(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 May 2007 (24.05.2007)

PCT

(10) International Publication Number
WO 2007/057346 A2

(51) International Patent Classification: **Not classified**

(21) International Application Number: PCT/EP2006/068300

(22) International Filing Date: 9 November 2006 (09.11.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

05110951.0	18 November 2005 (18.11.2005)	EP
60/741,116	1 December 2005 (01.12.2005)	US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF MAKING A LITHOGRAPHIC PRINTING PLATE

(57) Abstract: A method of making a lithographic printing plate comprising the steps of : a) providing a lithographic printing plate precursor comprising (i) a support having a hydrophilic surface or which is provided with a hydrophilic layer, (ii) a coating on said support, comprising a photopolymerizable layer, and, optionally, an intermediate layer between the photopolymerizable layer and the support, wherein said photopolymerizable layer comprises a polymerizable compound, a polymerization initiator and a binder, b) image-wise exposing said coating in a plate setter, c) optionally, heating the precursor in a preheating unit, d) developing the precursor off -press in a gumming unit by treating the coating of the precursor with a gum solution, thereby removing the non-exposed areas of the photopolymerizable layer from the support , wherein said polymerization initiator comprises a solubilizing group capable of solubilizing the initiator in the gum solution.

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METHOD OF MAKING A LITHOGRAPHIC PRINTING PLATE

[DESCRIPTION]

FIELD OF THE INVENTION

The present invention relates to a method for making a lithographic printing plate whereby a negative-working photopolymer printing plate precursor, having a photopolymerizable layer which comprises a polymerization initiator having a solubilizing group capable of solubilizing the initiator in the gum solution, is image-wise exposed and treated with a gum solution in a gumming station, whereby the plate is developed and gummed in a single step.

BACKGROUND OF THE INVENTION

In lithographic printing, a so-called printing master such as a printing plate is mounted on a cylinder of the printing press. The master carries a lithographic image on its surface and a printed copy is obtained by applying ink to said image and then transferring the ink from the master onto a receiver material, which is typically paper. In conventional, so-called "wet" lithographic printing, ink as well as an aqueous fountain solution (also called dampening liquid) are supplied to the lithographic image which consists of oleophilic (or hydrophobic, i.e. ink-accepting, water-repelling) areas as well as hydrophilic (or oleophobic, i.e. water-accepting, ink-repelling) areas. In so-called "driographic" printing, the lithographic image consists of ink-accepting and ink-abhesive (ink-repelling) areas and during driographic printing, only ink is supplied to the master.

Printing masters are generally obtained by the so-called computer-to-film (CtF) method, wherein various pre-press steps such as typeface selection, scanning, color separation, screening, trapping, layout and imposition are accomplished digitally and each color selection is transferred to graphic arts film using an image-setter. After processing, the film can be used as a mask for the exposure of an imaging material called plate precursor and after plate processing, a printing plate is obtained which can be used as a master. Since about 1995, the so-called 'computer-to-plate' (CtP) method has gained a lot of interest. This method, also called 'direct-to-plate', bypasses the creation of film because the digital document is transferred directly to a printing plate precursor by means of a so-called plate-setter. A printing plate precursor for CtP is often called a digital plate.

Digital plates can roughly be divided in three categories : (i) silver plates, which work according to the silver salt diffusion transfer mechanism; (ii) photopolymer plates which contain a photopolymerizable composition that hardens upon exposure to light and (iii) thermal plates of which the imaging mechanism is triggered by heat or by light-to-heat conversion. Thermal plates are mainly sensitized for infrared lasers emitting at 830 nm or 1064 nm. Photopolymers can be sensitized for blue, green or red light (i.e. wavelength range between 450 and 750 nm), for violet light (i.e. wavelength range between 350 and 450 nm) or for infrared light(i.e. wavelength range between 750 and 1500 nm). Laser sources have been increasingly used to expose a printing plate precursor which is sensitized to a corresponding laser wavelength. Typically, an Ar laser (488 nm) or a FD-YAG laser (532 nm) can be used for exposing a visible light sensitized photopolymer plate. The wide-scale availability of low cost blue or violet laser diodes, originally developed for data storage by means of DVD, has enabled the production of plate-setters operating at shorter wavelength. More specifically, semiconductor lasers emitting from 350 to 450 nm have been realized using an InGaN material. An infrared laser diode emitting around 830 nm or a Nd-YAG laser emitting around 1060 nm can also be used.

Typically, a photopolymer plate precursor comprises a support, a photopolymerizable coating and an overcoat. The photopolymerizable coating comprises a polymerizable compound, a polymerization initiator and a binder, and the overcoat comprises usually a polyvinylalcohol binder to hinder the penetration of oxygen in the coating. Upon image-wise exposure, free radicals formed by the initiator are not quenched by the oxygen and can initiate crosslinking and/or polymerization of the polymerizable compound, resulting in hardening or curing of the exposed areas. The exposed precursor is usually processed in alkaline developer having a pH > 10, whereby the overcoat and the photopolymerizable coating at the non-exposed areas are solubilized in the developer solution. US2004/0131974 discloses a method for making such a lithographic printing plate whereby, after image-wise exposure, the overcoat is removed with water in a prewashing step, resulting in a reduction of the formation of sludge in the alkaline developing solution and whereby staining is prevented at the non-image portions.

Currently, most commercial lithographic plates require an additional gumming process after the exposed plates is developed and before it is put on the press, in order to protect the plate from contamination, e.g. by oxidation, fingerprints, fats, oil or dust, or from damaging, e.g. by scratches during handling of the plate. Such an additional gumming step is not convenient for the end-user, because it is a time consuming step and requires an additional gumming station.

WO 02/101 469 discloses a method of processing an imageable element useful as alkaline-developable lithographic printing plate precursor wherein the element is developed and gummed with an aqueous alkaline developing-gumming solution comprising a water-soluble polyhydroxy compound having a specific structure.

EP 1 342 568 discloses a method for making a heat-sensitive lithographic printing plate wherein the image-wise heated precursor, comprising a coating of hydrophobic thermoplastic polymer particles which coalescence on heating, is developed with a gum solution. A practical embodiment for this type of printing plates was introduced by Agfa under the tradename Azura.

In US 6,027,857, US 6,171,735, US 6,420,089, US 6,071,675, US 6,245,481, US 6,387,595, US 6,482,571, US 6,576,401 and US 6,548,222 a method is disclosed for preparing a lithographic printing plate wherein a photopolymer plate, after image-wise exposure, is mounted on a press and processed on-press by applying ink and fountain to remove the unexposed areas from the support. Also US 2003/16577 and

US 2004/13968 disclose a method wherein a plate comprising a photopolymerizable layer can be processed in an on-press processing with fountain and ink or with a non-alkaline aqueous developer. An adhesion promoting compound can also added to the printing plate precursor for improving the developability of the on-press processing and for improving the durability of the plate in the printing process. Typically, these compounds have an ethylenically unsaturated bond and a functional group capable of adsorbing to the surface of the support. Other compounds and polymers can be used as adhesion promoting compound. The compound can be present in the photopolymerisble layer or in an intermediate layer between the support and the photopolymerisable layer as disclosed in EP 851 299, EP 1 091 251, US 2004/214105, EP 1 491 356, US 2005/39620, EP 1 495 866, EP 1 500 498, EP 1 520 694 and EP 1 557 262.

A first problem associated with on-press processing of such photopolymer printing plates is the lack of daylight stability, i.e. the image is not stable before processing and, therefore, the exposed plate needs to be processed within a short time after the exposure. However, since on-press processing is not possible during a print job, the end-user must wait until the previous print job has been completed before the exposed plate can be mounted on the press and processed. As a result, the exposure of the plate for the next print job must be delayed until just before the completion of the previous print job, so as to avoid that the unprocessed plate is affected by the ambient light. Alternatively, the exposed plate must be kept under safe-light conditions, but this again reduces the ease of use and convenience that are normally associated with e.g. violet- and infrared-sensitive photopolymer plates.

A second problem left unsolved in the prior art about on-press processable photopolymer plates is the lack of a visible image between exposure and processing. Although it is known to add a colorant to the photosensitive coating, so as to obtain a visible image after removal of the non-exposed areas of the coating by the processing, this does not allow to distinguish an exposed plate from an unexposed plate immediately after the image-wise exposure, let alone to inspect the image quality after the exposure, because the visible image is only revealed after the on-press processing. Moreover, on-press processable plates normally do not contain a colorant because the on-press removal of the non-printing areas of the coating may cause contamination of the fountain solution and/or the ink and it may take an unacceptable number of printed copies before the contamination by said colorant has disappeared.

A third problem associated with on-press processing with fountain and ink is an insufficient clean-out of the non-exposed areas.

In the unpublished patent application PCT/EP 2005/052298, filed on 18 May 2005, a method for making a lithographic printing plate is disclosed wherein the image-wise exposed precursor is developed with a gumming solution.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for making a lithographic printing plate by means of a photopolymer plate precursor, which is perceived by the user as a method which does not require a processing step and wherein the exposed plate can be kept in ambient light during an unlimited time before being mounted on the press. This object is realized by the method defined in claim 1, having the specific feature that the precursor, which comprises a photopolymerizable layer having a polymerization initiator which comprises a solubilizing group capable of solubilizing the initiator in the gum solution, is image-wise exposed and is treated with a gum solution in a gumming station comprising at least one gumming unit whereby the plate is developed and gummed in a single step. Since the plate is developed and gummed, the lithographic image can no longer be affected by ambient daylight. On the contrary, further exposure to daylight would only increase the polymerization degree of the exposed areas, i.e. would strengthen rather than deteriorate the image. In addition, the present inventors have observed that the precursor, having a photopolymerizable layer with this initiator, exhibits a high sensitivity and a good clean-out and the formation of images of high quality.

It is a further object of the present invention to provide a method for making a lithographic printing plate by means of a photopolymer plate precursor, which is perceived by the user as a method which does not require a processing step and wherein the exposed plate can be kept in ambient light during an unlimited time before being mounted on the press, and wherein a visible image is provided before mounting the plate on the press. This object is realized by adding a colorant to the coating of the photopolymer plate. Since the non-printing areas of the coating are removed in the gumming units, there is no risk of contamination of the fountain solution or ink during the start of the print job.

Other specific embodiments of the invention are defined in the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there is provided a steps of:

a) providing a lithographic printing plate precursor comprising
  (i) a support having a hydrophilic surface or which is provided with a hydrophilic layer,
  (ii) a coating on said support, comprising a photopolymerizable layer, and, optionally, an intermediate layer between the photopolymerizable layer and the support,

wherein said photopolymerizable layer comprises a polymerizable compound, a polymerization initiator and a binder,

b) image-wise exposing said coating in a plate setter,

c) optionally, heating the precursor in a preheating unit,

d) developing the precursor off-press in a gumming unit by treating the coating of the precursor with a gum solution, thereby removing the non-exposed areas of the photopolymerizable layer from the support,

wherein said polymerization initiator comprises a solubilizing group capable of solubilizing the initiator in the gum solution.

In the present invention, the printing plate precursor is image-wise exposed off-press by means of a plate setter, i.e. a laser exposure apparatus suitable for image-wise exposing a precursor. The precursor used in the method of the present invention is negative-working whereby at the exposed areas the coating is hardened. Here, "hardened" means that the coating becomes insoluble or non-dispersible for the gum solution and may be achieved through polymerization and/or crosslinking of the coating.

After imaging, the plate precursor is optionally heated, hereinafter also referred to as "pre-heat" or "preheat", to enhance or to speed-up the polymerization and/or crosslinking reaction. This preheat step is carried out at a temperature of preferably 80°C to 150°C and during a dwell time of preferably 5 seconds to 1 minute. The preheating unit is preferably provided with heating elements such as IR-lamps, UV-lamps, heated air, a heated metal roll, etc.

Subsequently the plate precursor is treated, i.e. developed and gummed, in a gumming station which comprises at least one gumming unit, preferably two gumming units, namely a first and a second gumming unit. In the gumming unit(s), a gum solution is applied to the coating of the precursor whereby the non-exposed areas of the photopolymerizable layer is removed from the support and whereby the hydrophilic surface of the support at the non-exposed areas are protected by adsorption of gum in a single step. The development with a gum solution has the additional benefit that, due to the remaining gum on the plate at the non-exposed areas, an additional gumming step is not required to protect the surface of the support at the non-exposed areas. As a result, the precursor is processed and gummed in one single step and the obtained lithographic image on the plate will not be affected by ambient daylight or by contamination.

The method of the present invention has the additional advantage that the precursor, having a photopolymerizable layer with this initiator, exhibits a high sensitivity and a good clean-out and the formation of images of high quality.

In the printing step, the plate is mounted on the plate cylinder of the printing press and the printing process is started.

The gum solution

A gum solution is typically an aqueous liquid which comprises one or more surface protective compounds that are capable of protecting the lithographic image of a printing plate against contamination, e.g. by oxidation, fingerprints, fats, oils or dust, or damaging, e.g. by scratches during handling of the plate. Suitable examples of such compounds are film-forming hydrophilic polymers or surfactants. The layer that remains on the plate after treatment with the gum solution preferably comprises between 0.005 and 20 g/m^2 of the surface protective compound, more preferably between 0.010 and 10 g/m^2, most preferably between 0.020 and 5 g/m^2.

In the present description, all concentrations of compounds present in the gum solution are expressed as percentage by weight (wt.% or % w/w) relative to the ready-to-use gum solution, unless otherwise indicated. A gum solution may be normally supplied as a concentrated solution which is diluted by the end user with water to a ready-to-use gum solution before use according to the instructions of the supplier, usually 1 part of the gum is diluted with 1 part to 10 parts of water.

Preferred polymers for use as protective compound in the gum solution are gum arabic, pullulan, cellulose derivatives such as carboxymethylcellulose, carboxyethylcellulose or methylcellulose, (cyclo)dextrin, poly(vinyl alcohol), poly(vinyl pyrrolidone), polysaccharide, homo- and copolymers of acrylic acid, methacrylic acid or acrylamide, a copolymer of vinyl methyl ether and maleic anhydride, a copolymer of vinyl acetate and maleic anhydride or a copolymer of styrene and maleic anhydride. Highly preferred polymers are homo- or copolymers of monomers containing carboxylic, sulfonic or phosphonic groups or the salts thereof, e.g. (meth)acrylic acid, vinyl acetate, styrene sulfonic acid, vinyl sulfonic acid, vinyl phosphonic acid or acrylamidopropane sulfonic acid.

