(54) Abstract Title: Photopolymer composition curable by ambient light

(57) The invention provides a composition comprising a solid photopolymer e.g. a photopolymer resin, which is adapted to be curable in ambient light. Also included in the present invention are methods of making a photopolymer printing plate for use in e.g. stamp production. The solid photopolymer may be a liquid at temperatures above 50 degrees C and a gel at temperatures below 50 degrees C, and may be an unsaturated polyester resin, and unsaturated polyurethane resin etc.
COMPOSITIONS AND METHODS RELATING TO PHOTOPOLYMER

The present invention relates to a method of making printing plates for, for example, business and craft use. The present invention also relates to photopolymer compositions useful for making for example printing plates.

Background

Currently, photopolymer printing plates are in practice hardened by exposure to radiation predominantly emitted in the ultra violet part of the spectrum. The light source may be composed of a set of UV light emitting fluorescent tubes emitting mainly UVA energy between 340nm and 390nm, typically peaking at 365nm. The image is then created by the interposition of a masking element between the photopolymer and the light source. This mask prevents the light from reaching the photopolymer in the parts where it is black and thus the photopolymer remains uncured. The uncured material is then typically removed by washing in a solvent. These parts are where there will be no ink transference in the finished plate. The clear areas of the mask allow light through which hardens the photopolymer and these become the parts that transfer ink to make the image.

Conventional photopolymer used in the manufacture of hand stamps and flexographic printing plates has a reactivity, measured by determining the depth of cure in mm when exposed to light of a typical intensity of between 6-12 mW/cm² at a wavelength of 340nm for 30 seconds, giving 0.8-1.4mm of cured polymer. When this photopolymer is exposed to daylight of much lower intensity the rate of cure is far too long to be practically useful.

There are disadvantages in using UV light to cure photopolymer to produce printing plates. The use of UV light to cure photopolymers results in a need to for specially designed equipment. Furthermore, there is a potential danger risk of UV damage to a user's eyes when using UV light in the curing process. This is of particular importance if the user is unskilled or untrained in the art of curing of photopolymers, for example, to make printing plates.

Photocentric Limited of Peterborough, England has produced liquid photopolymers which are curable in ambient light and thus which overcome some of the disadvantages associated with UV-curable photopolymers. These ambient light-curable liquid photopolymers are described in GB2422678. The liquid photopolymer described therein
comprises visible light curing photoinitiators and, optionally when sealed in a plastic sachet, can be used to make stamps. This system has been commercialised in the Imagepac® home stamp making system produced by Photocentric Limited of Peterborough, England.

In the system disclosed in GB2422678, the sachet is compressed between two planar parallel sheets of light transmitting material prior to hardening to force the sachet to adopt the desired shape of the resultant stamp, since the sachet of liquid photopolymer may take on any physical shape gravity or other forces dictate. The sachet is then exposed to daylight from one side to produce a solid floor or support to the image part of the stamp, and from the other side to produce a relief or the image forming part of the stamp. Thus, the user typically uses a method of clamping or restraining the sachet of liquid into the required shape. The user typically first exposes the floor to the stamp to support the relief.

BRIEF DESCRIPTION OF THE INVENTION

In a first aspect of the present invention, there is provided a composition comprising a solid photopolymer resin which is adapted to be curable in ambient light to form a printing plate. Included in the invention are such compositions comprises one or more ambient light activated photoinitiators.

In a second aspect of the invention, there is provided a method of making a composition as described herein, comprising mixing a photopolymer resin which is solid at room temperature with an ambient light activated photoinitiator.

In a further aspect of the invention, there is provided a method of making a printing plate comprising exposing the composition of the present invention to an ambient light source. In one embodiment, the method comprises: uniformly exposing a first face of the composition to form a floor; and then imagewise exposing a second face of the composition to form a printing surface. In one embodiment, the method is for making a hand stamp or the like.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", means
including but not limited to, and is not intended to (and does not) exclude other moieties, additives, components, integers or steps.

Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith.

**Detailed Description**

A first aspect of the present invention relates to a composition comprising a solid photopolymer resin which is adapted to be curable in ambient light to form a printing plate. The resin may be cured to form a printing plate made from the cured photopolymer. The invention includes the use of such compositions to make a relief plate, useful for example in flexography, hand stamps or craft stamps. The printing plates may consist entirely of the cured polymer resin or may additionally contain, in particular, a backing plate.

In embodiments, the resin is in the form of a sheet which may be converted to a relief printing plate using imagewise exposure to ambient light. After exposure, the resin may go through usual post-exposure processing, and in particular uncured resin is removed to form the relief pattern.

The present invention is concerned with solid photopolymer resin compositions which are adapted to be curable in ambient light. The term "solid photopolymer" as used herein includes, although is not limited to, photopolymers which are non-fluid, for example photopolymers which have a gel or gel-like structure prior to curing. That is to say, in embodiments of the present invention, the photopolymer resin is a gel. A gel may have a similar density to a liquid but have the structural coherence of a solid. Typically, the photopolymer of the present disclosure is a gel at room temperature prior to exposure. Preferably, the photopolymer of the present invention is a solid up to about
30°C, particularly up to about 35°C, and more particularly is a solid up to about 40°C. In embodiments of the invention, the photopolymer is a solid up to about 50°C. A solid photopolymer resin as used in the present invention may be a liquid at temperatures higher than about 50°C.

The term "solid photopolymer" as used herein excludes photopolymers which are liquid at room or ambient temperature. Room temperature can be typically considered to be from about 10°C to about 30°C. In one embodiment, the solid photopolymer used in the present methods, products and compositions is a photopolymer which is a solid up to about 50°C prior to curing but which may be a liquid at temperatures above about 50°C (prior to curing).

Examples of solid photopolymers resin which are gel-like that can be used in the present invention include those which are produced from, for example, unsaturated polyester resins, unsaturated polyurethane resins, unsaturated polyamide resins and unsaturated poly(meth)acrylate resins, for example polyether urethane polymers, polyether polyester urethane copolymers e.g. polyether polyester urethane methacrylate.

In one embodiment, the composition which comprises an ambient light activated photoinitiator. In one embodiment, the photoinitiator is active at a wavelength above about 370nm, optionally at above 400nm. In one embodiment, the solid photopolymer is selected from a heat pressed sheet photopolymer, a solvent-cast sheet photopolymer and an extruded sheet photopolymer. In one embodiment, the photoinitiator is selected from an aromatic phosphine oxide compound, a metallocene compound, a titanocene compound, a camphor quinone compound and combinations thereof. Further examples of photoinitiators which may be used in the present invention are described below.

In one embodiment, the solid photopolymer is a liquid photopolymer at temperatures above 50°C and a gel at temperatures of less than about 50°C. In an embodiment, the composition comprises a gelling agent. In one embodiment, the photopolymer is a liquid and free flowing at greater than 50°C and is a solid at less than 50°C, in particular at room temperature.

In one embodiment, the compositions include a gelling agent, for example polyethylene glycol, stearic acid esters, hydroxy stearic acid, polysaccharides and acylamino acid-amine salts, condensation products of benzaldehyde and polyol such as pentaerythritol,
mannitol, xylitol, sorbitol and the like. In one embodiment, the daylight curable gel photopolymers are substantially soluble in the composition at less than about 130°C and solidify to a gel state on cooling and remain a gel until reheated to at least 50°C. The photopolymers may undergo reverse liquid to gel states on heating and cooling. In one embodiment, the photopolymers, when modified so as to be curable by ambient light, can resist deformation by a force of less than 50kPa at 25°C and are substantially transparent to daylight. In one embodiment, the photopolymer as modified has an elasticity of greater than about 1% e.g. 2%, 3% or greater.

