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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 September 2016 (01.09.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/134972 A1

(51) International Patent Classification:
C08F 220/08 (2006.01) *C08F 230/08* (2006.01)
B29C 67/00 (2006.01)

(21) International Application Number:
PCT/EP2016/052826

(22) International Filing Date:
10 February 2016 (10.02.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15156100.8 23 February 2015 (23.02.2015) EP

(71) Applicant: **PHILIPS LIGHTING HOLDING B.V.** [NL/NL]; High Tech Campus 45, 5656 AE Eindhoven (NL).

(72) Inventors: **LUB, Johan**; High Tech Campus 5, 5656AE Eindhoven (NL). **HIKMET, Rifat, Ata, Mustafa**; High Tech Campus 5, 5656AE Eindhoven (NL).

(74) Agent: **VERWEIJ, Petronella, Daniëlle**; High Tech Campus 5, 5656 AE Eindhoven (NL).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

(54) Title: SILICONE MIXTURE CONTAINING ACRYLATES FOR INKJET AND DISPENSER 3D PRINTING

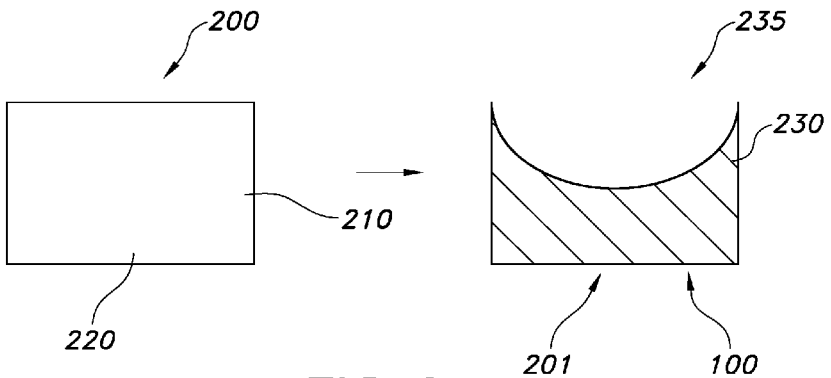


FIG. 2a

(57) Abstract: The invention provides a method for producing a 3D printed object (100) comprising 3D printing using a 3D printer (500) a composition (200) comprising polymerizable compounds (210) to provide a printed composition (201), wherein the polymerizable compounds (210) comprise polysiloxanes (220) comprising polymerizable acrylate groups (225) covalently linked to the polysiloxanes (220), and polymerizing at least part of the total number of acrylate groups (225) of the printed composition (201) to provide said 3D printed object (100) with polymerized polysiloxanes (230).

WO 2016/134972 A1

Silicone mixture containing acrylates for inkjet and dispenser 3D printing

FIELD OF THE INVENTION

The invention relates to a method for producing a 3D object. Further, the invention relates to such 3D object *per se*.

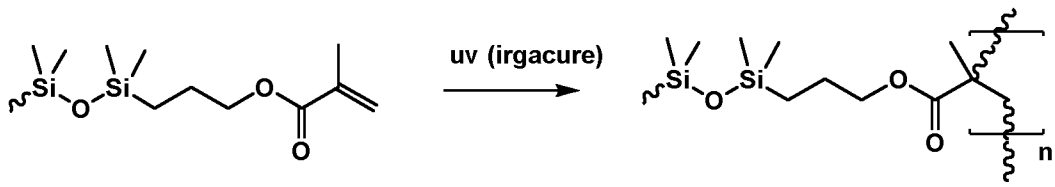
BACKGROUND OF THE INVENTION

Printing of optical components is known in the art. WO2014108364, of LUXEXCEL, for instance, describes a method for printing an optical element comprising the steps of ejecting at least one droplet of printing material comprising silicone towards a substrate in a first step and curing the droplet deposited on the substrate in a second step. The deposited droplet is cured in the second step by ultraviolet irradiation or by infrared irradiation. The printing material of the at least one droplet is heated at least to 75 °C, preferably at least to 100 °C and particularly preferably at least to 150 °C before and/or while ejecting the droplet during the first step.

