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(54) **Laser-engravable element for use in flexographic printing plates and hand or coding stamps**

(57) The invention relates to a laser-engravable element for use in a flexographic printing plate or a hand or coding stamp comprising a thermoset crosslinked copolymer obtainable from polyether urethane (meth)acrylate pre-polymer and (meth)acrylic monomer, oligomer and/or polymer. Such element is preferably used for making hand or coding stamps. The invention further pertains to a method of laser engraving comprising en-

graving a pattern into the surface of the element, the pattern being formed by decomposing and/or evaporating part of the copolymer of the element by means of irradiating with a laser beam, optionally followed by a wash step to remove remains of decomposed copolymer.

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Description

[0001] The present invention relates to a laser-engravable element for use in a flexographic printing plate or a hand or coding stamp, to a stamp die made of the same by laser engraving, to a flexographic and hand or coding stamp comprising said stamp die, and to a method of laser engraving the element.

[0002] Laser-engravable elements for flexographic printing plates are known in the art. For instance in US 5,259,311 a method is disclosed for laser engraving of photopolymer printing plates. This method relates to the making of patterned flexographic printing plates only. The only material disclosed is CYREL® , which is a material of unknown composition obtainable by the E.I. DuPont Company, USA.

[0003] In US 5,798,202 laser engraving of flexographic printing plates was disclosed, using a large number of elastomeric layers for making the printing plate. Particularly, copolymers of butadiene and styrene, copolymers of isoprene and styrene, styrene-diene-styrene triblock copolymers, such as polystyrene-polybutadiene-polystyrene (SBS), polystyrene-polyisoprene-polystyrene (SIS), or polystyrene-poly(ethylenebutylene)-polystyrene (SEES), and non-crosslinked polybutadiene and polyisoprene; nitrile elastomers; polychloroprene; polyisobutylene and other butyl elastomers; chlorosulfonated polyethylene; polysulfide; polyalkylene oxides; polyphosphazenes; elastomeric polymers and copolymers of acrylates and methacrylates; elastomeric polyurethanes and polyesters; elastomeric polymers and copolymers of olefins such as ethylene-propylene copolymers and non-crosslinked EPDM; elastomeric copolymers of vinyl acetate and its partially hydrogenated derivatives were disclosed.

[0004] In EP 1,228,864 laser-engravable plates for use in flexographic printing were disclosed comprising a layer consisting of cured (meth)acrylate polymer. The use of acrylamides, styrene, vinyl acetate, and their partially hydrogenated derivatives, including amphoteric interpolymers were generically disclosed. Gelatin- and cellulose-esters and -ethers and elastomeric materials such as polymers and copolymers of butadiene and isoprene were also disclosed as suitable polymers.

[0005] Laser-engravable elements for hand and coding stamps are known in the art. Common materials for such elements are selected from natural and synthetic rubbers, as well as the hereinbefore-mentioned elastomers, and combinations thereof.

[0006] The making of hand or coding stamps requires that no hazardous, toxic, flammable and/or bad-smelling gas comes free during the engraving process. It is further of importance that particles that are formed or come free during the engraving process do not adhere to the layer and to prevent damage of the printing image, can easily be removed by a simple washing process. It is also an advantage when materials for making hand or coding stamps can also be used for making flexographic printing plates, i.e. it is also an objective of the invention to use materials that can equally well be used for hand stamps and flexographic printing plates. It is also important to use materials that enable fast engraving process times. Finally, the materials should satisfy the usual other requirements, such as being tack- and dust-free, ozone resistant, having good ink absorption and transfer of ink, showing no desiccation, and having long life times. There is thus a need for plates than can easily be used for hand or coding stamps, without having the disadvantages of the prior art materials of printing plates.

[0007] It was found that materials that are known for making flexographic printing plates are less suitable for making laser-engravable hand or coding stamps, in that they do not satisfy all, or at least most, of the hereinabove-mentioned requirements. It is the object of the invention to provide suitable materials that satisfy at least most of these requirements and which can be used for both making hand and coding stamps.

[0008] To this end it was found that a laser-engravable element for use in a hand or coding stamp could be used comprising a thermoset crosslinked copolymer obtainable from polyether urethane (meth)acrylate pre-polymer and (meth)acrylic monomer, oligomer and/or polymer. Such element, which is usually in the form of a plate, sheet, or film is particularly suitable for making hand or coding stamps.