In one embodiment, the photopolymer comprises a gelling agent which is soluble in the composition at less than about 130°C, more preferably less than 120°C. In one embodiment, the photopolymer forms a gel state on cooling and remain gel-like on reheating from ambient to at least 50°C. Typically, the gelling agent undergoes reverse liquid to gel states on heating and cooling (prior to curing).

In one embodiment, the gelling agent is stable, that is to say it does not decompose which allows the gel photopolymer composition to retain its gel property for a period of at least one year, preferably greater than two years. The concentration of the gelling agent in the composition is between about 0.1% and about 10% by weight based on the total composition weight. More preferably it is between about 1% and about 5%. The concentration of gelling agent depends upon the type of gelling agent used in the compositions of the present invention.

In one embodiment, the photopolymer is selected from an unsaturated polyester resin, an unsaturated polyurethane resin, an unsaturated polyamide resin, an unsaturated poly(meth)acrylate resin and combinations thereof. In one embodiment, the photopolymer resin has a viscosity of less than 10,000mPas at 100°C.

In some embodiments, the solid photopolymer of the present invention is not a gel but is a solid in the more traditional sense, e.g. Cyre® manufactured by DuPont or Nyloflex® manufactured by BASF, when modified to cure under ambient light. In one embodiment, the photopolymer is in the form of a solid sheet or block.

In one embodiment, the composition of the present invention may comprise photopolymer as described in, for example, GB 2338238 (Cooke) when modified to be cured under ambient light. GB2338238 does not disclose a composition which is
suitable for use to produce printing plates which are produced using ambient light. Instead, the compositions are only suitable for curing in actinic light.

In one embodiment, the composition comprises a photopolymer, as described in EP 0453307, when modified to be cured under ambient light, in which a photocurable gel suitable for use as a printing plate undergoes a reversible reaction on heating and cooling. The compositions of EP 0453307 comprise polymers with moieties of isotactic and syndiotactic polymethyl methacrylate dissolved in photopolymerizable ethylenically unsaturated compounds and may also include 'oil gelating agents'. EP0453307 does not disclose a composition which may be used to form a printing plate when exposed to ambient light nor does it disclose printing plates or methods of producing printing plates using ambient light. Thus, in one embodiment, the composition comprises a photopolymer having isotactic polymethyl methacrylate moieties or syndio tactic polymethyl methacrylate moieties or combinations thereof.

In an embodiment, the composition comprises a photopolymer which may be manufactured as described in US 2760863 (Plambeck), when modified to be cured under ambient light, and can be formed by conventional solvent-casting, extrusion or hot press process. However, this is not a preferred embodiment since the exposed printing plate must be washed out in solvents which is not particularly environmentally friendly and it is not desirable for untrained personnel to handle solvents.

In an embodiment, the composition comprises water washable sheet photopolymer as described in US 4023973 (Japan Synthetic Rubber Co), when modified to be cured under ambient light. The compositions described in US 4023973 are not adapted to being cured by ambient light.

Typically, the photopolymer resin has a hardness of between about 20 and about 90 Shore A. In one embodiment, the composition is adapted to form a moulding or embossing die when cured, is curable to a hardness of about 90 Shore A +/- 10 Shore A. In some embodiments, the composition has a hardness, when cured, of up to 50 Shore A, 60 Shore A, 70 Shore A, 80 Shore A or 90 Shore A or a particular hardness from about 50 Shore A to about 90 Shore A.
The composition may be adapted to form a printing plate. In one embodiment, the composition is in the form of a block or a sheet. In one embodiment, the composition is of a thickness that results in a plate of between about 0.5mm and about 5mm.

The composition may further comprise a plastic cover over at least one surface of the composition, wherein optionally the plastic cover transmits light.

In a further aspect of the invention, there is provided a combination of the composition according to any preceding claim together with a masking element.

In one embodiment, the daylight curable photopolymer composition comprises photoinitiators which are active in the visible part of the spectrum i.e. 350 nm or more and typically more than 370nm, and even more typically more than 400nm. The composition may comprise a solid photopolymer preparation. Known solid photopolymer preparations contain UV activated photoinitiators and therefore are not adapted to be curable in ambient light. Thus, the photopolymer of the present invention may be crosslinked or polymerised by ambient light activated photoinitiators that are predominantly active in the visible part of the spectrum.

The use of ambient light activated photoinitiators provides benefits to the user in that they can now make printing plates without costly, specially designed exposure equipment. The light required to harden the solid photopolymer of the present invention is readily available from a 60W standard light bulb.

In the present invention, the composition may comprise ambient light, e.g. daylight, activated photoinitiators as described in the preceding paragraphs. If conventional UV activated photoinitiators are used, the exposure times required to cure the photopolymer in natural or artificial ambient light are elevated beyond those practically acceptable. For example, if the photopolymer is manufactured utilising 1% benzophenone (a UV photoinitiator) as the photoinitiator, the depth of cure with a 60W light as the illumination source for a time of 60 minutes would be of the order of 0.2mm. Increasing the concentration of benzophenone was not found to substantially increase the rate of cure. Practically, to be functionally usable the photoinitiators must initiate hardening to a depth of 1mm in about 2 minutes, and thus the composition must contain photoinitiators active in the same part of the spectrum as the light source.
In one embodiment, the composition of the present invention comprises photoinitiators which are free radical generators and initiate radicals either by molecular cleavage or by hydrogen abstraction. In alternative embodiments, the photoinitiator is a photoinitiator that interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction are in general hydrogen abstraction or photoinduced electron transfer.

Typically, the photoinitiator is present in the composition in a concentration of between about 0.1% to about 10% by weight based on the total weight of the composition. More typically, the composition comprises a photoinitiator in a concentration of between about 0.5% to about 5%, optionally between about 0.5% to about 3%. In one embodiment, the photoinitiator is in a concentration of about 1% by weight.

It is a further development of embodiments of this invention is that the photopolymer has been modified to improve its usability in both sunlight and artificial ambient light. In this respect, it is desirable that the photopolymer reacts under ambient artificial light with sufficient speed to cure to a suitable depth in a reasonable period of time such that a user can complete each stage of its operation without excessive waiting, whilst at the same being stable in manufacture, transit and in use.

In one embodiment, the photopolymer composition comprises a combination of UV photoinitiators and visible light activated photopolymers.

Photoinitiators that are predominantly active in the visible part of the spectrum are then typically combined with UV activated photoinitiators to provide activation under visible light and depth of cure. Acrylated phosphine oxides typically exhibit extinction coefficient maxima in the far UV to near visible region of the electromagnetic spectra, typically 390-420nm. The inclusion of this type of initiator in the formulation allows the product to cure both under UV and ambient light. The inclusion of these types of photoinitiators can be as a blend with other types to ensure activity in both the UV-A and the near visible region of the electromagnetic spectrum. A typical example of a blend is Irgacure® 2022, a liquid blend of bisacyl phosphine oxide and alpha hydroxy ketone produced and marketed by Ciba Geigy.

