 200 microns in width, and are present in a coverage of from 1 to 1,000 particles per square millimetre.
6. A light-sensitive printing plate precursor as claimed in Claim 5, wherein said particles are present in a coverage of from 5 to 500 particles per mm².
7. A light-sensitive printing plate precursor as claimed in Claim 2, substantially as hereinbefore described with reference to any of the Samples of the Examples.
8. A process of producing a light-sensitive printing plate precursor as claimed in any preceding claim, which comprises spray-coating an aqueous solution or liquid dispersion containing said polymer onto the light-sensitive layer of the precursor, and drying the aqueous liquid.
9. A process for producing a precursor as claimed in Claim 8, wherein said polymer comprises from 10 to 30 wt. % of said aqueous liquid.
10. A process of producing a light-sensitive printing plate precursor as claimed in Claim 8, substantially as hereinbefore described with reference to any of the Examples.
11. A process of preparing a printing plate which comprises imagewise exposing by vacuum contact a precursor as claimed in any of Claims 1 to 7 or made by a process as claimed in Claim 8, 9 or 10 and developing the exposed light-sensitive layer.