[0009] According to the invention it is preferred to use a copolymer that is obtained from 10 to 65 wt.%, preferably 20 to 35 wt.% of (meth)acrylic compounds, including monomers and oligomers, wherein the well-known terms "(meth) acrylic" and "(meth)acrylate" stand for "acrylic or methacrylic" and "acrylate or methacrylate," respectively, and 35 to 95 wt%, preferably 65 to 80 wt.% of a polyether urethane (meth)acrylate pre-polymer, up to a total of 100 wt.% of polymerized and polymerizable compounds.

[0010] The (meth)acrylic compound is selected from at least one of mono- or polyfunctional (meth)acrylate alkyl esters, (meth)acrylate hydroxyalkyl esters, polyethylene glycol (meth)acrylate, and unsubstituted or N-alkyl, N-hydroxy-alkyl, or N-alkylene substituted (meth)acrylamide. Examples are 2-ethylhexyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, diethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, neopentylglycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol penta- or hexa(meth)acrylate, or wethoxylated or propoxylated derivatives thereof, (meth)acrylamide, N-methylol(meth)acrylamide, methylene bis(meth)acrylamide, and the like.

[0011] Particular useful are mixtures of these (meth)-acrylic compounds. Most suitable are the methacrylate derivatives such as methacrylate esters including methyl methacrylate (MMA), hydroxymethyl methacrylate (HMMA), hy-

droxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA), polyether acrylate compounds such as dialcohol derivatives like 1,6-hexanediol diacrylate (1,6-HDDA), tetraethyleneglycol diacrylate (TEGDA), and other polyethylene glycol acrylate derivatives, methacrylate oligomers, and the like, and mixtures thereof. Up to 100 wt.% of these (meth)acrylic compounds may be monomers.

[0012] The polyether urethane (meth)acrylate pre-polymer compound is preferably a pre-polymer, such as unsaturated polyester resin, unsaturated polyurethane resin, unsaturated polyamide resin, unsaturated polyacrylate/methacrylate resin, polyether urethane acrylate/methacrylate polymer, polyether polyester urethane acrylate copolymer, and hydroxy-terminated hydrogenated polybutadiene resin. Particularly suitable are polyether urethane or polyester urethane based photopolymer compositions, such as those commercially available as Verbatim® liquid photopolymers from Chemence Ltd.

[0013] To the polymerizing mixture additives may be added, such as photo-initiators, stabilizers, such as thermal polymerization stabilizers, light absorbers, dyes, pigments, and the like.

[0014] Suitable photo-initiator systems include benzil and derivatives thereof, benzoin and derivatives thereof, such as methyl, ethyl, isopropyl, or n-butyl ether of benzoin; acetophenone and derivatives of acetophenone, such as 2,2-diethoxy-acetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone; ketoxime esters of benzoin; triazines; and diimidazoles, anthraquinones such as 2-ethylantraquinone, and a hydrogen donor; benzophenone and derivatives thereof, such as 2-methylbenzophenone, 2-methoxy-benzophenone, and tertiary amines; Michler's ketone alone and with benzophenone; thioxanthenes; and 3-ketocoumarins, 1-hydroxy-cyclohexylphenylketone, xanthone, thioxanthone, 2-chloroxanthone, and 2-isopropylxanthone, and the like, or mixtures thereof.

[0015] Sensitizing agents (light absorbers) can also be included with the photo-initiator systems discussed above. In general, sensitizing agents are those materials that absorb radiation at a wavelength different than that of the reaction-initiating component, and are capable of transferring the absorbed energy to that component. Thus, the wavelength of the activating radiation can be adjusted.

[0016] Stabilizers may be used, particularly thermal polymerization inhibitors, such as phenol derivatives including p-methoxyphenol, hydroquinone and derivatives thereof, benzoquinone and derivatives thereof, 2,6-di-t-butyl-p-cresol, nitroso compounds, and the like.

[0017] The composition of the invention typically contains about 20 to 95 wt.% of polyether urethane (meth)-acrylate pre-polymer and about 20 to 95 wt.% of (meth)-acrylic monomer, both based the total weight of the photopolymer composition. The photo-initiator is typically used in a quantity of from about 0.0001 wt.% to about 10 wt.%, preferably about 0.1 wt.% - 7 wt.%, based the total weight of the photopolymer composition. A thermal stabilizer can be used in a quantity of from 0 - 1 wt.%, preferably from 0.005 to 0.5 wt.%, based the total weight of the photopolymer composition.