In one embodiment of the present invention, the visible light activated photoinitiator may be an organic aromatic carbonyl compound, for example, unsubstituted or substituted benzophenones e.g. benzophenone, 4-bromobenzophenone, 4,4'-
dichlorobenzophenone, 4,4'-dimethoxybenzophenone, 4-methylbenzophenone, 4-hydroxybenzophenone, 3,5-dihydroxybenzophenone, 4-phenylbenzophenone and deoxybenzophenone; unsubstituted or substituted acetophenones e.g. acetophenone, 4-methylacetophenone, 3,5-dimethylacetophenone, 4-methoxyacetophenone, 2-chloroacetophenone, 4-chloroacetophenone, 2-chloro-3-nitroacetophenone, 2-chloro-5-nitroacetophenone, 2,6-dimethoxyacetophenone, 4-hydroxyacetophenone, α-phenylacetophenone and α,α-dichloroacetophenone; unsubstituted or substituted aromatic ketones e.g. deoxybenzoin, phenyl naphthyl ketone, benzoin methyl ether, benzoin ethyl ether, benzoin n-propyl ether, benzoin isopropyl ether, benzoin n-butyl ether, benzoin isobutyl ether, benzoin t-butyl ether and other alkyl ethers of benzoin, and α-diketones such as benzil; and various quinone compounds e.g. p-benzoquinone, 2,5-dimethyl-p-benzoquinone, 2,6-dichloro-p-benzoquinone, 9,10-anthraquinone, 2-methyl-9,10-anthraquinone, 2-ethyl-9,10-anthraquinone, 2-bromo-9,10-anthraquinone, 2-ethyl-5,6,7,8-tetrahydroanthraquinone, 1,4-naphthoquinone, 2,3-dichloronaphthoquinone, 2,3-dimethyl-1,4-naphthoquinone, 2-ethyl-1,4-naphthoquinone, phenanthraquinone and 1,2-naphthoquinone.

In one embodiment, the blend of photoinitiator is aromatic bisacylated phosphine oxides which afford coverage across the region of 370-440nm of the electromagnetic spectrum; e.g. blends sold under the trade name Lucerine (BAPO-1; BASF), and bis(2,4,6-trimethylbenzoyl) phenyl phosphine oxide (BAPO-3) and their commercially available blends.

In one embodiment the photoinitiator is an organometallic-based visible light photoinitiator e.g. a titanocene compounds e.g. cyclopentadienyl bis 2,6 Difluoro-pyrrol. The trade name of such Irgacure 784 which is manufactured by Ciba. Examples of other titanocene compounds include a titanocene compound in bis(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)diphenyltitanium, bis(cyclopentadienyl)bis(2,3,4,5,6-pentafluoro-phen-1-yl)titanium, bis(cyclopentadienyl)bis(2,3,5,6-tetrafluorophen-1-yl)titanium, bis(cyclopentadienyl) bis(2,4,6-trifluorophen-1-yl)titanium, bis(cyclopentadienyl)bis(2,6-difluorophen-1-yl)titanium, bis(cyclopentadienyl)bis(2,4-difluorophen-1-yl)titanium, bis(methylcyclopentadienyl)bis(2,3,4,5,6-pentafluorophen-1-yl)titanium, bis(methyl-cyclopentadienyl)-bis(2,3,5,6-tetrafluorophen-1-yl)titanium, bis(methylcyclopenta-diencylbis(2,4-difluorophen-1-yl)titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(pyr-1-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(methylsulfonamido)-
In one embodiment, the photoinitiator is selected from bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-pentyl-2,2-dimethylbutanoyl)amino]phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-hexyl)-2,2-dimethylbutanoyl]phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-methylbutyl)amino]phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-methylpentanoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-ethylcyclohexyl)carbonylamino]phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-ethylisobutyrylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,2,5,5-tetramethyl-1,2,5-diazadisilolidin-1-y1)phenyl]titanium,
(bis-cyclo-pentadienyl)bis[2,6-difluoro-3-(octylsulfonamido)phenyl]titanium, 
bis(cyclopenta-di-enyl)bis[2,6-difluoro-3-(4-tolylsulfonamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(4-dodecylphenylsulfonlamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(4-(1-pentylhexyl)phenylsulfonamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(ethylsulfonlamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-((4-bromophenyl)sulfonlamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-naphthylsulfonlamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(hexadecylsulfonlamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-methyl-(4-dodecylphenyl)sulfonlamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-methyl-4-(1-pentylhexyl)-phenyl)sulfonlamido]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-hexyl-4-tolylsulfonlamido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(pyrrol-2,5-dione-1-yl)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3,4-dimethyl-3-pyrrrolidine-2,5-dione-1-yl)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(phthalimido)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-isobutoxycarbonylamino)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(ethoxy)carbonylamino)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-chloroethoxy)carbonylamino)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-chloroethoxy)carbonylamino)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(phenoxycarbonylamino)phenyl]titanium, 
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-phenoxythiourea)phosphorylamino]titanium, 
(bis-cyclo-pentadienyl)bis[2,6-difluoro-3-(3-phenoxythiourea)phosphorylamino]titanium.
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-butyli-thioureido)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-phenylureido)-phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-butyli-thioureido)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N,N-diacyetylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3,3-dimethylureido)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(acetylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(butylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(butylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(decanylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(octadecanolamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(isobutylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-ethylhexanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-methylbutanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-methylbutanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,2-dimethylbutanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-ethyl-2-methyl-heptanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(cylohexycarbonylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,2-dimethyl-3-chloropropanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-phenylpropanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-chloromethyl-2-methyl-3-chloropropanoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(3,4-xyloylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(4-ethylbenzoylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,4,6-mesitylcarbonylamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(benzoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-3-phenylpropyl)benzoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-3-ethylheptyl)-2,2-dimethylpentanoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-isobutyl-(4-tolylalamo)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-isobutylbenzoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cylohexylmethypivaloylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(oxolan-2-ylmethyl)benzoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-isobutylbenzoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-3-phenylpropyl-(4-toluylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(oxolan-2-ylmethyl)-(4-toluy)-amino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(4-toluylmethyl)benzoylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-4-toluylmethyl)-(4-toluylamino)phenyl]titanium,
bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-butylbenzoylamino)phenyl]titanium,
diaryl)bis[2,6-difluoro-3-(N-butyloxyethyl)benzoyl]amino]phenyl]titanium, bis(cyclopenta-
diaryl)bis[2,6-difluoro-3-(N-benzyl)benzoylamine]phenyl]titanium, bis(cyclopenta-
diaryl)bis[2,6-difluoro-3-(N-2,4-dimethylpentyl)-2,2-dimethylpentanoylamino]phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,4-dimethylpentyl)-2,2-dimethylpentanoylamino]phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(4-tolyl)amino]phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,2-dimethylpentanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,2-dimethyl-3-ethoxypropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(2,2-dimethyl-3-allyloxypropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-
difluoro-3-(N-allylacetylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(2-ethylbutanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cyclohexylmethylbenzoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cyclohexylmethyl-4-tolyl)amino]phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-2-ethylhexyl)benzoylamino]phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-isopropylbenzoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-