Examples of surfactants for use as surface protective agent include anionic or nonionic surfactants. The gum solution may also comprise one or more of the above hydrophilic polymers as surface protective agent and, in addition, one or more surfactants to improve the surface properties of the coated layer. The surface tension of the gum solution is preferably from 20 to 50 mN/m.

The gum solution comprises preferably an anionic surfactant, more preferably an anionic surfactant whereof the anionic group is a sulphonic acid group.

Examples of the anionic surfactant include aliphates, abietates, hydroxyalkanesulfonates, alkanesulfonates, dialkylsulfosuccinates, straight-chain alkylbenzenesulfonates, branched alkylbenzenesulfonates, alkylnaphthalenesulfonates, alkylphenoxypolyoxyethylenepropylsulfonates, salts of polyoxyethylene alkylsulfophenyl ethers, sodium N-methyl-N-oleyltaurates, monoamide disodium N-alkylsulfosuccinates, petroleum sulfonates, sulfated castor oil, sulfated tallow oil, salts of sulfuric esters of aliphatic alkylesters, salts of alkylsulfuric esters, sulfuric esters of polyoxyethylenealkylethers, salts of sulfuric esters of aliphatic monoglycerides, salts of sulfuric esters of polyoxyethylenealkylphenylethers, salts of sulfuric esters of polyoxyethylenestyrylphenylethers, salts of alkylphosphoric esters, salts of phosphoric esters of polyox-yethylenealkylethers, salts of phosphoric esters of polyoxyethylenealkylphenylethers, partially saponified compounds of styrenemaleic anhydride copolymers, partially saponified compounds of olefin-maleic anhydride copolymers, and naphthalenesulfonateformalin condensates. Particularly preferred among these anionic surfactants are dialkylsulfosuccinates, salts of alkylsulfuric esters and alkylnaphthalenesulfonates.

Specific examples of suitable anionic surfactants include sodium dodecylphenoxybenzene disulfonate, the sodium salt of alkylated naphthalenesulfonate, disodium methylene-dinaphtalene-disulfonate, sodium dodecyl-benzenesulfonate, sulfonated alkyl-diphenyloxide, ammonium or potassium perfluoroalkylsulfonate and sodium dioctyl-sulfosuccinate.

Suitable examples of the nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkyl aryl ethers wherein the aryl group may be a phenyl group, a naphthyl group or an aromatic heterocyclic group, polyoxyethylene polystyryl phenyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, polyoxyethylene polyoxypropylene block polymers, partial esters of glycerinaliphatic acids, partial esters of sorbitanaliphatic acid, partial esters of pentaerythritolaliphatic acid, propyleneglycolmonoaliphatic esters, partial esters of sucrosealiphatic acids, partial esters of polyoxyethylenesorbitanaliphatic acid, partial esters of polyoxyethylenesorbitolaliphatic acids, polyethyleneglycolaliphatic esters, partial esters of poly-glycerinaliphatic acids, polyoxyethylenated castor oils, partial esters of polyoxyethyleneglycerinaliphatic acids, aliphatic diethanolamides, N,N-bis-2-hydroxyalkylamines, polyoxyethylene alkylamines, triethanolaminealiphatic esters, and trialkylamine oxides. Particularly preferred among these nonionic surfactants are polyoxyethylene alkylphenyl ethers, polyoxyethylene alkylnaphthyl ethers and poloxyethylene-polyoxypropylene block polymers. Further, fluorinic and siliconic anionic and nonionic surfactants may be similarly used.

Two or more of the above surfactants may be used in combination. For example, a combination of two or more different anionic surfactants or a combination of an anionic surfactant and a nonionic surfactant may be preferred. The amount of such a surfactant is not specifically limited but is preferably from 0.01 to 30 wt.%, more preferably from 0.05 to 20 wt.%.

According to the present invention the gum solution has a pH-value preferably between 3 and 9, more preferably between 4.5 and 8.5, most preferably between 5 and 7. The pH of the gum solution is usually adjusted with a mineral acid, an organic acid or an inorganic salt in an amount of from 0.01 to 15 wt.%, preferably from 0.02 to 10 wt.%. Examples of the mineral acids include nitric acid, sulfuric acid, phosphoric acid and metaphosphoric acid. Especially organic acids are used as pH control agents and as desensitizing agents. Examples of the organic acids include carboxylic acids, sulfonic acids, phosphonic acids or salts thereof, e.g. succinates, phosphates, phosphonates, sulfates and sulfonates. Specific examples of the organic acid include citric acid, acetic acid, oxalic acid, malonic acid, p-toluenesulfonic acid, tartaric acid, malic acid, lactic acid, levulinic acid, phytic acid and organic phosphonic acid.

The gum solution further comprises preferably an inorganic salt. Examples of the inorganic salt include magnesium nitrate, monobasic sodium phosphate, dibasic sodium phosphate, nickel sulfate, sodium hexametaphosphate and sodium tripolyphosphate. An alkali-metal dihydrogen phosphate such as KH_2PO_4 or NaH_2PO_4 is most preferred. Other inorganic salts can be used as corrosion inhibiting agents, e.g. magnesium sulfate or zinc nitrate. The mineral acid, organic acid or inorganic salt may be used singly or in combination with one or more thereof.

In accordance with another embodiment of the present invention, the gum solution as developer in the processing of the plate comprises preferably a mixture of an anionic surfactant and an inorganic salt. In this mixture the anionic surfactant is preferably an anionic surfactant with a sulphonic acid group, more preferably an alkali-metal salt of a mono- or di-alkyl substituted diphenylether-sulphonic acid, and the inorganic salt is preferably a mono or dibasic phosphate salt, more preferably an alkali-metal dihydrogen phosphate, most preferably KH_2PO_4 or NaH_2PO_4.

In accordance with another embodiment of the present invention, the gum solution comprising a mixture of an anionic surfactant and an inorganic salt has preferably a pH-value between 3 and 9, more preferably between 4 and 8, most preferably between 5 and 7.

Besides the foregoing components, a wetting agent such as ethylene glycol, propylene glycol, triethylene glycol, butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, glycerin, trimethylol propane and diglycerin may also be present in the gum solution. The wetting agent may be used singly or in combination with one or more thereof. In general, the foregoing wetting agent is preferably used in an amount of from 1 to 25 wt.%.

Further, a chelate compound may be present in the gum solution. Calcium ion and other impurities contained in the diluting water can have adverse effects on printing and thus cause the contamination of printed matter. This problem can be eliminated by adding a chelate compound to the diluting water. Preferred examples of such a chelate compound include organic phosphonic acids or phosphonoalkanetricarboxylic acids. Specific examples are potassium or sodium salts of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic acid, 1-hydroxyethane-1,1-diphosphonic acid and aminotri(methylenephosphonic acid). Besides these sodium or potassium salts of these chelating agents, organic amine salts are useful. The preferred amount of such a chelating agent to be added is from 0.001 to 5 wt.% relative to the gum solution in diluted form.

Further, an antiseptic and an anti-foaming agent may be present in the gum solution. Examples of such an antiseptic include phenol, derivatives thereof, formalin, imidazole derivatives, sodium dehydroacetate, 4-isothiazoline-3-one derivatives, benzoisothiazoline-3-one, benztriazole derivatives, amidineguanidine derivatives, quaternary ammonium salts, pyridine derivatives, quinoline derivatives, guanidine derivatives, diazine, triazole derivatives, oxazole and oxazine derivatives. The preferred amount of such an antiseptic to be added is such that it can exert a stable effect on bacteria, fungi, yeast or the like. Though depending on the kind of bacteria, fungi and yeast, it is preferably from 0.01 to 4 wt.% relative to the gum solution in diluted form. Further, preferably, two or more antiseptics may be used in combination to exert an aseptic effect on various fungi and bacteria. The anti-foaming agent is preferably silicone anti-foaming agents. Among these anti-foaming agents, either an emulsion dispersion type or solubilized type anti-foaming agent may be used. The proper amount of such an anti-foaming agent to be added is from 0.001 to 1.0 wt.% relative to the gum solution in diluted form.

Besides the foregoing components, an ink receptivity agent may be present in the gum solution if desired. Examples of such an ink receptivity agent include turpentine oil, xylene, toluene, low heptane, solvent naphtha, kerosine, mineral spirit, hydrocarbons such as petroleum fraction having a boiling point of about 120°C to about 250°C, diester phthalates (e.g., dibutyl phthalate, diheptyl phthalate, di-n-octyl phthalate, di(2-ethylhexyl) phthalate, dinonyl phthalate, didecyl phthalate, dilauryl phthalate, butylbenzyl phthalate), aliphatic dibasic esters (e.g., dioctyl adipate, butylglycol adipate, dioctyl azelate, dibutyl sebacate, di(2-ethylhexyl) sebacate dioctyl sebacate), epoxidated triglycerides (e.g., epoxy soyabean oil), ester phosphates (e.g., tricresyl phosphate, trioctyl phosphate, trischloroethyl phosphate) and plasticizers having a solidification point of 15°C or less and a boiling point of 300°C or more at one atmospheric pressure such as esters of benzoates (e.g., benzyl benzoate). Examples of other solvents which can be used in combination with these solvents include ketones (e.g., cyclohexanone), halogenated hydrocarbons (e.g., ethylene dichloride), ethylene glycol ethers (e.g., ethylene glycol monomethyl ether, ethylene glycol monophenyl ether, ethylene glycol monobutyl ether), aliphatic acids (e.g., caproic acid, enathic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, heptadecylic acid, stearic acid, nonadecanic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, heptacosanoic acid, montanic acid, melissic acid, lacceric acid, isovaleric acid) and unsaturated aliphatic acids (e.g., acrylic acid, crotonic acid, isocrotonic acid, undecyclic acid, oleic acid, elaidic acid, cetoleic acid, erucic acid, butecidic acid, sorbic acid, linoleic acid, linolenic acid, arachidonic acid, propiolic acid, stearolic acid, clupanodonic acid, tariric acid, licanic acid). Preferably, it is an aliphatic acid which is liquid at a temperature of 50°C, more preferably has from 5 to 25 carbon atoms, most preferably has from 8 to 21 carbon atoms. The ink receptivity agent may be used singly or in combination with one or more thereof. The ink receptivity agent is preferably used in an amount of from 0.01 to 10 wt.%, more preferably from 0.05 to 5 wt.%. The foregoing ink receptivity agent may be present as an oil-in-water emulsion or may be solubilized with the aid of a solubilizing agent.

The viscosity of the gum solution can be adjusted to a value of e.g. between 1.7 and 5 mPa.s, by adding viscosity increasing compounds, such as poly(ethylene oxide) or polyvinylalcohol, e.g. having a molecular weight between 10^4 and 10^7. Such compounds can be present in a concentration of 0.01 to 10 g/l.

A baking gum has a similar composition as described above, with the additional preference towards compounds that do not evaporate at the usual bake temperatures. Baking gum solutions or baking gumming solutions can be aqueous solutions of sodium dodecyl phenoxy benzene disulphonate, alkylated naphthalene sulphonic acid, sulphonated alkyl diphenyl oxide, methylene dinaphtalene sulphonic acid, etc. Other gumming solutions contain a hydrophilic polymer component and an organic acid component. Still other baking gumming solutions contains the potassium salt of the hydroxyethylidene diphosphonic acid. Still other baking gumming solutions contain a sulphosuccinamate compound and phosphoric acid.

The contact angle between the baking gum solution and the plate is preferably lowered by adding at least one surfactant. Preferred surfactants are non-ionic polyglycols and perfluorated aliphatic polyester acrylates.

The viscosity of the baking gum solution is brought at a value of 1.7 cP to 5 cP, more preferably 2 to 4.5 cP by adding at least one viscosity increasing compound. Preferred viscosity increasing compounds are hydrophilic polymer compounds, more preferably polyethylene oxides. Said polyethylene oxides have preferably a molecular weight between 100,000 and 10,000,000, more preferably between 500,000 and 5,000,000. They are preferably used in a concentration of 0.01 to 10 g/l, more preferably of 0.05 to 5 g/l.

In another embodiment the baking gumming solutions comprises (a) water, (b) at least one hydrophilic polymer and (c) at least one component selected from the group consisting of water soluble organic acids comprising at least two acid functions and being selected form the group consisting of a benzene carboxylic acid, a benzene sulphonic acid, a benzene phosphonic acid, an alkane phosphonic acid and water soluble salts thereof. The mentioned compounds (b) and (c) which are dissolved in the aqueous solution in accordance with the present invention are such that they do not evaporate at the customary baking temperatures. The protective layer which is formed remains water-soluble, even after baking, and can be readily removed without damaging the printing plate.

Component (b) comprises in particular the following hydrophilic polymers : N-polyvinyl-pyrrolidone, polyvinylmethylether, copolymers containing ethylene units and maleic anhydride units, homopolymers or copolymers containing vinyl phosphonic acid units, vinyl methyl phosphinic acid units and/or acrylic acid units and/or a polyalkylene glycol, such as polyethylene glycol.

Component (c) comprises in particular : benzene disulphonic acids, benzene polycarboxylic acids having from 3 to 6 carboxyl groups, alkane diphosphonic acids which having from 1 to 3 carbon atoms in the alkane group, carboxyl group containing alkane diphosphonic acids which have from 5 to 9 carbon atoms in the alkane group, and/or one of the water-soluble salts of these acids (preferably alkali metal salts or ammonium salts). Specific examples of component (c) include benzene-1,3-disulphonic acid, benzene-1,2,4-tricarboxylic acid (trimellitic acid), benzene 1,2,4,5-tetracarboxylic acid (pyromellitic acid), benzene hexacarboxylic adid (mellitic acid), methane diphosphonic acid (diphosphono methane), 4,4-diphosphono-heptane-1,7-dioic acid (3,3-diphosphone-pimeic acid), and the sodium salts of these acids. In other embodiments the baking gumming solution for use can additionally contain hydroxy-polycarboxylic acids, such as citric acid and/or the salts thereof, water soluble alkanediols having at least 4 carbon atoms, such as hexanediol-(1,6) and surfactants (preferably anionic or non-ionic surfactants) such as alkyl aryl sulphonates, alkyl phenol ether sulphonates and a natural surfactant (e.g. Saponin). Specific examples of suitable baking gum solutions, ingredients and concentrations thereof, can be found in e.g. EP-A 222 297, EP-A 1 025 992, DE-A 2 626 473 and US 4,786,581.