[0018] The copolymers of the present invention are crosslinked. The crosslinking makes the polymers of the invention solvent resistant, which makes the stamps therefore very suitable for solvent-based inks, for instance inks containing up to 10 wt.% of alcohol. The polymers are also resistant to water-based inks, oil-based inks, and UV-inks.

[0019] The laser engraving comprises engraving a pattern into the surface of the element, the pattern being formed by decomposing and/or evaporating part of the cured polymer of the element by means of irradiating with a laser beam, optionally followed by a wash step to remove remains of decomposed copolymer.

[0020] Thus the element composed of the above copolymer may be converted to a stamp die by laser engraving a pattern into the element. A plate can be made of the element as such or of the stamp die obtained thereof, which both may be provided with a backing layer. The plates such obtained is a basic plate, which in accordance with the patent is used for making hand or coding stamps and which can be mounted in a stamp holder. The plates can also be used for making flexographic printing plates. The basic plate may contain additional layers, which array of layers may optionally be applied onto a backing layer. With the aid of a laser, such as an CO₂ laser or a YAG laser, a desired printing pattern (image) is formed on the plate, so that the exposed parts will be heated, resulting in evaporation, decomposition or both of the polymer(s). In a subsequent processing step the entire plate may be washed or rinsed, preferably with water, to remove remains of the polymer(s) that are formed as particles in the heated parts of the plate. Other cleaning methods such as brushing may also be used. The parts not treated with the laser remain as printing image on the plate.

[0021] The polymers of the invention are liquid polymers that can be cured, preferably with UV light, and can be polymerized to form plates of different degrees of hardness by changing the components in the mixture. Example of such a mixture are verbatim® (ex Chemence), APR® (ex Asahi, Japan), and similar materials for example obtainable by McDermid Inc., USA.

[0022] In accordance with a preferred embodiment, the method according to the invention is carried out on a completely cured photopolymeric plate fabricated in one step, and which is immediately ready for laser treatment.

[0023] The backing layer is preferably provided with an adhesive that adheres very well to the cured polymer. In order to provide a good contact between the backing layer and the photopolymer, and in order to adjust to the required plate thickness, this treatment may be performed by applying pressure.

[0024] Generally, the polymer layer according to the invention can be used as a top layer provided to one or more other layers. Such other layer may be a polymeric layer including rubber, but also textile, paper, carton, metal, adhesive

and metal foil, and the like may be used. Such embodiment is known in the art as cupping.

[0025] It has been shown that the method according to the invention makes it possible to produce very fine patterns on the plate. A traditional and known laser suitable for carrying out the present method, a CO₂ or YAG laser, is able to achieve a Didot screen of 60. In practice a Didot screen of 40-60 is usual (a Didot screen of 56 corresponds with a raster of 150 lpi (lines per inch)). When the element is black, for instance by mixing dyes or pigments in the polymer mixture, also a YAG laser can be used. The power consumed will generally range from 10-3000 watt, preferably from 20-1000 watt, more preferably from 25-500 watt. With a photopolymeric plate of A2 size, a CO₂ laser will generally have a power consumption ranging from 25-250 watt. These lasers are generally known in the art.

[0026] Hand and coding stamps as such are known in the art. Usually, the stamping layer is fixed to a wooden, plastic, or metal stamp holder or platen, directly or via a backing layer, for instance with glue or with double-sided adhesive tape, and the platen is mounted in the stamp holder. Hand and coding stamps may be executed as self-inking stamps, for instance by using a rotating stamp base.

[0027] The term "laser-engravable" as used herein refers to reinforced materials capable of absorbing laser radiation such that those areas of the materials, which are exposed to a laser beam of sufficient intensity, become physically detached with sufficient resolution and relief depth. It will be understood that if the laser radiation is not absorbed by the reinforced material directly, then it may be necessary to add a laser radiation absorbing component as described below. The term "physically detached" means that the material so exposed is either removed or is capable of being removed by any means such as by vacuum cleaning or washing or by directing a stream of gas across the surface to remove the loosened particles, or by infra-red laser irradiation of non-printing parts on the stamp, followed by removal thereof by spraying, centrifuging, and/or suction techniques.

[0028] The element composed of the above copolymer can be made by any method for making such elements. For instance, a method is pouring the liquid photopolymer composition, together with optional photo-initiator, stabilizers, dyes, and the like, into a mold, for instance a glass mold optionally provided with a backing foil. After having poured the polymer into the mold the upper side may be protected by a protective foil. Exposing the liquid polymer to UV light then cures it to a thermoplastic polymer and simultaneous exposure to UVC light eliminates possible tackiness. The mold has a pre-determined thickness to provide polymer layers of a desired thickness. The elements thus obtained are ready for laser engraving. Other methods lead to similar results, but may have advantages in terms of processability, fastness, reproducibility, etc.