In one embodiment, the photopolymer composition comprises bis(cyclopenta-
diaryl)bis[2,6-difluoro-3-(N-benzylbenzoylamino)phenyl]titanium, bis(cyclopenta-
diaryl)bis[2,6-difluoro-3-(N-benzyl-4-tolyl)amino]phenyl]titanium, bis(cyclopean-
tadienyl)bis[2,6-difluoro-3-(N-benzyl-4-tolyl)amino]phenyl]titanium, bis(cyclopenta-
diaryl)bis[2,6-difluoro-3-(N-2,4-dimethylpentyl)-2,2-dimethylpentanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(4-methylphenylmethyl)-2,2-dimethylpentanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-2-
methoxyethyl)-2,2-dimethylpentanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cyclohexylmethyl-2-ethyl-2-methylheptanoylamino)aminophenyl]titanium, bis(cyclo-
pentadienyl)bis[2,6-difluoro-3-(N-butyl-(4-chlorobenzoyl)amino)phenyl]titanium, bis-
(cyclopentadienyl)bis[2,6-difluoro-3-(N-hexyl-(2-ethyl-2-methylbutanoyl)-amino)-
phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cyclohexyl-2,2-dimethyl-
pentanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-oxolan-2-
ylethyl)-2,2-dimethylpentanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cyclohexyl-2-chlorobenzoyl)amino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(3,3-dimethyl-2-azetidinon-1-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-isocyanatom phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-ethyl-(4-tolylsulfonyl)amino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-hexyl-(4-tolylsulfonyl)amino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-butyl-(4-tolylsulfonyl)amino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-isobutyl-(4-tolylsulfonyl)amino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-butyl-(2,2-dimethyl-3-chloropropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(3-phenylpropanoyl)-2,2-dimethyl-3-chloropropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cyclohexylmethyl-(2,2-dimethyl-3-chloropropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-isobutyl-(2,2-dimethyl-3-chloropropanoyl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-butyl-(2-chloromethyl-2-methyl-3-chloropropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(butylthiocarbonylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(phenylthiocarbonylamino)phenyl]titanium or bis(methylcyclopentadienyl)bis[2,6-difluoro-3-(N-hexyl-2,2-dimethylbutanoylamino)phenyl]titanium.

In other embodiments, the photoinitiator is selected from bis(methylcyclopentadienyl)bis[2,6-difluoro-3-(N-hexyl-2,2-dimethylpentanoylamino)phenyl]titanium, bis(methylcyclopentadienyl)bis[2,6-difluoro-3-(N-ethylacetylamino)phenyl]titanium, bis(methylcyclopentadienyl)bis[2,6-difluoro-3-(N-ethylpropionylamino)phenyl]titanium, bis(trimethylsilylpentadienyl)bis[2,6-difluoro-3-(N-butyl-2,2-dimethylpropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(2-methoxyethyl)-trimethylsilylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-butylhexyldimethylsilylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-ethyl-(1,1,2-trimethylpropyl)dimethylsilylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-ethoxymethyl-3-methyl-2-azethi- odinon-1-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-allyl-
oxymethyl-3-methyl-2-azetidin-1-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(3-chloromethyl-3-methyl-2-azetidin-1-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-benzyl-2,2-dimethylpropanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(5,5-dimethyl-2-pyrroldinon-1-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(6,6-diphenyl-2-piperidinon-1-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(2,3-dihydro-1,2-benzisothiazol-3-one(1,1-dioxide)-2-yl)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-hexyl-4-chlorobenzoylamino)phenyl]titanium, bis(cyclopenta-dietyl)bis[2,6-difluoro-3-(N-hexyl-(2-chlorobenzoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-isopropyl-(4-chlorobenzoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(4-methylphenylmethyl)-(4-chlorobenzoylamino)phenyl]titanium.

Further embodiments include the use of one or more of the following photoinitiators:

bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(4-methylphenylmethyl)-(2-chlorobenzoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-benzyl-2,2-dimethylpentanoylamino)phenyl]titanium, bis(cyclopenta-dietyl)bis[2,6-difluoro-3-(N-(2-ethylhexyl)-4-tolyl-sulfonylamino)phenyl]titanium, bis(cyclopenta-dietyl)bis[2,6-difluoro-3-(N-(3-oxaheptyl)benzoylamino)phenyl]titanium, bis(cyclopenta-dietyl)bis[2,6-difluoro-3-(N-(3,6-dioxadecyl)benzoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(trifluoromethyl-sulfonylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(trifluoromethyl-acetilamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(2-chloro-benzo-yl)amino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(4-chlorobenzoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(3,6-dioxadecyl)-2,2-dimethylpentanoylamino)phenyl]titanium, bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-(3,7-dimethyl-7-methoxyoctyl)benzoylamino)phenyl]titanium, and bis(cyclopentadienyl)bis[2,6-difluoro-3-(N-cyclohexylbenzoylamino)phenyl]titanium.

In one embodiment the photoinitiator is selected from camphorquinone and 1-phenyl-1,2-propanedione, monoacylphosphine oxide, bisacylphosphine oxide, diaryliodonium salt and triarylsulfonium salt. In one embodiment, the photoinitiator may comprise a mixture of compounds, for example a mixture of one or more of the above named compounds.
In one embodiment, the photopolymer composition further comprises an activator which can be used together with a photoinitiator to enhance curing efficiency. In one embodiment, the activators may comprise tertiary amine and sulfinate compounds. Examples of activators which could be used in the present invention include, but are not limited to, e.g. ethyl 4-(N,N-dimethylamino) benzoate, 2-(ethylhexyl)-4-(N,N-dimethylamino) benzoate, N,N-dimethylaminomethyl methacrylate, N,N-dimethylaminophenethyl alcohol, sodium benzenesulfinate, and sodium toluenesulfinate.

In one embodiment, the photopolymer composition comprises a combination of camphoroquinone and a tertiary amine such as ethyl 4-(N,N-dimethylamino) benzoate, 2-(ethylhexyl)-4-(N,N-dimethylamino) benzoate, N,N-dimethylaminomethyl methacrylate, and N,N-dimethylaminophenethyl alcohol. In another embodiment, the composition comprises a combination of camphoroquinone and bisacylphosphine oxide and/or monoacylphosphine oxide.

In one embodiment, the photopolymer composition further comprises one or more performance-enhancing additives including, for example, esters of acrylic or methacrylic acid, stabilisers, defoamers, dyes and high molecular weight fatty acids. Examples of fatty acids which are particularly effective in ensuring a dry, tack-free surface after post-curing of the washed plate include for example myristic acid.

In a further embodiment of this invention, the solid photopolymer can be filled into sachets which have a rigid substrate on only one side. This substrate is typically made of a rigid material such as metal or plastic. It is then coated with a composition that will adhere to the photopolymer when illuminated with daylight. Typically the substrate could be aluminium, steel or polyester. The photopolymer material is filled to provide a level of curable solid that is between about 0.1mm and about 1mm thick, more typically between about 0.3mm and about 0.5mm thick. This plate then is exposed through only one side, that side being the opposite side to the rigid substrate, with daylight generated by a 60W bulb for a time of typically 15 minutes at a height of 20cm. The uncured material is washed off in water and detergent and the plate is placed back under water and under the light for a further 15 minutes to harden and become tack-free.

In one embodiment, the photopolymer resin composition comprises an imaging face and an opposing support face, wherein the support face comprises a layer of exposed i.e. cured photopolymer. The composition may be supplied to the user with a pre-exposed
support face. This support face may have a depth which provides adequate support to the image part of the imaging face and thick enough to provide integrity to the stamp, preferably, the support face is also thin enough such that the floor does not transfer ink when depressed onto the surface to be stamped. In one embodiment the support face is at least 0.5mm in depth and no more than about 0.5mm less than the total thickness. It is desirable that the floor is between ¼ and ⅓ of the total thickness of the stamp.