The support

A particularly preferred lithographic support is an electrochemically grained and anodized aluminum support. Graining an anodizing of aluminum supports is well known. The acid used for graining can be e.g. nitric acid or sulfuric acid. The acid used for graining preferably comprises hydrogen chloride. Also mixtures of e.g. hydrogen chloride and acetic acid can be used. The relation between electrochemical graining and anodizing parameters such as electrode voltage, nature and concentration of the acid electrolyte or power consumption on the one hand and the obtained lithographic quality in terms of Ra and anodic weight (g/m^2 of Al_2O_3 formed on the aluminum surface) on the other hand is well known. More details about the relation between various production parameters and Ra or anodic weight can be found in e.g. the article "Management of Change in the Aluminium Printing Industry" by F. R. Mayers, published in the ATB Metallurgie Journal, volume 42 nr. 1-2 (2002) pag. 69.

The anodized aluminum support may be subject to a so-called post-anodic treatment to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with a sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or may be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulfonic acid, polyvinylbenzenesulfonic acid, sulfuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulfonated aliphatic aldehyde.

Another useful post-anodic treatment may be carried out with a solution of polyacrylic acid or a polymer comprising at least 30 mol% of acrylic acid monomeric units, e.g. GLASCOL E15, a polyacrylic acid, commercially available from ALLIED COLLOIDS.

The grained and anodized aluminum support may be a sheet-like material such as a plate or it may be a cylindrical element such as a sleeve which can be slid around a print cylinder of a printing press.

The support can also be a flexible support, which may be provided with a hydrophilic layer, hereinafter called 'base layer'. The flexible support is e.g. paper, plastic film or aluminum. Preferred examples of plastic film are polyethylene terephthalate film, polyethylene naphthalate film, cellulose acetate film, polystyrene film, polycarbonate film, etc. The plastic film support may be opaque or transparent.

The base layer is preferably a cross-linked hydrophilic layer obtained from a hydrophilic binder cross-linked with a hardening agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolyzed tetra-alkylorthosilicate. The latter is particularly preferred. The thickness of the hydrophilic base layer may vary in the range of 0.2 to 25 µm and is preferably 1 to 10 µm. More details of preferred embodiments of the base layer can be found in e.g. EP-A 1 025 992.

The coating

The coating on the support comprises at least one layer comprising a photopolymerizable composition, said layer hereinafter also referred to as "photopolymerizable layer". Said coating may further comprise an oxygen-barrier layer, which comprises a water-soluble or water-swellable polymer, on said photopolymerizable layer, said barrier layer hereinafter also referred to as "toplayer" or "overcoat" or "overcoat layer". Said coating may further comprise an intermediate layer between the photopolymerizable layer and the support.

The thickness of the coating preferably ranges between 0.4 and 10 g/m^2, more preferably between 0.5 and 5 g/m^2, most preferably between 0.6 and 3 g/m^2.

The photopolymeriazble layer comprises (i) a polymerizable compound, (ii) a polymerization initiator comprising a solubilizing group capable of solubilizing the initiator in the gum solution and capable of hardening said polymerizable compound in the exposed areas and (iii) a binder. The photopolymerizable layer may further comprise an adhesion promoting compound.

The photopolymerizable layer has a coating thickness preferably ranging between 0.4 and 5.0 g/m^2, more preferably between 0.5 and 3.0 g/m^2, most preferably between 0.6 and 2.2 g/m^2.

The adhesion promoting compound

The adhesion promoting compound is a compound capable of interacting with said support, preferably a compound having an addition-polymerizable ethylenically unsaturated bond and a functional group capable of interacting with the support, more preferably a functional group capable of interacting with a grained and anodised aluminium support. Under "interacting" is understood each type of physical and/or chemical reaction or process whereby, between the functional group and the support, a bond is formed which can be a covalent bond, an ionic bond, a complex bond, a coordinate bond or a hydrogen-bridge bond, and which can be formed by an adsorption process, a chemical reaction, an acid-base reaction, a complex-forming reaction or a reaction of a chelating group or a ligand. The adhesion promoting compound may be present in the photopolymerizable layer and/or in an intermediate layer between the photopolymerizable layer and the support.

The adhesion promoting compound may be selected from at least one of the low molecular weight compounds or polymeric compounds as described in EP-A 851 299 from lines 22 on page 3 to line 1 on page 4, EP-A 1 500 498 from paragraph [0023] on page 7 to paragraph [0052] on page 20, EP-A 1 495 866 paragraph [0030] on page 5 to paragraph [0049] on page 11, EP-A 1 091 251 from paragraph [0014] on page 3 to paragraph [0018] on page 20, and EP-A 1 520 694 from paragraph [0023] on page 6 to paragraph [0060] on page 19. Preferred compounds are those compounds which comprise a phosphate or phosphonate group as functional group capable of adsorbing on the aluminium support and which comprise an addition-polymerizable ethylenic double bond reactive group, especially those described in EP-A 851 299 from lines 22 on page 3 to line 1 on page 4 and EP-A 1 500 498 from paragraph [0023] on page 7 to paragraph [0052] on page 20. Also preferred are those compounds which comprises a tri-alkyl-oxy silane groups, hereinafter also referred to as "trialkoxy silane" groups, wherein the alkyl is preferably methyl or ethyl, or wherein the trialkyloxy silane groups are at least partially hydrolysed to silanol groups, as functional group capable of adsorbing on the support, especially silane coupling agents having an addition-polymerizable ethylenic double bond reactive group as described in EP-A 1 557 262 paragraph [0279] on page 49 and EP-A 1 495 866 paragraph [0030] on page 5 to paragraph [0049] on page 11.

The adhesion promoting compound may be present in the photopolymerizable layer in an amount ranging between 1 and 50 wt%, preferably between 3 and 30 wt%, more preferably between 5 and 20 wt% of the non-volatile components of the composition.

The adhesion promoting compound may be present in the intermediate layer in an amount of at least 50 wt%, preferably at least 80 wt%, more preferably at least 90 wt%, most preferably 100 wt% of the non-volatile components of the composition.

The optionally intermediate layer has a coating thickness preferably ranging between 0.001 and 1.5 g/m^2, more preferably between 0.003 and 1.0 g/m^2, most preferably between 0.005 and 0.7 g/m^2.

The polymerization initiator

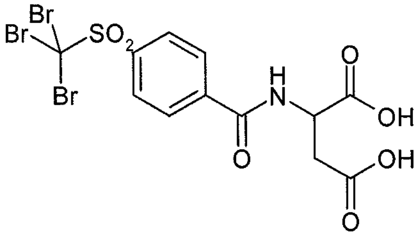
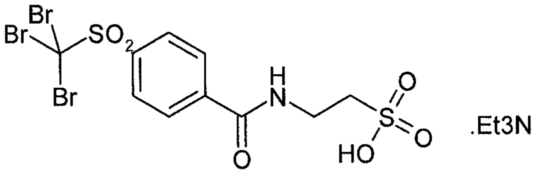
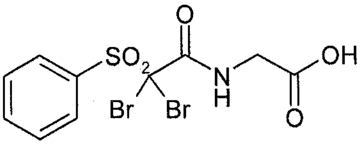
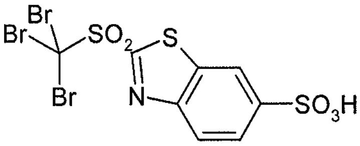
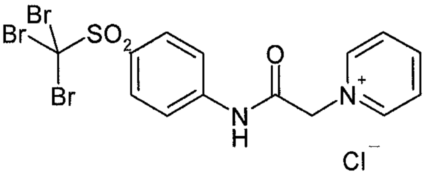
According to the present invention, the photopolymerizable layer comprises a polymerization initiator which comprises a solubilizing group capable of solubilizing the initiator in the gum solution and which is capable of hardening said polymerizable compound in the exposed areas. Solubilizing means that the initiator can be dissolved in the gum solution or can be dispersed in the gum solution.

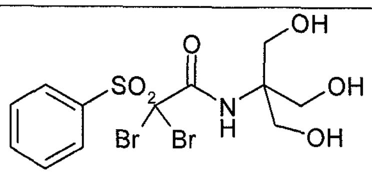
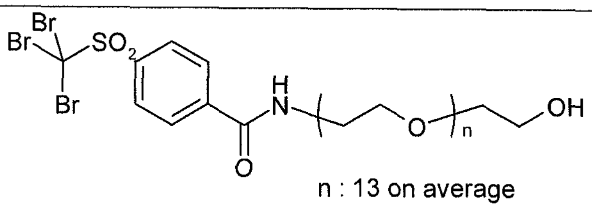
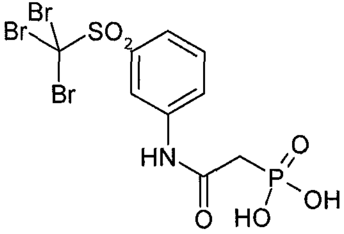
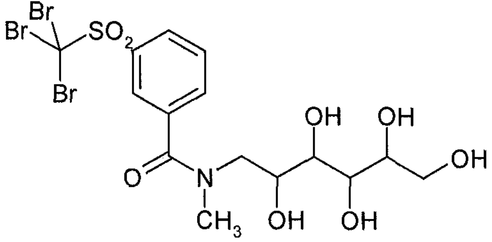
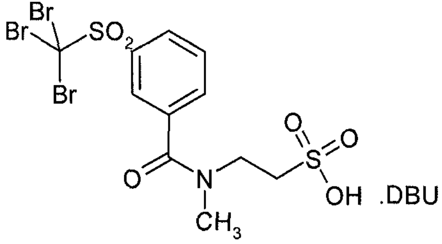
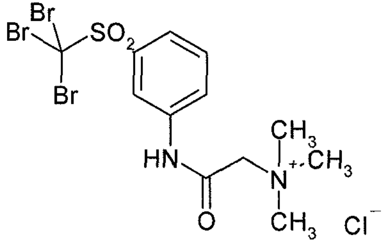
According to a preferred embodiment, said initiator comprises at least one of the following compounds selected from an alfa-di- or tri-bromo alkyl sulphone, a tri-bromo acetamide, a di-aryl iodonium, a di-aryl alkyl sulphonium, a tri-aryl sulphonium, a tri-bromo aryl ketone, a tri-bromo heteroaryl ketone or a tri-halo methyl triazine, wherein each of these compounds further comprises a solubilizing group capable of solubilizing the initiator in the gum solution. Di- and tribromoalkylsulfones which comprises a solubilizing group capable of solubilizing the initiator in the gum solution, are a particularly preferred initiators. According to another preferred embodiment of the present invention, said initiator comprises a hexa-aryl bisimidazol which comprises a solubilizing group capable of solubilizing the initiator in the gum solution.

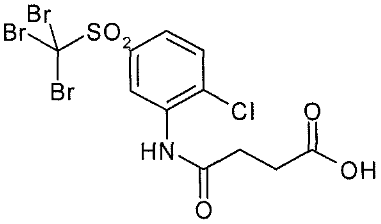
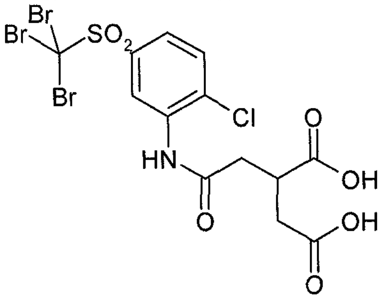
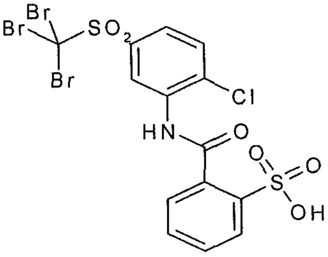
According to the present invention, the solubilizing groups can be an anionic group, a cationic group or a polyalkyleneoxyde group. The solublizing group is prefereably one of the following groups: a carboxylic acid or a salt thereof, a sulfonic acid or a salt thereof, a sulfuric acid hemi ester or a salt thereof, a phosphonic acid or a salt thereof, a phosphoric acid derivative or a salt thereof, an acyl sulfonamide or a salt thereof, a phenol, an ammonium salt, a sulfonium salt, a phosphonium salt, an oligo ethylene oxide, an hydroxylgroup and an oligohydroxy group (i.e. an alkyl or aryl group substituted by two or more hydroxyl groups); particularly preferred are a carboxylic acid group or a salt thereof, or a sulfonic acid group or a salt thereof. The initiator of the present invention comprises at least one of said solubilizing group, optionally bond to the initiator by a linking group. The initiator of the present invention may also comprising two or more of said solubilizing groups.

Specific examples of initiators according to the present invention are given below, without being limited to those.

di- and tribromoalkyl sulfones :

BS-1	
BS-2	
BS-3	
BS-4	
BS-5	

BS-6	
BS-7	 n : 13 on average
BS-8	
BS-9	
BS-10	
BS-11	

BS-12	
BS-13	
BS-14	

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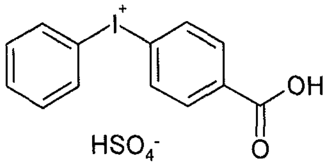
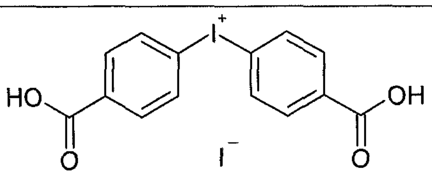
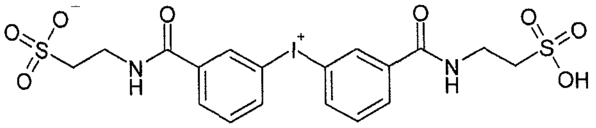
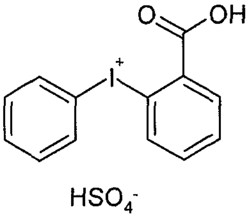
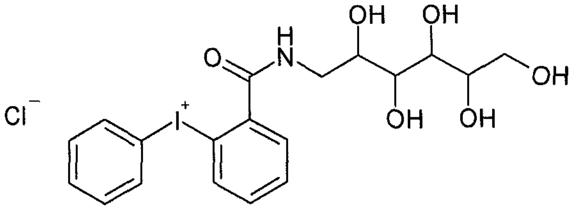
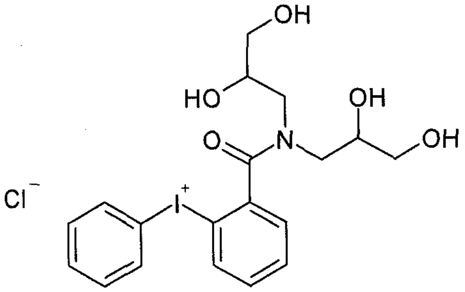
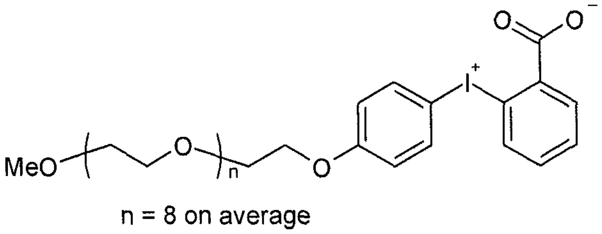
Iodonium-1	
Iodonium-2	