SUMMARY OF THE INVENTION

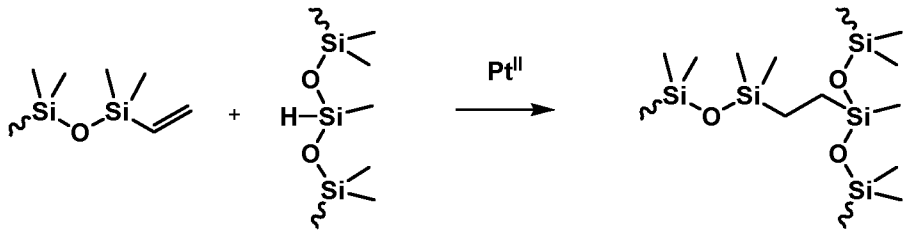
Additive manufacturing is a growing field of materials processing. It can be used for rapid prototyping, customization, late stage configuration, or making small series in production. For 3D inkjet printing or dispensing, a liquid monomer mixture may be used and by photo polymerization the shape is then fixed before the following layer is deposited.

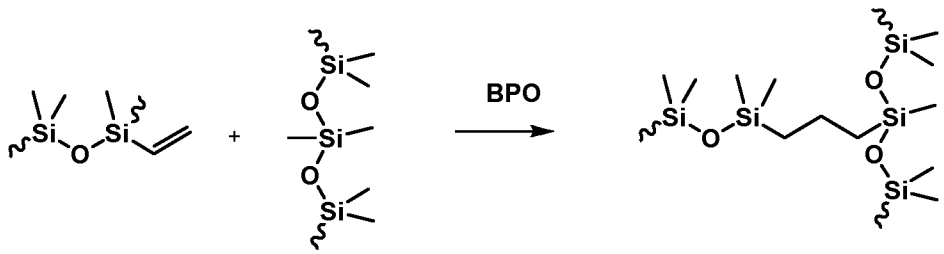
3D inkjet printing and 3D dispension are additive manufacturing technologies used for modeling, prototyping, and production applications. These technologies work on an "additive" principle by laying down a liquid in the forms of drops or by a continuous flow, respectively, of a polymerizable liquid which is photopolymerized on “the flow”. By using for example acrylates, polymerization (see scheme below, wherein photo- polymerization of silicone acrylates is shown, in correspondence with the invention) can be fast enough to obtain the 3D structure. The use of these pure acrylates is – however - not desired as they do not show the high stability of silicones.



This cross-link (obtained) is herein also indicated as "acrylate-based cross-link".

For making optical components in lighting applications, silicones have proven to be very relevant materials. They are optically and thermally very stable and highly transparent. They are one of the preferred materials in LED technology. The materials are normally processed in a mold, thermal crosslinking stabilizing the form. Two main chemical mechanisms are applied, hydrosilylation (in general with a catalyst such as a Pt catalyst) and peroxide initiated cross-linking (such as with a peroxide catalyst) of vinyl silicones, which mechanisms are shown below, respectively:





These cross-links are herein also indicated as "siloxanes cross-links". Both indicated processes (via e.g. the Pt catalyst or via e.g. the BPO catalyst) are thermal processes. Photochemical alternatives have been proposed but need extremely low wavelength instead of the 360 nm normally used in industrial applications and very high intensities. Thus these processes are not applicable for the 3D manufacturing processes.

Generally acrylates are used in such a process which shows rapid photo polymerization. However, as indicated above, acrylates are not suitable in lighting applications as they do not show the high photo-stability of silicone polymers. As also indicated above, silicones are a very interesting class of materials with applications in lighting, healthcare and consumer lifestyle. The rubbery properties are interesting in several

healthcare applications and the light stability and transparency are very important properties for application in LED technology. However, as also indicated above it appeared that pure silicone material has disadvantages in 3D printing, amongst others in terms of processing and/or in terms of strength of the printed 3D object. Further, the use of mixtures of silicones and acrylates appears also to induce disadvantages in terms of processing as they cannot easily be mixed.