The support face is typically formed from uniformly exposed a surface of the photopolymer resin. The term "uniformly exposing" means that a masking element or photographic negative is not laid over the product to cause imagewise curing. Usually, the photopolymer composition is supported on a substantially horizontal surface, for example of a desk or table, such that it has an upper face exposed to ambient light to cause curing. In one embodiment, a first, upper, face is cured free of any masking element to form the support face, after which the composition is inverted to expose to ambient light a second, opposed face, which has a masking element placed over it to form the image face used to create the image transferred by the stamp.

In one embodiment, the composition comprises a plastic cover which protects the composition. This plastic film may transmit daylight without substantive diffraction or impedance, in which case the plastic film does not need to be removed before curing of the composition. The plastic can be selected from known plastics that transmit ambient light or daylight e.g. polythene, polyester and polypropylene etc.

In other embodiments of the present invention, the plastic cover may be removed from the composition prior to exposure of the imaging face of the product to ambient light. As a result, the imaging face of the composition is able to contact the masking element with limited air between the two, thus ensuring that light diffraction is minimised. Therefore, the present invention may offer the user enhanced imaging. When containing liquid polymer in plastic, light transmission is the most important of the required properties. Since the plastic used in the composition of the present invention does not necessarily need to transmit light (although in some embodiments in which the plastic is not removed before exposure, light transmission of the plastic will be of importance) the type of plastic can be chosen for other desired properties, e.g. rigidity, resistance to denting and sealability. Thus, in some embodiments of the present invention, the plastic may confer functional qualities to the composition, e.g. rigidity, resistance to denting and sealability.
In one embodiment, the product comprising the composition is typically of approximately a standard paper size, e.g. an ISO paper size or US standard size (8½" x 11"), for example they may be of about the following dimensions in millimetres, e.g. of the following dimensions ± 10mm, e.g. ± 5mm such as, for example, ± 2mm:

<table>
<thead>
<tr>
<th>Size</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>297 x 420</td>
</tr>
<tr>
<td>A4</td>
<td>210 x 297</td>
</tr>
<tr>
<td>A5</td>
<td>148 x 210</td>
</tr>
<tr>
<td>A6</td>
<td>105 x 148</td>
</tr>
<tr>
<td>A7</td>
<td>105 x 74</td>
</tr>
</tbody>
</table>

In embodiments, the composition, and therefore the printing plate made from the composition, is of no greater than standard US paper size, or no greater than A3, A4, A5, A6 or A7 size, in all cases ± 10 mm, e.g. ± 5mm such as, for example, ± 2mm.

In one embodiment the composition comprises a solid photopolymer sheet or block which has the dimensions provided above. It was found that solid photopolymer of an area up to an A4 size (210mm x 297mm) can be practically exposed using a 60W lightbulb. By practically, it is meant that the exposure time has to be performed within an acceptable time period. The photopolymer can be manufactured with very high concentrations of photoinitiators, but their relative effect declines after an optimal concentration is reached. A light source can be elevated further away from the photopolymer to provide even light over a wider and wider area. However, lack of intensity couple with the reducing effect of the additional photoinitiators combine to produce a maximum usable size for a 60W bulb of about A4. It is possible to increase the bulb power, but these are not rated safe for standard lamp use because of the excessive heat generated. If the 60W bulb is positioned further away than about 25cm the exposure time increases to longer than about 15 minutes, which is considered undesirable. In embodiments where the light source is further away than about 25 or 30 cm and/or the photopolymer is of a size larger than about A4 size, the concentration of ambient light activated photoinitiators may be increased in order to enable the photopolymer to be cured by the ambient light source.

In embodiments of the present invention, the use of a solid photopolymer which is adapted to be curable in ambient light simplifies the stamp making process.
Embodiments of the present invention enable a user to expose a stamp on one side only, through their negative (or artwork mask), the other side having a layer that has been pre-exposed by the manufacturer. The resultant product provides advantages of cost and time over current methodologies.

Artwork can be produced directly from a printer connected to a personal computer, then simply laid on top of the imaging side of ambient light curable photopolymer block and exposed under ambient light e.g. a lightbulb. Any area of photopolymer which is masked from the ambient light source and therefore that has not been crosslinked or polymerised by the daylight may then be washed away in water.

In a further aspect of the present invention, there is provided a kit for producing a printing plate which comprises a product of the present invention as described herein and a material which is suitable as a masking element. The kit may also comprise an instruction leaflet which details how to make a printing plate from the product.

The present invention also provides a method of making a printing plate comprising exposing the composition of the present invention to an ambient light source. In one embodiment, the method comprises uniformly exposing a first face of the composition to form a layer; and then imagewise exposing a second face of the composition to form a printing surface. If the composition comprises a plastic cover, the method may further comprise removing at least one side of said cover before exposing the composition to ambient light.

In one embodiment, the ambient light source is selected from sunlight, daylight and artificial ambient light, e.g. a light bulb. In one embodiment, the method further comprises hardening the plate, wherein hardening the plate comprises an additional step of exposing the composition to ambient light or to heat e.g. from a hot air gun.

In one embodiment, the plate is post-exposed, e.g. under water. In one embodiment, the printing plate is a hand stamp and the method further comprises assembling a hand stamp from the plate.

The present invention also provides a method of making a composition as described herein, comprising mixing a photopolymer which is solid at room temperature with an
ambient light activated photoinitiator. In one embodiment, the photopolymer is mixed with the photoinitiator at a temperature at which the photopolymer is a liquid, and further wherein the mixture is cooled to a temperature at which it is a solid.

In one embodiment, the method further comprises one or more of the following steps:

(a) casting a liquid photopolymer composition onto a transparent sheet at a temperature above its pouring point;

(b) injection moulding a liquid photopolymer composition into a mould of the desired thickness for a stamp.

(c) extruding a liquid photopolymer composition into a sheet of the desired thickness for a printing plate;

(d) hot pressing a solid photopolymer into a sheet of the desired thickness for a printing plate; and

(e) filling a liquid photopolymer composition into plastic and cooling between plates set at the desired thickness for a printing plate.

In one embodiment, the solid ambient light curable photopolymer compositions can be shaped and formed as a solid layer of suitable thickness according to conventional solvent casting, i.e. dissolving the composition in a solvent, shaping the solution into a film or plate and removing the solvent. In other embodiments, extrusion calendaring or hot press techniques can also be used where the photocurable composition is extruded between two rollers at a maintained temperature set a given distance apart that dictates the total plate thickness. In an embodiment, when the photopolymer resin is liquid at high temperatures, the hot liquid photopolymer composition can be poured into a plastic tray to cool and take on the proportions of the tray when cooled. This tray can then be sealed with a plastic lidding film to make it suitable for shipment.

In one embodiment, the method comprises irradiating a surface of the composition with ambient light to cure the photopolymer resin, so that the product provided to a user has a support layer.