Iodonium-3	
Iodonium-4	
Iodonium-5	
Iodonium-6	
Iodonium-7	

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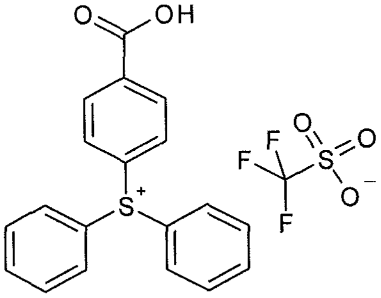
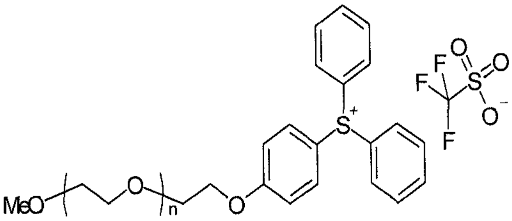
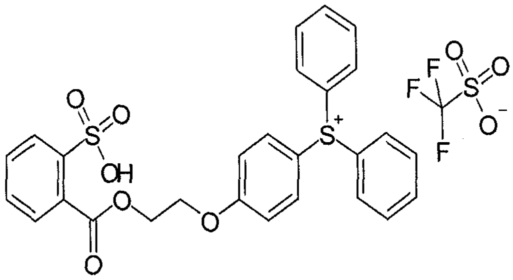
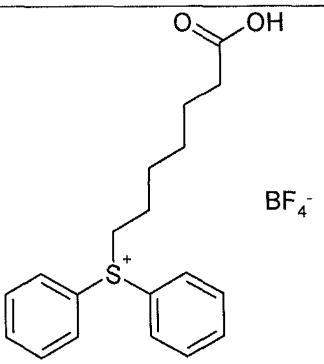
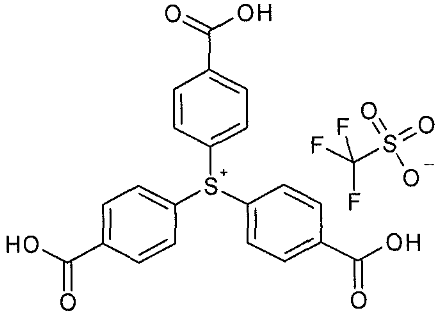
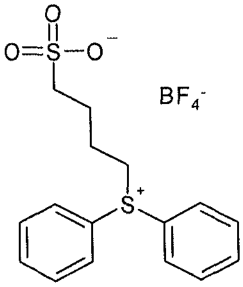
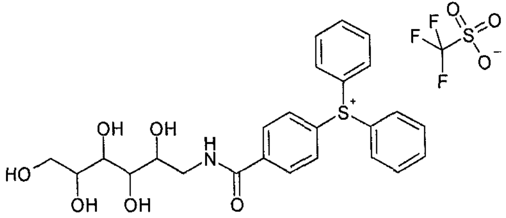
Sulf-1	
Sulf-2	 n = 8 on average
Sulf-3	
Sulf-4	

Sulf-5	
Sulf-6	
Sulf-7	

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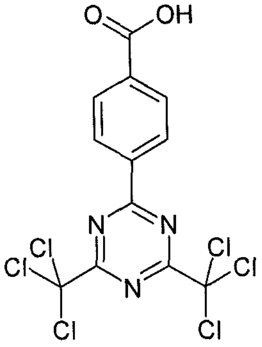
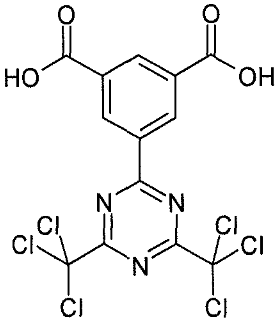
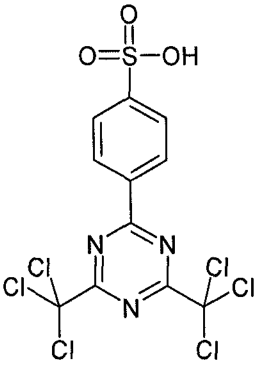
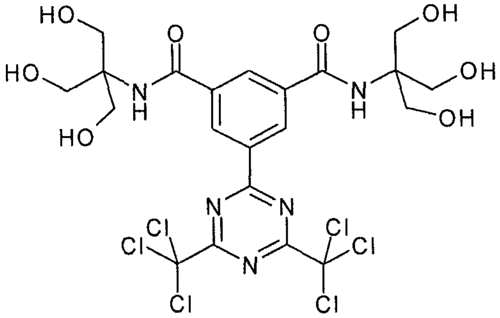
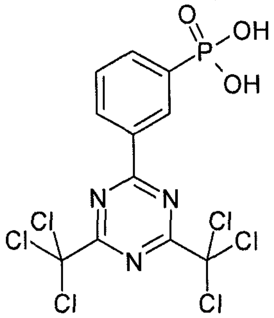
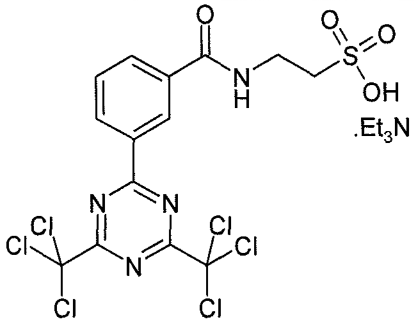
Tria-1	

Tria-2	
Tria-3	
Tria-4	
Tria-5	

Tria-6	

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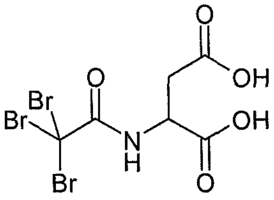
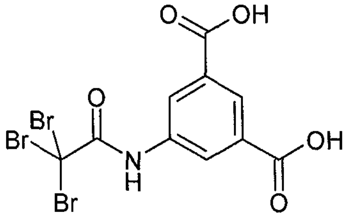
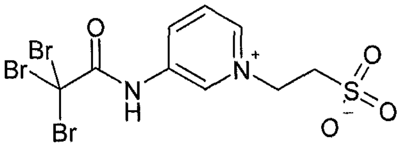
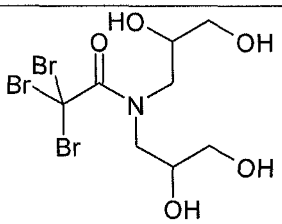
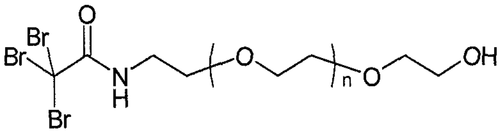
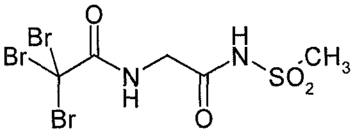
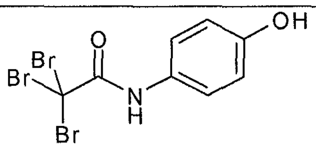
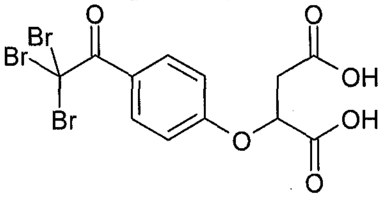
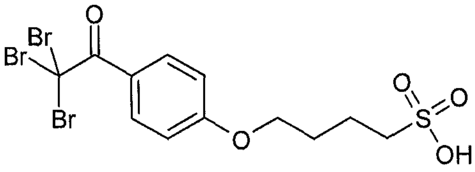
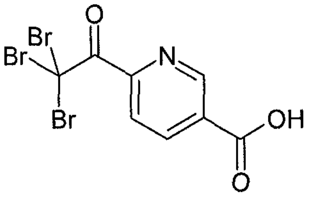
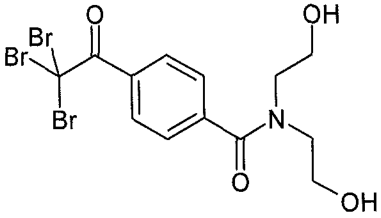
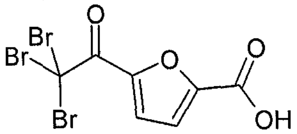
Acet-1	
Acet-2	
Acet-3	
Acet-4	

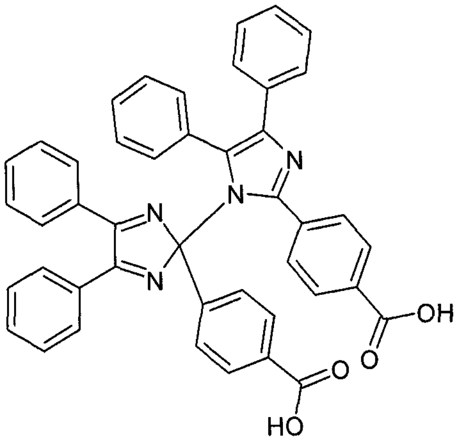
Acet-5	 n : 12 on average
Acet-6	
Acet-7	

Tribromomethyl aryl and heteroaryl ketones :

TBAK-1	
TBAK-2	
TBAK-3	

TBAK-4	
TBAK-5	

A hexa-aryl bisimidazol:

HABI-1	

According to another preferred embodiment of the present invention, the photopolymerizable layer further comprises an IR-dye, capable of interacting with said initiator to form initiating radicals by exposure to IR-light or heat. Initiating radicals means radicals which are capable of starting the crosslinking or polymerization reaction resulting in a hardening of the coating at the exposed areas. According to another preferred embodiment of the present invention, the photopolymerizable layer, comprising a hexa-aryl bisimidazol initiator with said solubilizing group, further comprises a violet sensitizing dye capable of interacting with said initiator to from initiating radicals by exposure to violet light.

The polymerizable compound and other polymerization initiators

The photopolymerizable layer may also comprise a polymerizable compound and optionally another polymerization initiator.

The polymerizable monomer or oligomer may be a monomer or oligomer comprising at least one epoxy or vinyl ether functional group and said initiator is a Bronsted acid generator capable of generating free acid, optionally in the presence of a sensitizer, upon exposure, hereinafter said initiator also referred to as "cationic photoinitiator" or "cationic initiator".

Suitable polyfunctional epoxy monomers include, for example, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohex-ane carboxylate, bis-(3,4 -epoxycyclohexymethyl) adipate, difunctional bisphenol Aepichlorohydrin epoxy resin and multifunctional epichlorohydrinitetraphenylol ethane epoxy resin.

Suitable cationic photoinitiators include, for example, triarylsulfonium hexafluoroantimonate, triarylsulfonium hexafluorophosphate, diaryliodonium hexafluoroantimonate, and haloalkyl substituted s-triazine. It is noted that most cationic initiators are also free radical initiators because, in addition to generating Bronsted acid, they also generate free radicals during photo or thermal decomposition.

The polymerizable monomer or oligomer may be a ethylenically unsaturated compound, having at least one terminal ethylenic group, hereinafter also referred to as "free-radical polymerizable monomer", and said initiator may be a compound, capable of generating free radical, optionally in the presence of a sensitizer, upon exposure, hereinafter said initiator also referred to as "free radical initiator".

Suitable free-radical polymerizable monomers may include, for example, multifunctional (meth)acrylate monomers (such as (meth)acrylate esters of ethylene glycol, trimethylolpropane, pentaerythritol, ethoxylated ethylene glycol and ethoxylated trimethylolpropane, multifunctional urethanated (meth)acrylate, and epoxylated (meth)acrylate), and oligomeric amine diacrylates. The (meth)acrylic monomers may also have other double bond or epoxide group, in addition to (meth)acrylate group. The (meth)acrylate monomers may also contain an acidic (such as carboxylic acid) or basic (such as amine) functionality.

Any free radical initiator capable of generating free radical directly or in the presence of a sensitizer upon exposure can be used as a free radical initiator of this invention. Suitable free-radical initiators include, for example, the derivatives of acetophenone (such as 2,2-dimethoxy-2-phenylacetophenone, and 2-methyl-l-[4-(methylthio) phenyl-2-morpholino propan-l-one); benzophenone; benzil; ketocoumarin (such as 3-benzoyl-7-methoxy coumarin and 7-methoxy coumarin); xanthone; thioxanthone; benzoin or an alkyl-substituted anthraquinone; onium salts (such as diaryliodonium hexafluoroantimonate, diaryliodonium triflate, (4-(2-hydroxytetradecyl-oxy)-phenyl) phenyliodonium hexafluoroantimonate, triarylsulfonium hexafluorophosphate, triarylsulfonium p-toluenesulfonate, (3-phenylpropan-2-onyl) triaryl phosphonium hexafluoroantimonate, and N-ethoxy(2-methyl)pyridinium hexafluorophosphate, and onium salts as described in U.S. Pat.Nos. 5,955,238,6,037,098, and 5,629,354); borate salts (such as tetrabutylammonium triphenyl(n-butyl)borate, tetraethylammonium triphenyl(n-butyl)borate, diphenyliodonium tetraphenylborate, and triphenylsulfonium triphenyl(n-butyl)borate, and borate salts as described in U.S. Pat. Nos. 6,232,038 and 6,218,076,); haloalkyl substituted s-triazines (such as 2,4-bis(trichloromethyl)-6-(p-methoxy-styryl)-s-triazine, 2,4-bis(trichloromethyl)-6-(4-methoxy-naphth-l-yl)-s-triazine, 2,4-bis(trichloromethyl)-6-piperonyl-s-triazine, and 2,4-bis(trichloromethyl)-6-[(4 -ethoxy-ethylenoxy)-phen-1-yl]-s-triazine, and s-triazines as described in U.S. Pat. Nos. 5,955,238, 6,037,098, 6,010,824 and 5,629,354); and titanocene (bis(etha.9-2,4-cyclopentadien-1-yl) bis[2,6-difluoro-3-(lH-pyrrol-1-yl)phenyl) titanium). Onium salts, borate salts, and s-triazines are preferred free radical initiators. Diaryliodonium salts and triarylsulfonium salts are preferred onium salts. Triarylalkylborate salts are preferred borate salts. Trichloromethyl substituted s-triazines are preferred s-triazines.