Hence, it is an aspect of the invention to provide an alternative method for producing a 3D object, such as an optical component, which method preferably further at least partly obviates one or more of above-described drawbacks. It is also an aspect of the invention to provide an alternative 3D object, such as an optical component, which optical component preferably further at least partly obviates one or more of above-described drawbacks.

Amongst others, the invention provides a silicone material that can be used in a rapid polymerization process which is needed in technologies such as additive manufacturing (3D printing). Here we therefore suggest the use of mixture of silicones some of which contain acrylate groups which can be photopolymerised leading to gelation of the material enabling deposition of layers on top of each other while the rest of the monomers can be thermally cured leading to the total polymerization of the system for obtaining silicon rubber with good stability. Especially, it is herein proposed to replace part of the reactive groups of the materials described above by (meth)acrylate groups. By addition of e.g. an UV photoinitiator, it is possible to print these materials and photopolymerize part of the deposited materials such that flow is supressed (by formation of a gel) and the form of the printed materials is retained. After or during the deposition, the samples are solidified under thermally induced reactions of hydrosilylation or peroxide initiated crosslinking.

Hence, in a first aspect the invention provides a method for producing a 3D printed object ("object" or "3D object"). The method comprises the step of providing a composition comprising a curable polysiloxane. The curable polysiloxane comprises polymerizable acrylate groups covalently linked to the curable polysiloxane. Furthermore, the curable polysiloxane is curable by one or more of (a) a hydrosilylation reaction and (b) a peroxide curing. The composition further comprises a photo polymerization catalyst and one or more of (a1) a hydrosilylation catalyst and (b1) a peroxide catalyst. The method also comprises the step of 3D printing using a 3D printer the composition to provide a printed composition. Finally, the method comprises the steps of photo polymerizing at least part of the total number of said (polymerizable) acrylate groups of the printed composition to

provide said 3D printed object with polymerized polysiloxane, and providing heat to the printed composition to solidify said 3D printed object under thermally induced reactions of hydrosilylation or peroxide initiated crosslinking.

With such method it is possible to provide 3D printed objects, having the advantage of the 3D printing technology that allows that substantially any shape may be created (which is not the case with conventional assembly), and it is possible that the silicone materials can be printed which may lead to 3D objects that can be used for optical applications, as the silicone material may substantially be optically stable and also transmissive for light. The acrylate group based polymerization forms the basis of the formation of the structure of the printed composition.

Further, the polysiloxanes allow a further stabilization of the printed composition because reactive groups are included that may form cross-links by curing. The polysiloxanes may comprise a mixture of at least two types of polysiloxanes, viz. vinyl functional polysiloxanes and hydroxysiloxanes. More especially, the polysiloxanes may comprise polysiloxane molecules comprising acrylate groups for acrylate polymerization and may comprise polysiloxane molecules comprising curable groups, such as vinyl functional polysiloxanes and hydroxysiloxanes. Further, the polysiloxanes may comprise polysiloxane molecules comprising acrylate groups for acrylate polymerization and optionally also one or more of curable groups (i.e. a single polysiloxane having at least two different functional groups).

Silicones, more precisely called polymerized siloxanes or polysiloxanes, are mixed inorganic-organic polymers with the chemical formula $[(R_1,R_2)SiO]_n$ (not taking into account the terminal groups), where R is a group such as for example hydrogen, hydrocarbon or fluorocarbon, especially methyl, ethyl, or phenyl. Especially, one or more R groups of one or more Si backbone elements and Si terminal elements comprise one or more of hydrocarbon and fluorocarbon. One or more of these side groups may also have cross-linking functionality, such as a vinyl group. Especially, one or more R groups of one or more Si backbone elements and Si terminal elements may comprise an acrylate group (for cross-linking) or an acrylate-based cross-link (after cross-linking)

These polymerized siloxanes or polysiloxanes materials consist of an inorganic silicon-oxygen backbone (···-Si-O-Si-O-Si-O-···) with organic side groups attached to the silicon atoms, which are four-coordinate. As the R side groups may in principle be different, instead of the formula $[(R_2)SiO]_n$ also the formula $[(R1,R2)SiO]_n$ (not taking into account the terminal groups), might be applied.