[0029] More particularly, a common procedure for making stamps according to the invention is a process comprising a first step of preparing a mold for the liquid photopolymer to be poured into, followed by exposure to UV light by irradiating with actinic light. Usually a removable transparent plastic foil is placed over a horizontal glass support of an exposure unit (i.e. a device for irradiating the photopolymer with curing radiation). A mould is formed with a foam tape, laid onto the cover foil. The containment wall has the desired thickness of the cured photopolymer sheet. Liquid photopolymer is then poured into the mould. Any entrapped air bubbles are then removed and a semi-rigid backing sheet, which is coated to adhere to the cured polymer, is then carefully placed over the liquid. In practice air is completely excluded from the front and back surfaces of the liquid photopolymer by having the photopolymer layer positioned between plastic foils. The cured photopolymer sheet thus obtained is the laser-engravable element, which is ready for laser engraving to a stamp die.

[0030] It will be obvious that a plate is used which exhibits a difference in height between the printing and the non-printing parts. This height (or relief) may be adapted as desired, the height being determined mainly by the type of material to be stamped or printed, as well as by the type of plate material. In general, the plate thickness will vary from 0.5 to 10 mm. A plate thickness from 0.76 to 6.35 mm is preferred. The height of the relief may vary from 0.4 to 9.9 mm. A height of 0.66 to 6.15 mm is preferred.

[0031] According to the invention, a stamp can be formed with a laser, wherein the laser removes the non-printing parts from the surface of the plate. The height of the relief can be easily controlled. The laser can very simply be controlled directly by means of a digital system in which it is possible to have a simple coupling between a program for designing a pattern for the plate, and the laser. A person skilled in the art of computer programming is capable of doing this.

[0032] The invention is illustrated by the following example.

[0033] Hand stamps were made of A: Verbatim® (mixture according to the invention), B: polyamide-based material according to the prior art (Nyloflex®, ex BASF), and C: rubber according to the prior art (Trodax®, ex Frans Just & Söhne, Austria or Swing®, ex Schmidt Gummiwarenfabrik, Germany).

[0034] Verbatim® is a material obtainable by Chemence Ltd. United Kingdom with the composition (in wt.%):

high MW urethane methacrylate pre-polymer	about 40
methacrylate ester	about 30
2-hydroxypropyl methacrylate	about 10

(continued)

triethylene glycol dimethacrylate	about 10
polyethylene glycol methacrylate derivative	about 10
tetradecanoic acid	<5
acrylated oligomer	<3
benzophenone derivative	<1

[0035] The properties of A, B, and C were compared (see Table) showing an overall improvement of composition A with regard to B and C.

Table

Property	A	B	C
Engraving process time	Short	Short	Long
Release of toxic gas during the engraving process	No	Yes	No
Adherence of particles after the engraving process	No (liquid residue)	Yes (hard particles)	No (dust)
Water removable residues	Yes	No	Yes
Smell during the engraving process	No	Yes	Yes
Flash point (flammability)	Very high (inflammable)	Low	Very low
Air assist device required on the laser engraver	No	No	Yes
Prefiltered active charcoal-type device required in combination with the laser engraver	No	Yes	Yes

Claims

1. A laser-engravable element for use in a flexographic printing plate or a hand or coding stamp comprising a thermoset crosslinked copolymer obtainable from polyether urethane (meth)acrylate pre-polymer and (meth)acrylic monomer, oligomer, and/or polymer.
2. A stamp die obtainable by laser engraving a pattern into the element of claim 1.
3. A plate comprising the element of claim 1 or the stamp die of claim 2 and optionally a backing layer.
4. A hand or coding stamp comprising the element of claim 1 or the stamp die of claim 2, which is directly or through a backing layer secured to a platen which is mounted in a stamp holder, or directly secured in the stamp holder.
5. A method of laser engraving the element of claim 1 comprising engraving a pattern into the surface of the element, the pattern being formed by decomposing and/or evaporating part of the copolymer of the element by means of irradiating with a laser beam, optionally followed by a wash step to remove remains of decomposed copolymer.



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EUROPEAN SEARCH REPORT

Application Number
EP 03 10 4032

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The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 26 March 2004	Examiner Vogel, T
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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