The known photopolymerization initiators can be used in the composition of the present invention, in a preferred embodiment of the present invention the photopolymerizable composition according to the present invention comprises a hexaaryl-bisimidazole (HABI; dimer of triaryl-imidazole) compound as a photopolymerization initiator alone or in combination with further photoinitiators.

A procedure for the preparation of hexaarylbisimidazoles is described in DE 1470 154 and their use in photopolymerizable compositions is documented in EP 24 629, EP 107 792, US 4 410 621, EP 215 453 and DE 3 211 312. Preferred derivatives are e. g. 2,4,5,2',4',5'-hexaphenylbisimidazole, 2,2'-bis(2-chlorophenyl)-4,5,4',5'-tetraphenylbisimidazole, 2,2'-bis(2-bromophenyl)-4,5,4',5'-tetraphenylbisimidazole, 2,2'-bis(2,4-dichlorophenyl)-4,5,4',5'-tetraphenylbisimidazole, 2,2'-bis(2-chlorophenyl)-4,5,4',5'-tetrakis(3-methoxyphenyl)bisimidazole, 2,2'-bis(2-chlorophenyl)-4,5,4',5'-tetrakis(3,4,5-trimethoxyphenyl)-bisimidazole, 2,5,2',5'-tetrakis(2-chlorophenyl)-4,4'-bis(3,4-dimethoxyphenyl)bisimidazole, 2,2'-bis(2,6-dichlorophenyl)-4,5,4',5'-tetraphenylbisimidazole, 2,2'-bis(2-nitrophenyl)-4,5,4',5'-tetraphenylbisimidazole, 2,2'-di-o-tolyl-4,5,4',5'-tetraphenylbisimidazole, 2,2'-bis(2-ethoxyphenyl)-4,5,4',5'-tetraphenylbisimidazole and 2,2'-bis(2,6-difluorophenyl)-4,5,4',5'-tetraphenylbisimidazole. The amount of the HABI photoinitiator typically ranges from 0.01 to 30 % by weight, preferably from 0.5 to 20 % by weight, relative to the total weight of the non volatile components of the photopolymerizable composition.

A very high sensitivity can be obtained in the context of the present invention by the combination of an optical brightener as sensitizer and a hexaarylbisimidazole as photoinitiator.

Suitable classes of photoinitiators other than hexaarylbisimidazole compounds may include aromatic ketones, aromatic onium salts, organic peroxides, thio compounds, ketooxime ester compounds, borate compounds, azinium compounds, metallocene compounds, active ester compounds and compounds having a carbon-halogen bond, but preferably the composition comprises a non-boron comprising photopolymerization initiator and particularly preferred the photopolymerization initiator comprises no boron compound. Many specific examples of photoinitiators suitable for the present invention can be found in EP-A 1 091 247. Other preferred initiators are trihalo methyl sulphones.

Preferably hexaarylbisimidazole compounds and/or metallocene compounds can be used alone or in combination with other suitable photoinitiators, in particular with aromatic ketones, aromatic onium salts, organic peroxides, thio compounds, ketoxime ester compounds, azinium compounds, active ester compounds or compounds having a carbon halogen bond.

The polymerizable monomer or oligomer may be a combination of a monomer or oligomer comprising at least one epoxy or vinyl ether functional group and a polymerizable ethylenically unsaturated compound, having at least one terminal ethylenic group, and said initiator may be a combination of a cationic initiator and a free-radical initiator. A monomer or oligomer comprising at least one epoxy or vinyl ether functional group and a polymerizable ethylenically unsaturated compound, having at least one terminal ethylenic group, can be the same compound wherein the compound contains both ethylenic group and epoxy or vinyl ether group. Examples of such compounds may include epoxy functional acrylic monomers, such as glycidyl acrylate. The free radical initiator and the cationic initiator can be the same compound if the compound is capable of generating both free radical and free acid. Examples of such compounds include various onium salts such as diaryliodonium hexafluoroantimonate and s-triazines such as 2,4-bis(trichloromethyl)-6-[(4-ethoxyethylenoxy)-phen-1-yl]-s-triazine which are capable of generating both free radical and free acid in the presence of a sensitizer.

The photopolymerizable layer may also comprise a multifunctional monomer. This monomer contains at least two functional groups selected from an ethylenically unsaturated group and/or an epoxy or vinyl ether group. Particular multifunctional monomers for use in the photopolymer coating are disclosed in US 6,410,205 , US 5,049,479 , EP 1079276 , EP 1369232 , EP 1369231 EP 1341040 , US 2003/0124460 , EP 1241002 , EP 1288720 and in the reference book including the cited refences : Chemistry & Technology

UV & EB formulation for coatings, inks & paints - Volume 2 - Prepolymers andReactive Diluents for UV and EB Curable Formulations by N.S. Allen, M.A. Johnson, P.K.T. Oldring, M.S. Salim - Edited by P.K.T. Oldring - 1991 - ISBN 0 947798102. Particularly preferred are urethane (meth)acrylate multifunctional monomers, which can be used alone or in combination with other (meth)acrylate multifunctional monomers.

The photopolymerizable layer may also comprise a co-initiator. Typically, a co-initiator is used in combination with a free radical initiator and/or cationic initator. Particular co-initiators for use in the photopolymer coating are disclosed in US 6,410,205 , US 5,049,479 , EP 1079276 , 1369232 , EP 1369231 EP 1341040 , US 2003/0124460 , EP 1241002 , EP 1288720 and in the reference book including the cited refences : Chemistry & Technology UV & EB formulation for coatings, inks & paints - Volume 3 -Photoinitiators for Free Radical and Cationic Polymerisation by K.K. Dietliker - Edited by P.K.T. Oldring - 1991 - ISBN 0 947798161.

The photopolymerizable layer may also comprise an inhibitor. Particular inhibitors for use in the photopolymer coating are disclosed in US 6,410,205, EP 1288720 and the unpublished patent application EP-A 04101955, filed on 6/5/2004.

The binder of the photopolymerizable layer

The photopolymerizable layer may further comprise also another binder. This binder can be selected from a wide series of organic polymers. Compositions of different binders can also be used. Useful binders include for example chlorinated polyalkylene (in particular chlorinated polyethylene and chlorinated polypropylene), polymethacrylic acid alkyl esters or alkenyl esters (in particular polymethyl (meth)acrylate, polyethyl (meth)acrylate, polybutyl (meth)acrylate, polyisobutyl (meth)acrylate, polyhexyl (meth)acrylate, poly(2-ethylhexyl) (meth)acrylate and polyalkyl (meth)acrylate copolymers of (meth) acrylic acid alkyl esters or alkenyl esters with other copolymerizable monomers (in particular with (met)acrylonitrile, vinyl chloride, vinylidene chloride, styrene and/or butadiene), polyvinyl chloride (PVC, vinylchloride/(meth)acrylonitrile copolymers, polyvinylidene chloride (PVDC), vinylidene chloride/(meth)acrylonitrile copolymers, polyvinyl acetate, polyvinyl alcohol, polyvinyl pyrrolidone, copolymers of vinyl pyrrolidone or alkylated vinyl pyrrolidone, polyvinyl caprolactam, copolymers of vinyl caprolactam, poly (meth)acrylonitrile, (meth)acrylonitrile/styrene copolymers, (meth)acrylamide/alkyl (meth)acrylate copolymers, (meth)acrylonitrile/butadiene/styrene (ABS) terpolymers, polystyrene, poly(α-methylstyrene), polyamides, polyurthanes, polyesters, methyl cellulose, ethylcellulose, acetyl cellulose, hydroxy-(C_1-C_4-alkyl)cellulose, carboxymethyl cellulose, polyvinyl formal and polyvinyl butyral. Particulary preferred binders are polymers having vinylcaprolactam, vinylpyrrolidone or alkylated vinylpyrrolidone as monomeric units. Alkylated vinylpyrrolidone polymers can be obtained by grafting alfa-olefines onto the vinylpyrrolidone polymer backbone. Typical examples of such products are the Agrimer AL Graft polymers commercially available from ISP. The length of the alkylation group may vary from C_4 to C_{30}. Other useful binders are binders containing carboxyl groups, in particular copolymers containing monomeric units of α,β-unsaturated carboxylic acids or monomeric units of α,β-unsaturated dicarboxylic acids (preferably acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid, maleic acid or itaconic acid). By the term "copolymers" are to be understood in the context of the present invention as polymers containing units of at least 2 different monomers, thus also terpolymers and higher mixed polymers. Particular examples of useful copolymers are those containing units of (meth)acrylic acid and units of alkyl (meth)acrylates, allyl (meth)acrylates and/or (meth)acrylonitrile as well as copolymers containing units of crotonic acid and units of alkyl (meth)acrylates and/or (meth)acrylonitrile and vinylacetic acid/alkyl (meth)acrylate copolymers. Also suitable are copolymers containing units of maleic anhydride or maleic acid monoalkyl esters. Among these are, for example, copolymers containing units of maleic anhydride and styrene, unsaturated ethers or esters or unsaturated aliphatic hydrocarbons and the esterification products obtained from such copolymers. Further suitable binders are products obtainable from the conversion of hydroxyl-containing polymers with intramolecular dicarboxylic anhydrides. Further useful binders are polymers in which groups with acid hydrogen atoms are present, some or all of which are converted with activated isocyanates. Examples of these polymers are products obtained by conversion of hydroxyl-containing polymers with aliphatic or aromatic sulfonyl isocyanates or phosphinic acid isocyanates. Also suitable are polymers with aliphatic or aromatic hydroxyl groups, for example copolymers containing units of hydroxyalkyl (meth)acrylates, allyl alcohol, hydroxystyrene or vinyl alcohol, as well as epoxy resins, provided they carry a sufficient number of free OH groups. Particular useful binder and particular useful reactive binders are disclosed in EP 1 369 232, EP 1 369 231, EP 1 341 040, US 2003/0124460, EP 1 241 002, EP 1 288 720, US 6,027,857, US 6,171,735 and US 6,420,089.

The organic polymers used as binders have a typical mean molecular weight M_W between 600 and 700 000, preferably between 1 000 and 350 000. Preference is further given to polymers having an acid number between 10 to 250, preferably 20 to 200, or a hydroxyl number between 50 and 750, preferably between 100 and 500. The amount of binder(s) generally ranges from 10 to 90 % by weight, preferably 20 to 80 % by weight, relative to the total weight of the non-volatile components of the composition.

Also particular suitable binders are copolymers of vinylacetate and vinylalcohol, preferably comprising vinylalcohol in an amount of 10 to 98 mol% vinylalcohol, more preferably between 35 and 95 mol %, most preferably 40 and 75 mol %, best results are obtained with 50 to 65 mol % vinylalcohol. The ester-value, measured by the method as defined in DIN 53 401, of the copolymers of vinylacetate and vinylalcohol ranges preferably between 25 and 700 mg KOH/g, more preferably between 50 and 500 mg KOH/g, most preferably between 100 and 300 mg KOH/g. The viscosity of the copolymers of vinylacetate and vinylalcohol are measured on a 4 weight % aqueous solution at 20°C as defined in DIN 53 015 and the viscosity ranges preferably between 3 and 60 mPa.s, more preferably between 4 and 30 mPa.s, most preferably between 5 and 25 mPa.s. The average molecular weight M_W of the copolymers of vinylacetate and vinylalcohol ranges preferably between 5 000 and 500 000 g/mol, more preferably between 10 000 and 400 000 g/mol, most preferably between 15 000 and 250 000 g/mol. Other preferred binders are disclosed in EP 152 819 B1 on page 2 lines 50-page 4 line 20, and in EP 1 043 627 B1 on paragraph [0013] on page 3.

In another embodiment the polymeric binder may comprise a hydrophobic backbone, and pendant groups including for example a hydrophilic poly(alkylene oxide) segment. The polymeric binder may also include pendant cyano groups attached to the hydrophobic backbone. A combination of such binders may also be employed. Generally the polymeric binder is a solid at room temperature, and is typically a non-elastomeric thermoplastic. The polymeric binder comprises both hydrophilic and hydrophobic regions, which is thought to be important for enhancing differentiation of the exposed and unexposed areas by facilitating developability. Generally the polymeric binder is characterized by a number average molecular weight (Mn)in the range from about 10.000 to 250.000, more commonly in the range from about 25.000 to 200.000. The polymerizable composition may comprise discrete particles of the polymeric binder. Preferably the discrete particles are particles of the polymeric binder which are suspended in the polymerizable composition. The presence of discrete particles tends to promote developability of the unexposed areas. Specific examples of the polymeric binders according to this embodiment are described in US 6.899.994, 2004/0260050, US2005/0003285, US2005/0170286 and US2005/0123853. In addition to the polymeric binder of this embodiment the imageable layer may optionally comprise one or more co-binders. Typical co-binders are water-soluble or water-dispersible polymers, such as, cellulose derivatives, poly vinyl alcohol, poly acrylic acid poly(meth)acrylic acid, poly vinyl pyrrolidone, polylactide, poly vinyl phosphonic acid, synthetic co-polymers, such as the co-polymer of an alkoxy polyethylene glycol (meth)acrylate. Specific examples of co-binders are described in US2004/0260050, US2005/0003285 and US2005/0123853. Printing plate precursors, the imageable layer of which comprises a binder and optionally a co-binder according this embodiment and described in more detail in US2004/0260050, US2005/0003285 and US2005/0123853, optionally comprises a topcoat and an interlayer.

Surfactant

Various surfactants may be added into the photopolymerizable layer to allow or enhance the developability of the precursor with a gum solution. Both polymeric and small molecule surfactants can be used. Nonionic surfactants are preferred. Preferred nonionic surfactants are polymers and oligomers containing one or more polyether (such as polyethylene glycol, polypropylene glycol, and copolymer of ethylene glycol and propylene glycol) segments. Examples of preferred nonionic surfactants are block copolymers of propylene glycol and ethylene glycol (also called block copolymer of propylene oxide and ethylene oxide); ethoxylated or propoxylated acrylate oligomers; and polyethoxylated alkylphenols and polyethoxylated fatty alcohols. The nonionic surfactant is preferably added in an amount ranging between 0.1 and 30% by weight of the coating, more preferably between 0.5 and 20%, and most preferably between 1 and 15%.