The fact that herein only R, or more precisely, R1,R2 are mentioned, does not exclude that different Si backbone elements may comprise the same side groups, but also more than two different types of side groups may be comprised by the silicone. Hence, R may for instance, but not limited to, be selected from the group consisting of methyl, phenyl, etc. Also halogens, mainly chlorine, are possible as side compound R. Further, $[R_2SiO]$, or $[-Si(R)_2-O-]$ refers to the silicone unit or silicone characterizing group (i.e. group that characterizes a silicone).

A siloxane is especially any chemical compound composed of units of the form R_2SiO, where R is for instance, but not limited to, a hydrogen atom, a hydrocarbon group, or one or more R_2SiO unit(s) combined with a terminal group. Siloxanes can have branched or unbranched backbones consisting of alternating silicon and oxygen atoms -Si-O-Si-O- with side chains R attached to the silicon atoms. Polymerized siloxanes with organic side chains ($R \neq H$) are commonly known as silicones or as polysiloxanes. Herein, these are also indicated as “siloxanes” or “siloxane polymers”. Representative examples are $[SiO(CH_3)_2]_n$ (polydimethylsiloxane) and $[SiO(C_6H_5)_2]_n$ (polydiphenylsiloxane). These compounds can be viewed as a hybrid of both organic and inorganic compounds. The organic side chains confer hydrophobic properties while the -Si-O-Si-O- backbone is purely inorganic. As indicated above, Si elements in the backbone are herein also indicated as Si backbone elements. A $[R_2SiO]_n$ siloxane comprises n Si backbone elements. Hence, any siloxane characterizing moiety R_2SiO provides one silicon backbone element (which has two side groups). Note that e.g. PDMS is $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$, has n+1 Si elements, thus in fact n+1 Si backbone elements. The most common polysiloxane is linear polydimethylsiloxane (PDMS; see above), a silicone oil. The second largest group of silicone materials is based on silicone resins, which are formed by branched and cage-like oligosiloxanes.

By varying the -Si-O- chain lengths, side groups, and cross linking, silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. Herein, after polymerization and (optional) curing, the printed composition is especially solid (though the printed composition (even after curing) may be flexible to some extend).

Herein, especially linear polysiloxanes are used as curable and/or cross-linkable siloxane polymers. However, also non-linear polysiloxanes may be used as curable and/or cross-linkable siloxane polymers. The term "curable and/or cross-linkable siloxane polymers" may also refer to a plurality of different types of curable and/or cross-linkable

siloxane polymers. In an embodiment, these curable and/or cross-linkable siloxane polymers are substantially identical. However, in another embodiment, the curable and/or cross-linkable siloxane polymers may comprise a plurality of different curable and/or cross-linkable siloxane polymers. For instance, they may differ in chain length, and/or they may differ in (the type of) side groups. Further, they may differ in the type of end group. The curable and/or cross-linkable siloxane polymers may have end groups that are configured to form cross-links upon curing. Note that additionally or alternatively, also one or more side groups per curable and/or cross-linkable siloxane polymer may be configured to form a cross-link upon curing. For instance, the side groups may include a vinyl group (or a hydrogen group). As can be understood from the above, the curable and/or cross-linkable siloxane polymers may comprise end groups and/or side groups that are configured to form cross-links upon curing. The weight average molar weight of the polysiloxanes used may especially be in the range of 2,000-200,000 g/mol.

The polysiloxanes may be cured via free-radical curing, such as with a peroxide catalyst (and heat), via condensation curing, such as with a tin salt catalyst and/or a titanium alkoxide catalyst (and heat), via addition curing, such as with a platinum catalyst (such as e.g. a 1,1,3,3-tetramethyl-1,3-divinyldisiloxane, platinum salt, dichloro(dicyclo-pentadienyl)platinum(II), other platinum(0) or platinum chloride complexes) and/or a rhodium catalyst (and heat), etc.. In the method according to the first aspect the invention, the polysiloxanes comprise curable polysiloxanes, curable by one or more of (a) a hydrosilylation reaction and (b) a peroxide curing, wherein the method further especially comprises: (i) providing said composition further comprising one or more of (a1) a hydrosilylation catalyst and (b1) a peroxide catalyst; and (ii) 3D printing said composition, and providing heat to the printed composition (to cure at least part of the total number of curable polysiloxanes).