In one embodiment, the present invention comprises pre-exposing of a face of the composition to form a support face. Thus, the support face of the composition can be pre-exposed to uniform light such that the user (i.e. the printing plate maker) only has to expose the composition on one side, namely an image face through the printed mask. This is an advantage in that simplifies the process for the user by halving the number of
exposure operations they have to perform. Typically, the creation of the floor is the most time critical of the two exposure operations, so by performing this automatically during manufacture it removes the most common way of making a bad quality stamp, i.e. over or under exposure of the floor. The floor or support is the time-critical exposure, the exposure through the negative or mask is not critical, as long as the time is over the minimum to avoid under-exposure the stamp quality does not deteriorate quickly with increase in time.

It is a further advantage of the present invention that a solid photopolymer which is adapted to be cured in ambient light, has pre-determined outer dimensions which correspond to the outer dimension of a finalised printing plate. As a result, there is no need to supply additional light transmitting clamping equipment to restrain the sachet, as is the case with liquid photopolymer preparations.

In one embodiment, the method of producing a printing plate further comprises exposing the composition under an ambient light source under water to harden or de-tack the printing plate and to remove air.

In one embodiment, the light source to expose the solid ambient light curable photopolymer is a lightbulb. In one embodiment, the light source may be a 60W lightbulb, particularly although not exclusively a lightbulb carried in a height adjustable lamp. In other embodiments, the light source may be daylight or an artificial light source, other than a 60W light bulb.

In order to obtain a good quality product, it is necessary to monitor the intensity of the light to which the photopolymer is exposed and thereby to determine an appropriate exposure time through the negative to form the image and through the base to form the support or floor if not supplied in pre-exposed format. The invention therefore provides a light intensity measuring apparatus in the event that the composition is not pre-exposed.

It is a further advantage of supplying the composition with a pre-exposed floor that this light measuring device can be simplified to just a timer as the amount of light through the negative is less critical.

An first face of the photosensitive composition, positioned facing upwards towards a light source, is uniformly exposed to ambient light, that is to light from the sun or from an
artificial source of visible light, such that the photopolymer cures to form a floor. This step may be done by a user when making the printing plate or alternatively is pre-cured by a manufacturer of the product to provide the support or floor. In this embodiment, the composition is sold to a user with a cured supporting floor. If the user produces the floor, when the floor has been formed, the composition must be inverted such that the unexposed, formerly lower, face of the composition is placed uppermost with the masking element above it.

Prior to curing the composition, whether to produce a floor or to produce the image surface, the user may first remove the plastic covering. Depending on the nature of the plastic, this may not be essential although may be preferred in order to obtain a good quality image.

The upper surface of the photopolymer is cured imagewise by exposure to ambient light through the negative to form a printing surface. Thereafter the plate is washed out then dried, to form a printing plate, e.g. a hand stamp plate.

Ambient light, that is either sunlight or artificial light from lamps within buildings, contains UV radiation of varying wavelengths and varying intensities. For a good quality product, each face of the composition should be exposed to an optimum amount of light. An embodiment of this invention therefore includes light measuring apparatus, so that it may be determined when a suitable exposure time has been reached at which the requisite amount of ambient light has been transmitted to the composition to produce a suitably cured plate. Usually, the light measuring apparatus determines the exposure time and causes a signal to be produced when the exposure time has been attained.

If it desired to obtain an excellent product, it is critical to govern the amount of light reaching the photopolymer in order to ensure an accurately obtained floor height, typically between 20% and 50% of the total plate height, and a relief that is neither over nor under exposed. For this reason it is a further embodiment of this invention that the apparatus includes a measuring device that can inform the user when the correct time has elapsed for the user to expose the image face and/or the support face and then to terminate the reaction. For good results, this electronic device must be situated adjacent to the face of the exposure unit so that it takes readings that are representative of the intensity of light that is reaching the plate.
This electronic device suitably measures the intensity of light over a number of short time intervals (suitably every 1 sec) to calculate the correct exposure time for each side of the photopolymer container. Light may be measured using a photodiode capable of sensing emission in the UVA region of the electromagnetic spectrum, nominally 315nm - 400nm. It was found that the ideal choice of photodiode was one doped to absorb in both the UV and visible regions of the electromagnetic spectrum.

The diode is linked to a counting processor. The photodiode measures the intensity, which may be measured in mW/cm², and gives a corresponding output to the processor that counts the output. The processor counts the energy to a predetermined quantity based on the activity of the final photopolymer formulation. The predetermined energy level may be determined empirically. Once the desired level has been reached the processor outputs to an audible output or other signal producing device to indicate the completion of the process. The sequence is repeated either two or three times in total for back (depending on whether the back is pre-exposed by the manufacturer), imagewise and post exposures of the composition.

The typical operation of the electronic device is described as follows.

If a support face is not pre-exposed, the method is as follows: a first switch is operated to start monitoring the first exposure, or floor exposure. In one embodiment, the switch is in the form of a button which is held until an initiation signal is produced (e.g. a chirp is sounded), denoting that the monitoring has started; failure to produce a chirp or initiation signal indicates a low battery or other malfunction. This first exposure takes place with the composition on a flat surface in ambient light conditions such that the image side is at the bottom, nearest the work surface. By this means the bottom side of the plate is obscured from light and no curing can take place through the image side. At the end of this exposure a completion signal will be given, e.g. the piezo electric buzzer or other audible signal will sound, suitably at regular intervals for up to 5 minutes to signal the end of that cycle. The buzzer may be silenced at this time by pressing either button.

If the support face of the composition is pre-exposed, the above steps do not need to be taken.

The composition is then positioned so that the image face is uppermost with a photographic negative or other form of masking element is held against the imaging
face. In one embodiment, the masking element, which is selectively black and clear and represents the design the printing plate is intended to produce can be printed directly from a printer.

The method comprises either lying the masking element directly on top of the imaging side of the composition either on the plastic containing the composition or making contact with the composition itself which eliminates the presence of an inner air gap which would impair the resultant printed image. If the negative is placed directly on top of the composition, the negative and the photopolymer make contact removing air that would otherwise be entrapped the polymer has a light adhesion to the negative which prevents it from moving. If the negative is placed on the plastic then it will be free to move and air can be entrapped between the surfaces, in this case a simple clamp made out of transparent material is required to compress the negative and the composition.

A further embodiment of this invention comprises a combination of the composition with a timer or light measuring device that is preset with the required times for a given height of lamp or calculates the actual intensity of the light required to harden the photopolymer on both the support and the image sides. In the event that the composition is provided with a pre-exposed support or floor then the user only has to expose one side through the negative which is less critical in accuracy and can be performed with a simple timer given a rough distance of the light away from the composition. Specifically if the composition has an exposed support layer then only one button needs to be depressed and the composition will be exposed on the non-exposed side through the negative for typically for about 10 minutes. If the composition does not have a pre-exposed support layer then it must be exposed within a clamp to compress the negative and the composition. A button must be depressed to signal calculation of the correct time, typically this will be between ½ and a 1/10th of the main exposure time, more typically between 1/5th and 1/8th. This time will typically be around 2 minutes and will create a support of the desired depth. Then the clamp must be reversed and the composition must be exposed through the negative for the second time. If the composition still has its plastic cover on, this is removed using scissors or a knife. The plate is then washed out by hand. This must take place very soon after completion of the last exposure as curing will continue whilst the composition is exposed to ambient light. The cured plate is placed in wash out liquid and washed out, e.g. is placed in a tray of warm water and detergent and washed out using a soft brush. After being washed out the polymer plate is placed in tray of shallow water which may include certain mineral salts to improve the
removal of surface tack. After about 10 minutes the plate has been post exposed and is ready to be dried, mounted and used for printing.
Various aspects of the invention will now be particularly described with reference to the following examples:

EXAMPLES

Example 1 Daylight curing gelled liquid photopolymer

Liquid photopolymer was manufactured without the addition of any photoinitiators as follows, 50g of triblock copolymer of polycaprylactone-polyoxytetramethylene-polycaprylactone (molecular weight 2000, CAPA 720 from Solvay with OH value of 56.5 mg KOH/g, an acid value of less than 0.02mg KOH/g and a water content of 0.01%) was mixed with 100g of a triblock, oxyethylene oxyethylene copolymer (molecular weight 2000 and an oxyethylene content of greater than 30% Poly G 55-56, from Olin), 14.8g of toluene diisocyanate (Lupranat from Elastogran) and 20 ppm of dibutylin dilaurate (Aldrich). This was reacted for 90 minutes at 65°C. 22.5g of polypropylene glycol mono methacrylate (PPM5S low inhibitor from International Speciality Chemicals Ltd) were added to the reaction and the mixture was further reacted at 80°C until practically all of the isocyanate was consumed. 38g of this oligomer were placed in a glass reacting vessel and to it was added; 5g of laurylmethacrylate, 5g of polypropylene glycol monomethacrylate, 1g of triethylene glycol dimethacrylate, 1g of trimethylolpropane trimethacrylate and 0.02g of 2,6 Di-tert-butyl-4-methylphenol (Topanol from ICI). Finally 0.9g of the daylight photoinitiator, Lucerine TPO and 1g of the gelling agent dibenzylidenemonosorbitolacetal (Disorbene from Roquette) were added to the mixture. It was mixed at 130°C until the mixture became clear and air was removed by centrifugation. With the mixture at above 60°C (to keep it liquid), but below 85°C (to prevent the plastic in the sachet from distorting), 39g were filled into an A6 (137mm x 109mm) sized sachet. The sachet was made of 80my cast polypropylene, but could be any plastic that could be easily sealed and transmits daylight. The sachet was sealed without air entrapment and then allowed to cool between two glass sheets in a planar parallel manner. One side of the resultant sachet was then exposed to light from a 60W bulb positioned 10 inches away for a total of 90 seconds to create a floor.

A design was printed from computer onto suitable transparency film (overhead projector film for ink jet printers, polyester vellum for laser printers). The sachet was cut around its perimeter. The film covering the other (non-exposed) side of the sachet was removed. The printed image (mask) was then placed on top of the imaging side (the non-exposed side) of the sachet. Light from a 60W lamp was then illuminated onto the
mask for a total of 10 minutes to form an image. The non-polymerised gel was then removed by brushing in hot water, and the remaining solid polymer was the image-forming part of the stamp. This stamp was placed under water again and under the 60W bulb for a further 10 minutes until its surface was hard and dry to touch. The rear side of the film was removed, the stamp then had a naturally sticky back it could be mounted onto a suitable holder, inked and stamped and presented the user with an excellent representation of the original design.

Example 2 – Daylight curing water washable sheet photopolymer formed in an open tray

A maleic anhydride adduct (bonded maleic anhydride content, 17% by weight) of a 1,2-polybutadiene having a viscosity-average molecular weight of 92,000, a vinyl content of 94%, and a crystallinity of 25% was converted to lithium salt (100% equivalent of maleic anhydride in the adduct was converted to lithium salt). The lithium salt was dissolved in a tetrahydrofuran-water (3:1 by volume) mixture to yield a solution containing 10% by weight of the lithium salt. A photosensitive resin composition was prepared by thoroughly mixing 40g of the said lithium salt solution, 3.1g of nonaethylene glycol dimethacrylate, and 0.7g of Lucerne TPO at the reflux temperature of tetrahydrofuran. The resulting composition was poured into an A6 sized plastic tray and allowed to stand for 24 hours, and then dried at 60°C for 5 hours to form a photosensitive solid layer approximately 2.3mm in depth. The tray was exposed to light from a 60W bulb through its base for 30 seconds. The light transmitting properties of the plastic tray are not material in the creation of the floor. A printed mask was then made and was placed on the upper side of the block and the same light source was irradiated through the mask side for 8 minutes. The block was removed from the tray and the non-polymerised gel was then removed by brushing in hot water. This plate was placed under water again and under the 60W bulb for a further 10 minutes until its surface was hard and dry to touch. The rear side of the block had a naturally sticky back (as it was cured in contact with the plastic tray and in the absence of air). The stamp could be mounted onto a suitable holder, inked and stamped and presented the user with an excellent representation of the original design.
Example 3 – Daylight curing water washable sheet photopolymer formed in heat press

A solution of polytetramethylene glycol (29.0 parts, G-850), dimethyl propionic acid (62.0 parts), hexamethylene diisocyanate (119.0 parts) and n-butyl tin dilaurate (5.0 parts) dissolved in tetrahydrofuran (300.0 parts) was placed in a 1litr flask equipped with a stirrer. The flask was heated to 65°C, with stirring, and the reaction was continued for 3 hours. Hydroxyethyl methacrylate (26.0 parts) was added and the mixture was reacted while heating to 65°C for 2 hours. A solution of terminal amino group-containing acrylonitrile and butadiene oligomer (184.0 parts, Hycar ATBNX 1300 times 16) dissolved in tetrahydrofuran (270.0 parts) in a separate container was added to the contents of the flask at room temperature with stirring. The polymer solution was then dried under reduced pressure to remove tetrahydrofuran and a hydrophilic polymer was obtained. This polymer (10.5 parts), nitrile-butadiene rubber (33 parts, acrylonitrile 35%, NIPUL-1042), butadiene rubber (22 parts) oligobutadiene acrylate (29 parts) and 1,6-hexanediol dimethacrylate (3 parts), and dimethylbenzylketal (2 parts) and Lucerne TPO (0.2 parts) as the photoinitiator were kneaded with toluene (40 parts) and water (10 parts) in a heating kneader at 105°C. The toluene and water were evaporated under reduced pressure. The obtained photosensitive resin composition was filled into a sachet comprising of a laminate of 125 my polyethylene terephthalate film with an inner heat seal coating comprising of PVDC compounds. This sachet was filled to an overall thickness of 2.3mm and was sealed without air entrapment. The sachet was compressed evenly in a heat press at 105°C and 100 kg/cm² for 1 min. The compressed and now solid block was removed and one side was irradiated in light from a 60W bulb for 30 seconds. The sachet was cut around all four sides and the film of the non-irradiated side was removed and replaced by a negative mask. Light from the same source was irradiated through the mask side for a further 8 minutes. The non-polymerised gel was then removed by brushing in hot water at 50°C for 8 minutes. The plate was then dried using a hair dryer for a further 12 minutes. The other side of plastic that was protecting the floor was removed, the stamp block was mounted, inked and shown to provide an excellent representation of the original printed negative.