Sensitizer

The photocurable composition may also comprise a sensitizer. Highly preferred sensitizers are violet light absorbing sensitizers, having an absorption spectrum between 350 nm and 450 nm, preferably between 370 nm and 420 nm, more preferably between 390 nm and 415 nm. Particular preferred sensitizers are disclosed in EP 1 349 006 paragraph [0007] to [0009], EP-A-3103499, filed on 22/09/2003, and WO2004/047930, including the cited references in these patent applications. Other highly preferred sensitizers are infrared light absorbing dyes, having an absorption spectrum between 750 nm and 1300 nm, preferably between 780 nm and 1200 nm, more preferably between 800 nm and 1100 nm. Particular preferred sensitizers are heptamethinecyane dyes, specially the dyes disclosed in EP 1 359 008 paragraph [0030] to [0032]. Other preferred sensitizers are blue, green or red light absorbing sensitizers, having an absorption spectrum between 450 nm and 750 nm. Useful sensitizers can be selected from the sensitizing dyes disclosed in US 6,410,205, US 5,049,479, EP 1 079 276, EP 1 369 232, EP 1 369 231, EP 1 341 040, US 2003/0124460, EP 1 241 002 and EP 1 288 720.

Colorant

The photopolymerizable layer or another layer of the coating may also comprise a colorant. The colorant can be present in the photopolymerizable layer or in a separate layer below or above the photopolymerizable layer. After processing with a gum solution, at least part of the colorant remains on the hardened coating areas, and a visible image can be produced on the support by removing the coating, including the colorant, at the non-exposed areas in the gum processing.

The colorant can be a dye or a pigment. A dye or pigment can be used as a colorant when the layer, comprising the dye or pigment, is colored for the human eye.

The colorant can be a pigment. Various types of pigments can be used such as organic pigments, inorganic pigments, carbon black, metallic powder pigments and fluorescent pigments. Organic pigments are preferred.

Specific examples of organic pigments include quinacridone pigments, quinacridonequinone pigments, dioxazine pigments, phthalocyanine pigments, anthrapyrimidine pigments, anthanthrone pigments, indanthrone pigments, flavanthrone pigments, perylene pigments, diketopyrrolopyrrole pigments, perinone pigments, quinophthalone pigments, anthraquinone pigments, thioindigo pigments, benzimidazolone pigments, isoindolinone pigments, azomethine pigments, and azo pigments.

Specific examples of pigments usable as colorant are the following (herein is C.I. an abbreviation for Color Index; under a Blue colored pigment is understood a pigment that appears blue for the human eye; the other colored pigments have to be understood in an analogue way):

- Blue colored pigments which include C.I. Pigment Blue 1, C.I. Pigment Blue 2, C.I. Pigment Blue 3, C.I. Pigment Blue 15 : 3, C.I. Pigment Blue 15 : 4, C.I. Pigment Blue 15 : 34, C.I. Pigment Blue 16, C.I. Pigment Blue 22, C.I. Pigment Blue 60 and the like; and C.I. Vat Blue 4, C.I. Vat Blue 60 and the like;
- Red colored pigments which include C.I. Pigment Red 5, C.I. Pigment Red 7, C.I. Pigment Red 12, C.I. Pigment Red 48 (Ca), C.I. Pigment Red 48 (Mn), C.I. Pigment Red 57 (Ca), C.I. Pigment Red 57 : 1, C.I. Pigment Red 112, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 168, C.I. Pigment Red 184, C.I. Pigment Red 202, and C.I. Pigment Red 209;
- Yellow colored pigments which include C.I. Pigment Yellow 1, C.I. Pigment Yellow 2, C.I. Pigment Yellow 3, C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14C, C.I. Pigment Yellow 16, C.I. Pigment Yellow 17, C.I. Pigment Yellow 73, C.I. Pigment Yellow 74, C.I. Pigment Yellow 75, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 95, C.I. Pigment Yellow 97, C.I. Pigment Yellow 98, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 114, C.I. Pigment Yellow 128, C.I. Pigment Yellow 129, C.I. Pigment Yellow 138, C.I. Pigment Yellow 150, C.I. Pigment Yellow 151, C.I. Pigment Yellow 154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 180, and C.I. Pigment Yellow 185;
- Orange colored pigments include C.I. Pigment Orange 36, C.I. Pigment Orange 43, and a mixture of these pigments.

Green colored pigments include C.I. Pigment Green 7, C.I. Pigment Green 36, and a mixture of these pigments;

- Black colored pigments include: those manufactured by Mitsubishi Chemical Corporation, for example, No. 2300, No. 900, MCF 88, No. 33, No. 40, No. 45, No. 52, MA 7, MA 8, MA 100, and No. 2200 B;

those manufactured by Columbian Carbon Co., Ltd., for example, Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255, and Raven 700; those manufactured by Cabot Corporation, for example, Regal 400 R, Regal 330 R, Regal 660 R, Mogul L, Monarch 700, Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300, and Monarch 1400; and those manufactured by Degussa, for example, Color Black FW 1, Color Black FW 2, Color Black FW 2 V, Color Black FW 18, Color Black FW 200, Color Black S 150, Color Black S 160, Color Black S 170, Printex 35, Printex U, Printex V, Printex 140 U, Special Black 6, Special Black 5, Special Black 4A, and Special Black 4.

Other types of pigments such as brown pigments, violet pigments, fluorescent pigments and metallic powder pigments can also be used as colorant. The pigments may be used alone or as a mixture of two or more pigments as colorant.

Blue colored pigments, including cyan pigments, are preferred.

The pigments may be used with or without being subjected to surface treatment of the pigment particles. Preferably, the pigments are subjected to surface treatment. Methods for surface treatment include methods of applying a surface coat of resin, methods of applying surfactant, and methods of bonding a reactive material (for example, a silane coupling agent, an epoxy compound, polyisocyanate, or the like) to the surface of the pigment. Suitable examples of pigments with surface treatment are the modified pigments described in WO 02/04210. Specifically the blue colored modified pigments described in WO 02/04210 are preferred as colorant in the present invention.

The pigments have a particle size which is preferably less than 10 µm, more preferably less than 5 µm and especially preferably less than 3 µm. The method for dispersing the pigments may be any known dispersion method which is used for the production of ink or toner or the like. Dispersing machines include an ultrasonic disperser, a sand mill, an attritor, a pearl mill, a super mill, a ball mill, an impeller, a dispenser, a KD mill, a colloid mill, a dynatron, a three-roll mill and a press kneader. Details thereof are described in " Latest Pigment Applied Technology" (CMC Publications, published in 1986).

A dispersing agent may be omitted in the preparation of dispersions of so-called self-dispersing pigments. Specific examples of self-dispersing pigments are pigments with are subjected to a surface treatment in such a way the pigment surface is compatible with the dispersing liquid. Typical examples of self-dispersing pigments in an aqueous medium are pigments which have ionic or ionisable groups or polyethyleneoxide chains coupled to the particle-surface. Examples of ionic or ionisable groups are acid groups or salts thereof such as carboxylic acid group, sulphonic acid, phosphoric acid or phosphonic acid and alkali metal salts of these acids. Suitable examples of self-dispersing pigments are described in WO 02/04210 and these are preferred in the present invention. The blue colored self-dispersing pigments in WO 02/04210 are preferred.

Typically, the amount of pigment in the coating may be in the range of about 0.005 g/m^2 to 2 g/m^2, preferably about 0.007 g/m^2 to 0.5 g/m^2, more preferably about 0.01 g/m^2 to 0.2 g/m^2, most preferably about 0.01 g/m^2 to 0.1 g/m^2.

The colorant can also be a dye. Any known dyes, such as commercially available dyes or dyes described in, for example, "Dye Handbook" (edited by the Organic Synthetic Chemistry Association, published in 1970) which are colored for the human eye, can be used as colorant in the photopolymerizable coating. Specific examples thereof include azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, anthraquinone dyes, phthalacyanine dyes, carbionium dyes, quinonimine dyes, methine dyes, and the like. Phthalocyanine dyes are preferrred. Suitable dyes are salt-forming organic dyes and may be selected from oil-soluble dyes and basic dyes. Specific examples thereof are (herein is CI an abbreviation for Color Index): Oil Yellow 101, Oil Yellow 103, Oil Pink 312, Oil Green BG, Oil Bue GOS, Oil Blue 603, Oil Black BY, Oil Black BS, Oil Black T-505, Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl

Violet, Rhodamine B (CI415170B), Malachite Green (CI42000), Methylene Blue (CI52015). Also, the dyes dislosed in GB 2 192 729 may be used as colorant.

Typically, the amount of dye in the coating may be in the range of about 0.005 g/m^2 to 2 g/m^2, preferably about 0.007 g/m^2 to 0.5 g/m^2, more preferably about 0.01 g/m^2 to 0.2 g/m^2, most preferably about 0.01 g/m^2 to 0.1 g/m^2.

Printing-out agent

The photopolymerizable layer or another layer of the coating may also comprise a printing-out agent, i.e. a compound which is capable of changing the color of the coating upon exposure. After image-wise exposing of the precursor, a visible image can be produced, hereinafter also referred to as "print-out image". The printing-out agent may be a compound as described in EP-A-1 491 356 paragraph [0116] to [0119] on page 19 and 20, and in US 2005/8971 paragraph [0168] to [0172] on page 17. Preferred printing-out agents are the compounds described in the unpublished PCT Application PCT/EP 2005/053141, filed on 1 July 2005, from line 1 page 9 to line 27 page 20. More preferred are the IR-dyes as described in the unpublished Patent Application EP 05 105 440.1, filed on 21 June 2005, from line 32 page 5 to line 9 page 32.

The contrast

The contrast of the image formed after image-wise exposure and processing with a gum solution is defined as the difference between the optical density at the exposed area to the optical density at the non-exposed area, and this contrast is preferably as high as possible. This enables the end-user to establish immediately whether or not the precursor has already been exposed and processed with a gum solution, to distinguish the different color selections and to inspect the quality of the image on the treated plate precursor.

The contrast increases with increasing optical density in the exposed area and/or decreasing optical density in the non-exposed areas. The optical density in the exposed area may increase with the amount and extinction coefficient of the colorant remaining in the exposed areas and the intensity of color formed by the printing-out agent. In the non-exposed areas it is preferred that the amount of colorant is as low as possible and that the intensity of color print-out agent is as low as possible. The optical density can be measured in reflectance by an optical densitometer, equipped with several filters (e.g. cyan, magenta, yellow). The difference in optical density at the exposed area and the non-exposed area has preferably a value of at least 0.3, more preferably at least 0.4, most preferably at least 0.5. There is no specific upper limit for the contrast value, but typically the contrast is not higher than 3.0 or even not higher than 2.0. In order to obtain a good visual contrast for a human observer the type of color of the colorant may also be important. Preferred colors for the colorant are cyan or blue colors, i.e. under blue color we understand a color that appears blue for the human eye.

The toplayer

The coating may comprise a top layer which acts as an oxygen barrier layer, hereinafter also referred to as "overcoat layer" or "overcoat". Preferred binders which can be used in the top layer are polyvinyl alcohol and the polymers disclosed in EP-A-3103498, filed on 22/09/2003, US 6,410,205 and EP 1 288 720, including the cited references in these patents and patent applications. The most preferred binder for the toplayer is polyvinylalcohol. The polyvinylalcohol has preferably an hydrolysis degree ranging between 74 mol % and 99 mol %. The weight average molecular weight of the polyvinylalcohol can be measured by the viscosity of an aqueous solution, 4 % by weight, at 20°C as defined in DIN 53 015, and this viscosity number ranges preferably between 3 and 26, more preferably between 3 and 15, most preferably between 3 and 10.

The coating thickness of the top layer is preferably between 0.25 and 1.75 g/m^2, more preferably between 0.25 and 1.3 g/m^2, most preferably between 0.25 and 1.0 g/m^2. In a more preferred embodiment of the present invention, the toplayer has a coating thickness between 0.25 and 1.75 g/m^2 and comprises a polyvinylalcohol having an hydrolysis degree ranging between 74 mol % and 99 mol % and a viscosity number as defined above ranging between 3 and 26.

In a preferred embodiment, the composition and the thickness of of the toplayer are optimised in order to obtain a high sensitivity, a good daylight stability and less or no sludge formation during processing. In order to reduce sludge, the toplayer comprises less polyvinylalcohol and polyvinylalcohol with a lower molecular weight, preferably a viscosity number of less than 26, more preferably less than 10is used and a thickness as low as possible but more than 0.25 g/m^2. In order to improve the sensitivity, the good oxygen barrier is desired, using a polyvinylalcohol with a high hydrolysis degree, preferably 88-98%, and a bigger thickness or the toplayer. In order to improve the daylight stability, small penetration of oxygen is desired by a using an oxygen barrier with reduced barrier property for oxygen, preferably by using a smaller thickness of the toplayer and with polyvinylalcohol having a lower hydrolysis degree. Due to a good balance of these elements, an optimised property for the precursor can be obtained.

The top layer may also comprise a component selected from the compounds of the gum solution as described above.

Exposure

The image-wise exposing step is carried out off-press in a plate setter, i.e. an exposure apparatus suitable for image-wise exposing the precursor by a laser such as a laser diode, emitting around 830 nm, a NdYAG laser, emitting around 1060 nm, a violet laser, emitting around 400 nm, or a gas laser such as Ar laser, or by a digital modulated UV-exposure, e.g. by means of digital mirror devices, or by a conventional exposure in contact with a mask. In a preferred embodiment of the present invention, the precursor is image-wise exposed by a laser emitting IR-light or violet light.

Preheating

After this image-wise exposing step the precursor is optionally heated in a preheating unit to enhance or to speed-up the polymerization and/or crosslinking reaction. This preheat step is carried out at a temperature of preferably 80°C to 150°C and during a dwell time of preferably 5 seconds to 1 minute. The preheating unit is preferably provided with heating elements such as IR-lamps, UV-lamps, heated air, a heated metal roll, etc.

Washing

After the exposing step or, when a preheating step is present, after the preheating step, the precursor may be washed in a prewashing station, whereby at least part of the toplayer can be removed by supplying a wash liquid, i.e. water or an aqueous solution, to the coating of the precursor. The washing liquid is preferably water, more preferably tap water.

The term aqueous includes water or mixtures of water with water-miscible organic solvents such as alcohols, e.g. methanol, ethanol, 2-propanol, butanol, iso-amyl alcohol, octanol, cetyl alcohol, etc.; glycols, e.g. ethylene glycol; glycerine; N-methyl pyrrolidone; methoxypropanol; and ketones, e.g. 2-ptopanone and 2-butanone; etc. The water-miscible organic solvent may be present in these mixtures of at most 50 % by weight, preferably less than 20 % by weight, more preferably less than 10% by weight, most preferably no organic solvent is present in the aqueous solution. The aqueous solution may further comprises a compound solubilized or dispersed in water or a mixture of water and a water-miscible solvent. Such compounds may be selected from the compounds of the gum solution as described above.

The wash liquid used in this step has preferably a temperature ranging between 15°C and 85°C, more preferably between 18°C and 65°C, most preferably between 20°C and 55°C.

The prewashing station may comprise at least one prewashing unit wherein the wash liquid is applied to the precursor by a spraying, jetting, dipping or coating technique, including spin coating, roll coating, slot coating or gravure coating, or by rubbing in with an impregnated pad or by pouring-in, either by hand or in an automatic apparatus. The spraying, jetting, dipping or coating technique are preferred.

An example of a spray nozzle which can be used in the spraying technique, is an air assisted spray nozzle of the type SUJ1, commercially available at Spraying Systems Belgium, Brussels. The spray nozzle may be mounted on a distance of 50 mm to 200 mm between nozzle and receiving substrate. The flow rate of the spray solution may be set to 7 ml/min. During the spray process an air pressure in the range of 4.80×10^5 Pa may be used on the spray head. This layer may be dried during the spraying process and/or after the spraying process. Typical examples of jet nozzles which can be used in the jetting technique, are ink-jet nozzles and valve-jet nozzles.

At least one of the prewashing units may be provided with at least one roller for rubbing and/or brushing the coating while applying the wash liquid to the coating.

The wash liquid used in the prewashing step can be collected in a tank and the washing liquid can be used several times. The wash liquid can be replenished by adding fresh water and/or fresh aqueous solution to the tank of the prewashing unit. Said fresh water and fresh aqueous solution are respectively water and aqueous solution which have not been used before for washing a precursor. In an alternative way, the wash liquid may be used once-only, i.e. only fresh water or fresh aqueous solution is applied to the coating by preferably a spraying or jetting technique. Preferably tap water is used in this alternative way.

The prewashing station may comprise two or more prewashing units, preferably two or three prewashing units.

In a preferred embodiment of the present invention, the prewashing station comprises a first and a second prewashing unit whereby the precursor is firstly washed in the first prewashing unit and subsequently washed in the second prewashing unit. The precursor can be firstly washed in the first prewashing unit with washing liquid which has been used in the second prewashing unit, and, subsequently, washed in the second prewashing unit with fresh water or fresh aqueous solution by preferably a spraying or jetting technique. In an alternative way, the first and second prewashing units preferably have the configuration of a cascade system, whereby the wash liquid used for washing the precursor in the first and second prewashing unit are respectively present in a first and a second tank, and whereby the wash liquid of the second tank overflows to the first tank when fresh water or fresh aqueous solution is added in the second prewashing unit.

In another embodiment of the present invention, the prewashing station may comprise a first, a second and a third prewashing unit whereby the precursor is firstly washed in the first prewashing unit, subsequently in the second prewashing unit and finally in the third prewashing unit. The precursor can be firstly washed in the first prewashing unit with washing liquid which has been used in the second prewashing unit, subsequently washed in the second prewashing unit with washing liquid which has been used in the third prewashing unit, and finally washed in the third prewashing unit with fresh water or fresh aqueous solution by preferably a spraying or jetting technique. In an alternative way, the first, second and third prewashing units preferably have the configuration of a cascade system, whereby the wash liquids used for washing the precursor in the first, second and third prewashing unit are respectively present in a first, a second and a third tank, and whereby the wash liquid of the third tank overflows to the second tank when fresh water or fresh aqueous solution is added in the third prewashing unit and the wash liquid of the second tank overflows to the first tank.

In another embodiment of the present invention, the wash liquid used in each of the prewashing units may be also regenerated by removing insoluble material present in the wash liquid. The presence of insoluble material in the wash liquid may caused by several reasons, e.g. by washing of a pigment containing coating, by evaporation of solvent or water of the washing liquid, or by sedimentation, coagulation or flocculation of components in the wash liquid. The insoluble material can be removed by several techniques such as filtration, ultrafiltration, centrifugation or decantation. A suitable apparatus for disposing a waste solution such as the wash liquid of the present invention is described in EP-A 747 773. The apparatus can be connected to the tank of a prewashing unit to regenerate the used wash liquid by circulation of the wash liquid over a filter or a filter membrane. The wash liquid can be circulated over the filter or filter membrane continuously, periodically or during the washing time, or the circulation is regulated by the measurement of the turbidity or transparency (i.e. optical transmission) of the wash liquid whereby the circulation starts when the turbidity exceeds an upper value and stops when a under value is reached. The upper and under turbidity value can be chosen in relation to the desired degree of purification, generally the optical transmission of the wash liquid is not lower than 50% of its value at starting, preferably not lower than 80%, more preferably not lower than 95%.

In the present invention, at least part of the toplayer, when present, can be removed in the washing step, preferably more than 50 % of the toplayer is removed, more preferably more than 80 %, most preferably more than 95 %. According to a preferred embodiment of the present invention, the photopolymerizable layer is substantially not extracted or solubilized in the washing step whereby the wash liquid used in the washing step does not contain components of the photopolymerizable layer in a concentration of less than 2 % by weight of, more preferably less than than 1 % by weight of these ingredients of the potopolymerizable layer, most preferably less than 0.5 % by weight. The components of the photopolymerizable layer which are preferably as much as possible omitted in the wash liquid are polymerizable monomer, multifunctional monomer, initiator, inhibitor and/or sensitizer.

Gum-processing

The precursor is developed in a gumming station by applying a gum solution to the coating of the precursor, thereby removing the non-exposed areas of the photopolymerizable layer from the support and gumming the plate in a single step. The gumming station comprises at least one gumming unit wherein the gum is applied to the precursor by a spraying, jetting, dipping or coating technique or by rubbing in with an impregnated pad or by pouring-in, either by hand or in an automatic apparatus.

An example of a spray nozzle which can be used in the spraying technique, is an air assisted spray nozzle of the type SUJ1, commercially available at Spraying Systems Belgium, Brussels. The spray nozzle may be mounted on a distance of 50 mm to 200 mm between nozzle and receiving substrate. The flow rate of the spray solution may be set to 7 ml/min. During the spray process an air pressure in the range of 4.80×10^5 Pa may be used on the spray head. This layer may be dried during the spraying process and/or after the spraying process. Typical examples of jet nozzles which can be used in the jetting technique, are ink-jet nozzles and valve-jet nozzles.

At least one of the gumming units may be provided with at least one roller for rubbing and/or brushing the coating while applying the gum to the coating. The gum used in the developing step can be collected in a tank and the gum can be used several times. The gum can be replenished by adding a replenishing solution to the tank of the gumming unit. In an alternative way, the gum solution may be used once-only, i.e. only starting gum solution is applied to the coating by preferably a spraying or jetting technique. Said starting gum solution is a gum solution which has not been used before for developing a precursor and has the same composition as the gum solution used at the start of the development.

Said replenishing solution is a solution which may be selected from a starting gum solution, a concentrated gum solution, a diluted gum solution, a solution of a non-ionic surfactant, water, a solution of a buffer having a pH ranging between 4 and 7 or a baking gum. A concentrated or diluted gum solution is a solution comprising a higher respectively lower concentration of gum additives as defined above. A concentrated gum solution can be added as replenishing solution when the concentration of active products is under a desired level in the gum solution. A diluted gum solution or water can be used when the concentration of active products is above a desired level in the gum solution or when the viscosity of the gum solution is increased or when the volume of the gum solution is under a desired level, e.g. due to evaporation of the solvent or water. A solution of a non-ionic surfactant or a solution of a buffer can be added when the gum solution needs a higher concentration of a surfactant or when the pH of the gum solution needs to be controlled at a desired pH value or at a desired pH value in a range of two pH values, e.g. between 4 and 7.

The addition of replenishing solution, i.e. the type and the amount of replenishing solution, may be regulated by the measurement of at least one of the following parameters such as the number and area of plate precursor developed, the time period of developing, the volume in each gumming unit (minimum and maximum level), the viscosity (or viscosity increase) of the gum solution, the pH (or pH change) of the gum solution, the density (or density increase) of the gum solution and the conductivity (or conductivity increase) of the gum solution, or a combination of at least two of them. The density (or density increase) of the gum solution can be measured with a PAAR densitymeter.

The gum solution used in this step has preferably a temperature ranging between 15°C and 85°C, more preferably between 18°C and 65°C, most preferably between 20°C and 55°C.

In a preferred embodiment of the present invention, the gumming station comprises a first and a second gumming unit whereby the precursor is firstly developed in the first gumming unit and subsequently developed in the second gumming unit. The precursor may be firstly developed in the first gumming unit with gum solution which has been used in the second gumming unit, and, subsequently, developed in the second gumming unit with starting gum solution by preferably a spraying or jetting technique. In an alternative way, the first and second gumming unit preferably have the configuration of a cascade system, whereby the gum solution used for developing the precursor in the first and second gumming unit are respectively present in a first and a second tank, and whereby the gum solution of the second tank overflows to the first tank when replenishing solution is added in the second gumming unit. Optionally, also to the first gumming unit a replenishing solution can be added and this replenishing solution may be the same or another replenishing solution than added to the second gumming unit, e.g. a diluted gum solution, a solution of a non-ionic surfactant or water can be added as replenisher to the first gumming unit.

In another embodiment of the present invention, the gumming station comprises a first, a second and a third gumming unit whereby the precursor is firstly developed in the first gumming unit, subsequently in the second gumming unit and finally in the third gumming unit. The precursor may be firstly developed in the first gumming unit with gum solution which has been used in the second gumming unit, subsequently developed in the second gumming unit with gum solution which has been used in the third gumming unit, and finally developed in the third gumming unit with starting gum solution by preferably a spraying or jetting technique. In an alternative way, the first, second and third gumming unit preferably have the configuration of a cascade system, whereby the gum solution used for developing the precursor in the first, second and third gumming unit are respectively present in a first, a second and a third tank, and whereby the gum solution of the third tank overflows to the second tank when replenishing solution is added in the third gumming unit, and whereby the gum solution of the second tank overflows to the first tank. Optionally, also to the second and/or first gumming unit(s) a replenishing solution may be added and this replenishing solution may be the same or another replenishing solution than added to the third gumming unit, e.g. a diluted gum solution, a solution of a non-ionic surfactant or water can be added as replenisher to the second or first gumming unit. In another option, two different replenishing solutions can also be added to one gumming unit, e.g. a starting gum solution and water.

In another embodiment of the present invention, the gum solution used in each of the gumming units may be regenerated by removing of insoluble material present in the gum solution of a gumming unit. The presence of insoluble material in the gum solution may be caused by several reasons, e.g. by developing of a pigment containing coating, by evaporation of solvent or water of the gum solution, or by sedimentation, coagulation or flocculation of components in the gum solution. The insoluble material can be removed continueously or in batch form by several techniques such as filtration, ultrafiltration, centrifugation or decantation. A suitable apparatus for disposing a waste developing solution such as the gum solution of the present invention is described in EP-A 747 773. The apparatus can be connected to the tank of a gumming unit to regenerate the used gum solution by circulation of the gum solution over a filter or a filter membrane. The gum solution can be circulated over the filter or filter membrane continuously, periodically or during the development time, or the circulation is regulated by the measurement of the turbidity or transparency (i.e. optical transmission) of the gum solution whereby the circulation starts when the turbidity exceeds an upper value and stops when a under value is reached. The upper and under turbidity value can be chosen in relation to the desired degree of purification, generally the optical transmission of the gum solution is not lower than 50% of its value at starting, preferably not lower than 80%, more preferably not lower than 95%.

Drying

According to another embodiment of the present invention, the plate can be dried after the gum-processing step in a drying unit. In a preferred embodiment the plate is dried by heating the plate in the drying unit which may contain at least one heating element selected from an IR-lamp, an UV-lamp, a heated metal roller or heated air. In a preferred embodiment of the present invention, the plate is dried with heated air as known in the drying section of a classical developing machine.

Baking

According to another embodiment of the present invention, the plate can be heated in a baking unit, optionally after drying the plate. In a preferred embodiment of the present invention, when the plate is heated in a baking unit, the precursor is developed by using a baking gum and the gum solution is preferably replenished by adding a replenishing baking gum. Said replenishing baking gum is a solution which may be selected from a starting baking gum, i.e. a solution having the same composition as the baking gum used at the start of the development, a concentrated baking gum or a diluted baking gum, i.e. a solution having a higher respectively lower concentration of additives than the starting baking gum, and water.

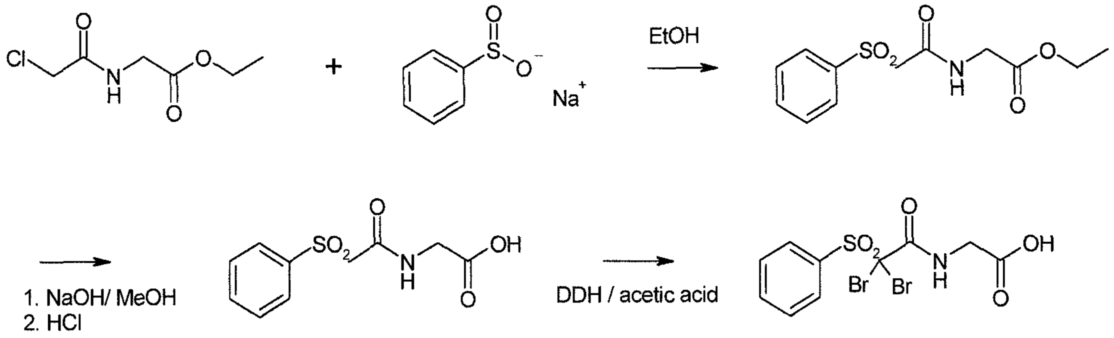
The baking unit may contain at least one heating element selected from an IR-lamp, an UV-lamp, a heated metal roller or heated air. The plate is preferably heated in the baking unit at a temperature above 150°C and less than the decomposition temperature of the coating, more preferably between 200°C and 295°C, most preferably between 250°C and 290°C. A longer heating time is usually used when a lower heating temperature is used, and a shorter heating time is used when a higher heating temperature is used. The plate is preferably heated over a time period of less than 10 minutes, more preferably less than 5 minutes, most preferably less than 2 minutes.

In a preferred embodiment of the present invention, the plate is heated by the method as described in EP-A 1 506 854. In another preferred embodiment of the present invention, the plate is heated by the method as described in WO 2005/015318.

In another embodiment of the present invention, the drying step and the heating step may be combined in one single step wherein the plate, after the gum-developing step, is dried and heated in an integrated drying-baking station.