Example 4 – Daylight curing 90 durometer water washable gelled photopolymer moulding plate

A container of 100g of 90 durometer photopolymer moulding resin was obtained, for instance from Exell of Italy. The photopolymer was supplied without the addition of
photoinitiators. To it was added 1% of the gelling agent dibenzylidenedemonosorbitolacetal, 0.6% 1-Hydroxy-cyclohexyl-phenyl-ketone for instance Irgacure 184 from Ciba and 0.7% camphor quinone from Aldrich. The solution was heated in a flask and stirred for 60 minutes. A sachet of A7 size (105 x 74mm) comprising of polypropylene on the imaging side and polyester coated with 5g/cm² photoinitiator compound comprising of 64.8% MEK, 0.8% 2-4-6 Trimethylbenzoyldiphenylphosphine oxide, 0.5% camphor quinone, 15.7% copolymer of vinylidene chloride and acrylonitrile and 18.2% of Vinylidene chloride - vinyl chloride copolymer on the support side was manufactured. Whilst the solution was above 60 degrees C, 3.8g of the solution was filled into the sachet. The sachet was then placed in a vacuum chamber to remove the excess air and the sachet was sealed by direct impulse heat sealing. This sachet was immediately placed between two glass sheets 0.4mm apart in a planar parallel manner. The sheet was cooled at room temperature for 10 minutes. The resultant gelled sachet was cut and the imaging side of polypropylene was peeled off. The negative comprising of the image that the desired stamp was to be made from was placed on the imaging side, lying it down so as not to entrap air. A 60 W bulb illuminated the sachet from a height of 20cm for 10 minutes. The sachet was then cut around its perimeter and the imaging side of plastic was removed. The sachet was washed out in warm water and detergent with a soft brush to remove the remaining liquid photopolymer. The cleaned plate was placed under water and under the same light for 10 minutes. The plate was dried and was pressed into paper as an embossing plate deriving a perfect image of the negative.
CLAIMS

1. A composition comprising a solid photopolymer resin which is adapted to be curable in ambient light to form a printing plate made from the cured photopolymer.

2. The composition of claim 1, which comprises an ambient light activated photoinitiator.

3. The composition of claim 2, wherein the photoinitiator is active at a wavelength above about 370nm, optionally at above 400nm.

4. The composition of claim 2 or claim 3 wherein the solid photopolymer is a heat pressed sheet photopolymer.

5. The composition of claim 2 or claim 3 wherein the solid photopolymer is a solvent-cast sheet photopolymer.

6. The composition of claim 2 wherein the solid photopolymer is an extruded sheet photopolymer.

7. The composition of any of claims 2 to 6, wherein the photoinitiator is selected from an aromatic phosphine oxide compound, a metalloocene compound, a titanocene compound, a camphor quinone compound and combinations thereof.

8. The composition of any preceding claim, wherein the solid photopolymer is a liquid photopolymer, at temperatures above 50°C and a gel at temperatures of less than about 50°C.

9. The composition of any of claims 1 to 7, which further comprises a gelling agent and further wherein the photopolymer is selected from an unsaturated polyester resin, an unsaturated polyurethane resin, an unsaturated polyamide resin, an unsaturated poly(meth)acrylate resin and combinations thereof.
10. The composition of claim 8 wherein the photopolymer is a liquid and free flowing at greater than 50°C and is a solid at less than 50°C, in particular at room temperature.

11. The composition of claim 10 wherein the photopolymer resin has a viscosity of less than 10,000mPas at 100°C.

12. The composition of any preceding claim, wherein the photopolymer resin has a hardness of between about 20 and about 90 Shore A.

14. The composition of any preceding claim, which is adapted to form a printing plate.

15. The composition of any preceding claim, which is in the form of a block or a sheet.

16. The composition of claim 14 or claim 15, which further comprises a plastic cover over at least one surface of the composition, wherein optionally the plastic cover transmits light.

17. The composition of any of claims 14 to 16, which is adapted to form a moulding or embossing die when cured, wherein the composition is curable to a hardness of about 90 Shore A +/- 10 Shore A.

18. The composition of any of claims 14 to 17, which is of a thickness that results in a plate of between about 0.5mm and about 5 mm.

19. A combination of the composition according to any preceding claim together with a masking element.

20. A method of making a printing plate comprising exposing the composition of any of claims 1 to 18 to an ambient light source.

21. A method of claim 20, which comprises:
uniformly exposing a first face of the composition to form a floor; and then imagewise exposing a second face of the composition to form a printing surface.
22. The method of claim 20 or claim 21, further comprising, if the composition comprises a plastic cover, removing at least one side of said cover before exposing the composition to ambient light.

23. The method of any of claims 20 to 22, wherein the ambient light source is selected from sunlight, daylight and artificial ambient light, e.g. a light bulb.

24. The method of any of claims 20 to 23, further comprising hardening the plate, wherein hardening the plate comprises an additional step of exposing the composition to ambient light or to heat e.g. from a hot air gun.

25. The method of any of claims 20 to 24 wherein the plate is post-exposed, wherein optionally the post-exposure step which is carried out under water.

26. The method of any of claims 20 to 25, wherein the printing plate is a hand stamp and the method further comprises assembling a hand stamp from the plate.

27. A method of making a composition according to any of claims 1 to 19, comprising mixing a photopolymer which is solid at room temperature with an ambient light activated photoinitiator.

28. The method of claim 27, wherein the photopolymer is mixed with the photoinitiator at a temperature at which the photopolymer is a liquid, and further wherein the mixture is cooled to a temperature at which it is a solid.

29. The method of claim 27 or claim 28, which further comprises one or more of the following steps:
   (a) casting a liquid photopolymer composition onto a transparent sheet at a temperature above its pouring point;
   (b) injection moulding a liquid photopolymer composition into a mould of the desired thickness for a stamp.
   (c) extruding a liquid photopolymer composition into a sheet of the desired thickness for a printing plate;
   (d) hot pressing a solid photopolymer into a sheet of the desired thickness for a printing plate; and
(e) filling a liquid photopolymer composition into plastic and cooling between plates set at the desired thickness for a printing plate.

29. The method of any of claims 26 to 28 comprising irradiating a surface of the composition with ambient light to cure the photopolymer, so that the product provided to a user has a support layer.
**Application No:** GB0714599.8  
**Examiner:** Mr Martin Price  
**Claims searched:** 1-29  
**Date of search:** 14 November 2008

**Patents Act 1977: Search Report under Section 17**

**Documents considered to be relevant:**

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<tr>
<th>Category</th>
<th>Relevant to claims</th>
<th>Identity of document and passage or figure of particular relevance</th>
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| X        | 1 at least         | GB 2422678 A  
Photocentric - see e.g. claims 1, 14 and 40 |
| X        | 1 at least         | WO 2007/138356 A1  
Photocentric - see e.g. claims 6 and 16 and page 17 line 3 |
| X        | 1 at least         | EP 1235107 A1  
Fuji Photo Film - see e.g. the abstract and claims 1 and 8 |
| X        | 1 at least         | WO 03/069411 A1  
Kodak - see e.g. claims 12-14 and page 18 paragraph 2 |
| X        | 1 at least         | EP 0453307 A3  
W.R. Grace - see e.g. claims 13 and 16 and page 8 lines 3-4 |
| X        | 1 at least         | JP 06242612 A  
Konishiroku Photo - see WPI abstract number 1994-319496 |

**Categories:**

- **X** Document indicating lack of novelty or inventive step
- **Y** Document indicating lack of inventive step if combined with one or more other documents of same category.
- **&** Member of the same patent family
- **A** Document indicating technological background and/or state of the art.
- **P** Document published on or after the declared priority date but before the filing date of this invention.
- **E** Patent document published on or after, but with priority date earlier than, the filing date of this application.

**Field of Search:**

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:

- C08F: G03F

Worldwide search of patent documents classified in the following areas of the IPC

- **EPODOC, WPI**

**International Classification:**
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