EXAMPLES

The synthesis of BS-3 :



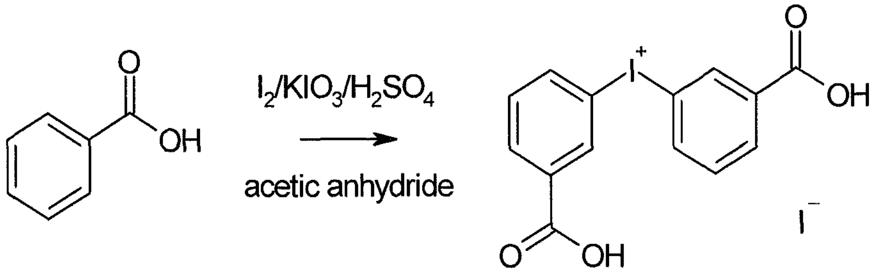
5 g (27.4 mmol) N-(chloroacetyl)-glycine ethyl ester (Aldrich) was dissolved in 50 ml methanol. 4.6 g (27.4 mmol) benzene sulfinic acid sodium salt was added and the mixture was refluxed for 16 hours. The precipitated sodium chloride was removed by filtration and the ethanol was evaporated under reduced pressure. The residue was treated with 80 ml hexane at 0°C. (2-benzenesulfonyl-acetamido)-acetic acid ethyl ester crystallized from the mixture, was isolated by fitration and dried. 7.8 g of the intermediate was isolated (92 %).

5 g (17.5 mmol) (2-benzenesulfonyl-acetamido)-acetic acid ethyl ester was dissolved in 30 ml methanol. 0.35 g (21.3 mmol) NaOH was added and the reaction was allowed to continue for 30 minutes at room temperature. The mixture was acidified to pH=2, using a 6N HCl-solution. (2-benzenesulfonyl-acetamido)-acetic acid precipitated from the medium, was isolated by filtration, washed with 5 ml methanol and dried. 2.45 g of (2-benzenesulfonyl-acetamido)-acetic acid was isolated (54 %).

2 g (7.8 mmol) (2-benzenesulfonyl-acetamido)-acetic acid was added to 13.2 ml acetic acid. 2.3 g (7.8 mmol) dibromo-dimethyl-hydantoin (DDH) was added and the mixture was slowly heated to 95°C. The reaction was allowed to continue for 90 minutes at 95°C. The

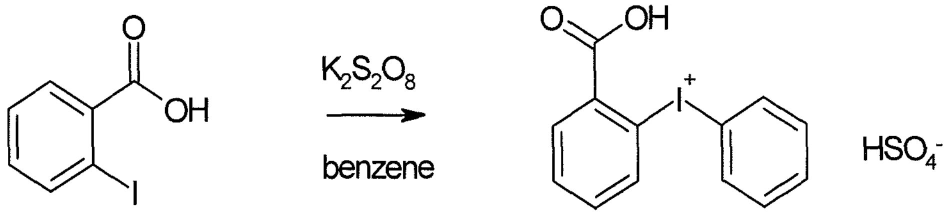
acetic acid was removed under reduced pressure and the residue crystallized upon standing. The residue was treated with 20 ml water and BS-3 was isolated by filtration , washed with water and dried. 2.3 g of BS-3 was isolated (71 %).

The synthesis of iodonium-2 :



A suspension of 7.7 g (30.4 mmol) iodine and 20 g (92.8 mmol) potassium iodate in 80 ml concentrated sulfuric acid was prepared. The suspension was cooled to 10 °C and 2 ml acetic anhydride and 38 g (312 mmol) benzoic acid was added while the temperature was kept below 10°C. The reaction was allowed to continue for 24 hours below 10°C, followed by 8 hours at room temperature. The reactionmixture was slowly added to 400 ml water. The crude diaryl iodonium salt was isolated by filtration. The isolated product was treated with 100 ml diethyl ether and water. The aqueous solution was treated with a solution of 25.8 g (155 mmol) potassium iodide and 0.1 g sodium dithionite. The mixture was stirred for 24 hours at room temperature. The product was isolated by filtration, washed twice with 25 ml water, twice with 25 ml diethyl ether and dried. 13.5 g of iodonium 2 was isolated (17.1%) (m.p. 150°C with decomposition).

The synthesis of iodonium-4 :



20 g (0.0807 mol) 2-iodo-benzoic acid was added to 80 ml HCl (conc.). The mixture was cooled to 10°C and 42 g (0.156 mol) potassium persulfate was added over 40 minutes while the temperature was kept at 10°C. The reaction was allowed to continue at 10°C for an additional 20 minutes. 75 ml benzene (**attention carcinogenic compound**) was added and the reaction was allowed to continue for 20 hours at room temperature. The reaction mixture was pourred into 200 ml ice and water. The mixture was stirred for 1 hour at room temperature. Iodonium-4 was isolated in an almost quantitave yield by filtration, washed with water and dried (m.p. 150°C).

Preparation of aluminum support S-1:

A 0.3 mm thick aluminum foil was degreased by spraying with an aqueous solution containing 26 g/l of NaOH at 65°C for 2 seconds and rinsed with demineralized water for 1.5 seconds. The foil was then electrochemically grained during 10 seconds using an alternating current in an aqueous solution containing 15 g/l of HCl, 15 g/l of SO_4^{2-} ions and 5 g/l of Al^{3+} ions at a temperature of 37°C and a current density of about 100 A/dm^2. The aluminum foil was then desmutted by etching with an aqueous solution containing 5.5 g/l of NaOH at 36°C for 2 seconds and rinsed with demineralized water for 2 seconds. The foil was subsequently subjected to anodic oxidation during 15 seconds in an aqueous solution containing 145 g/l of sulfuric acid at a temperature of 50°C and a current density of 17 A/dm^2, then washed with demineralized water for 11 seconds and post-treated for 3 seconds by spraying a solution containing 2.2 g/l of polyvinylphosphonic acid at 70°C, rinsed with demineralized water for 1 seconds and dried at 120°C for 5 seconds.

The support thus obtained was characterized by a surface roughness Ra of 0.37 µm, measured with interferometer NT1100, and had an anodic weight of 3.0 g/m^2.

Preparation of aluminum support S-2:

The preparation of this support is carried out in the same way as described for support S-1 with the exception that the polyvinyl phosphonic acid layer is partially removed by treatment with PD91, a water-based alkaline developer solution, commercially available from Agfa-Gevaert, followed by washing with water.

Preparation of intermediate layer I-1:

The coating composition for the intermediate layer I-1 was prepared by mixing the ingredients as specified in Table 1. The resulting solution was coated with a bar-coater on support S-2. After coating, the plate was dried for 1 minute at 120°C in a circulation oven. The resulting applied amount is 0.08 g/m^2.

Table 1: Compositions of the intermediate layer solutions and thickness of dried layer.

COMPOSITION / INGREDIENTS	I-1
Sipomer PAM 100 (1) (g)	1.0
Dowanol PM (2) (g)	125
Dry thickness (g/m^2)	0.08

(1) Sipomer PAM 100 is a phosphate functional speciality methacrylate monomer, obtained from RODIA. This compound was treated by extraction with methyl-tert-buthylether, collection of the mower phase, and subsequent addition of 250 ppm (parts per million) of para-methoxyphenol.

(2) Dowanol PM is propylene glycol monomethylether, trade mark of Dow Chemical Company.

Preparation of photosensitive layer P-1:

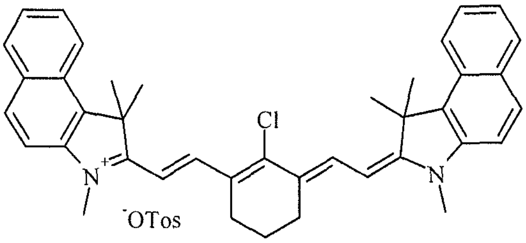
The coating composition for the photosensitive layer P-1 was prepared by mixing the ingredients as specified in Table 2. The resulting solution was coated with a bar-coater on the intermediate layer I-1. After coating, the plate was dried for 1 minute at 120°C in a circulation oven. The resulting thickness was 0.75 g/m^2.

Table 2: Compositions of the photosensitive layer solution.

COMPOSITION / INGREDIENTS	P-1
ALCOTEX 552P (1) (g)	3.75
IR-dye-01 (2) (g)	0.1775
BS-3 (3) (g)	0.2222
FST 426R (4) (g)	2.038
Edaplan LA411(7) (g)	0.375
Dowanol PM (g)	39.62
Dry thickness (g/m^2)	1.48

(1) Alcotex 552P is a 40% by weight solution in water of polyvinylalcohol having a hydrolysis degree of 55 mol%, commercially available from Synthomer

(2) IR-dye-01 has the following structure



wherein $^{-}$OTos represents a tosylate anion

(3) BS-3 is an initiator according to the present invention

(4) FST 426R is a solution in 2-butanone containing 88.2 % by weight of a reaction product from 1 mole of 2,2,4-trimethyl-hexamethylenediisocyanate and 2 moles of hydroxyethylmethacrylate (viscosity 3.30 mm^2/s at 25°C)

(5) Edaplan LA411 is a surfactant (solution of 10 % by weight in Dowanol PM® trade mark of Dow Chemical Company) obtained from Munzing Chemie.

Preparation of overcoat layer OC-1:

On top of the photosensitive layer P-1 a solution in water with the composition as defined in Table 3 was coated and was dried at 110°C for 2 minutes. The so-formed protective overcoat OC-1 has a dry thickness of 2.0 g/m^2.

Table 3: Composition of overcoat solution.

COMPONENT	OC-1
partially hydrolyzed polyvinylalcohol (degree of hydrolysis 88 %, viscosity 4 mPa•s in a solution of 4 wt.% at 20 °C) (g)	17.03
partially hydrolyzed polyvinylalcohol (degree of hydrolysis 88 %, viscosity 8 mPa•s in a solution of 4 wt.% at 20 °C) (g)	7.43
fully hydrolyzed polyvinylalcohol (degree of	14.87

hydrolysis 98 %, viscosity 6 mPa•s in a solution of 4 wt.% at 20 °C) (g)	
Acticide LA1206 (1) (g)	0.26
Metolat FC 355 (2) (g)	0.38
Lutensol A8 (90%) (3) (g)	0.032
Water (g)	960

(1) Acticide LA1206 is a biocide, commercially available from Thor

(2) Metolat FC 355 is an ethoxylated ethylenediamine, commercially available from Münzig Chemie

(3) Lutensol A8 (90% by weight) is a surface active agent, commercially available from BASF

Preparation of the printing plate

After drying of the overcoat layer, the plates were imaged with a Creo Trendsetter IR laser (830 nm) at different energies between 100 and 275 mJ/cm^2.

After exposure, the precursor was processed with Gum-1 solution.

Gum-1 is a solution prepared as follow:

To 750 g demineralised water
100 ml of Dowfax 3B2 (commercially available from Dow Chemical)
31.25 g 1,3-benzene disulphonic acid disodium salt (available from Riedel de Haan)
31.25 ml Versa TL77 (a polystyrene sulphonic acid available from Alco Chemical)
10.4 g trisodium citrate dihydrate,
2 ml of Acticide LA1206 (a biocide from Thor),
2.08 g of Polyox WSRN-750 (available from Union Carbide) were added under stirring and demineralised water was further added to 1000 g.

pH is between 7.2 and 7.8

After gum processing, the plates were mounted on a Heidelberg GTO52 printing press and a print job was started using K + E Novavit 800 Skinnex ink (trademark of BASF Drucksysteme GmbH) and Prima FS101 as fountain liquid, compressible blanket and by using offset paper. The plate exhibits a good clean -out, i.e. a complete removal of the coating at the non-exposed areas, and good prints were obtained on the press.

■

[CLAIMS]

1. A method of making a lithographic printing plate comprising the steps of:
   a) providing a lithographic printing plate precursor comprising
      (i) a support having a hydrophilic surface or which is provided with a hydrophilic layer,
      (ii) a coating on said support, comprising a photopolymerizable layer, and, optionally, an intermediate layer between the photopolymerizable layer and the support,

   wherein said photopolymerizable layer comprises a polymerizable compound, a polymerization initiator and a binder,
   b) image-wise exposing said coating by a laser in a plate setter,
   c) optionally, heating the precursor in a preheating unit,
   d) developing the precursor off-press in a gumming unit by treating the coating of the precursor with a gum solution, thereby removing the non-exposed areas of the photopolymerizable layer from the support,

   wherein said polymerization initiator comprises a solubilizing group capable of solubilizing the initiator in the gum solution.

2. A method according to claim 1, wherein said initiator comprises at least one of the following compounds selected from an alfa-di- or tri-bromo alkyl sulphone, a tri-bromo acetamide, a di-aryl iodonium, a di-aryl alkyl sulphonium, a tri-aryl sulphonium, a tri-bromo aryl ketone, a tri-bromo heteroaryl ketone or a tri-halo methyl triazine, wherein each of these compounds further comprises a solubilizing group capable of solubilizing the initiator in the gum solution.

3. A method according to claim 2, wherein said photopolymerizable layer further comprises an IR-dye, capable of interacting with said initiator to form initiating radicals by exposure to IR-light or heat.

4. A method according to any of the preceding claims, wherein said laser emits infrared light.

5. A method according to claim 1, wherein said initiator comprises a hexa-aryl bisimidazol which further comprises a solubilizing group capable of solubilizing the initiator in the gum solution.

6. A method according to claim 5, wherein said photopolymerizable layer further comprises an violet dye, capable of interacting with said initiator to form initiating radicals by exposure to violet-light.

7. A method according to any of claim 1, 2, 5 or 6, wherein said laser emits violet light.

8. A method according to any of the preceding claims, wherein said solubilizing group is an anionic group, a cationic group or a polyalkylene oxide group.

9. A method according to any of the preceding claims, wherein said solubilizing group is selected from one of the following groups: a carboxylic acid or a salt thereof, a sulphonic acid or a salt thereof, a sulfuric acid hemi ester or a salt thereof, a phosphonic acid or a salt thereof, a phosphoric acid derivative or a salt thereof, an acyl sulfonamide or a salt thereof, a phenol, an ammonium salt, a sulfonium salt, a phosphonium salt, an oligo ethylene oxide, a hydroxyl group or an oligohydroxy group.

10. A method according to any of the preceding claims, wherein said solubilizing group is a carboxylic acid or a salt thereof, a sulphonic acid or a salt thereof.

11. A method according to any of the preceding claims, wherein said solubilizing group is linked to said initiator by a linking

group.

12. A method according to any of the preceding claims, wherein said initiator comprises two or more of said solubilizing groups.

13. A method according to any of the preceding claims, wherein said gum solution has a pH-value ranging between 3 and 9.

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