Because heat is necessary to cure the silicones or polysiloxanes, the 3D printer may include a heating unit, especially for a dedicated heating of the printed composition. In general, the 3D printer may include a heating element to heat the composition, such that the composition may flow, and may thus be printed. Herein, the 3D printer may include a heating element (also) having the function to heat the composition downstream from a 3D printer nozzle. This may be a heating of the composition downstream from the nozzle but not yet deposited on a receiver item (or substrate) or on (other) printed composition and/or this may be a heating of the printed composition. Especially, this heating may be a local heating, e.g.

in a region substantially directly below the printer nozzle. Hence, in an embodiment the 3D printer further comprises a heating unit configured to heat said printed composition.

The composition may thus be solid at room temperature, but upon heating may become printable (i.e. especially flowable). Downstream from the printer nozzle, optionally further heating may be applied as indicated above. Especially, the composition and the method are chosen such that the curing time is substantially longer than the residence time of the printable material in the 3D printer used, such as in the range of > 1 minute and in the range of < 20 seconds, respectively. For instance, the method and the composition may be selected to have a curing time of the composition in the range of 10 time longer than the residence time of the printable composition. As indicated herein, the 3D printer may especially be an inkjet printer or a dispersion printer.

Above, it was first concentrated on the cross-linking or curing of the polysiloxanes. This leads to the formation of "siloxanes cross-links", a term herein used to indicate cross-links obtained by a hydrosilylation reaction or a peroxide initiated carbon bond formation. Now, we address the basic cross-linking of the polysiloxane chains via the acrylate groups. This leads to the formation of "acrylate-based cross-links".

For obtaining good strength and good optical properties it seems desirable that the amount of acrylate groups is not too low, but also not too high. Hence, in a specific embodiment the composition (i.e. of the polymerized siloxanes) comprises in the range of 0.5-8 wt.%, especially 1-5 wt.% acrylate groups, wherein the weight of the acrylate groups is defined as the weight of methacrylic acid. Methacrylic acid is defined as $C_4H_6O_2$ or $(CH_2)(CH_3)CCOOH$. When included in a polysiloxane, the acrylate group will especially be associated via the single bonded oxygen of the acid group, i.e. $(CH_2)(CH_3)CCOOR_1$, with R_1 being the polysiloxane. Further, when included in a polysiloxane, the remaining H atoms in above indicated formula are not necessarily H atoms, but can also be other atoms, i.e. $(C_2R_2R_3)C_3R_4R_5R_6)C_4C_1OOR_1$, with R_1 being the polysiloxane and R_2, R_3, R_4, R_5, and R_6 independently being selected from for instance the group consisting of H, an alkyl, an alkenyl, an alkynyl, an ether, an ester, a polysiloxane, etc., with especially at least one R_2, R_3, R_4, R_5, and R_6, and even more especially only one, being a polysiloxane. After cross-linking, at least one of R_2, R_3, R_4, R_5, and R_6 will comprise (another) polysiloxane molecule, covalently linked to the R1 polysiloxane molecule via the acrylate-based cross-link. C_4 indicates the carbon atom to which OOR_1, C_3 and C_2 are covalently bound (i.e. in the case of methacrylic acid, the carbon atom to which COOH, CH_3 and CH_2 are covalently bound). Hence, substantially any group or groups (including H) may be associated via the acrylate

group to the polysiloxanes. However, for estimating the amount of acrylate groups only the acrylate binding is taken into account, as R_1-R_6 may differ from application to application. Therefore, assuming e.g. a $(C_2R_2R_3)C_3R_4R_5R_6)C_4C_1OOR_1$ wherein e.g. R_1 and R_2 are polysiloxanes, the weight percentage of $C_2+C_3+C_1 + C_4 + 2*O +6H$ is evaluated, relative to the total weight of the composition. Hence, after printing, polymerizing (the acrylate groups) (and optionally curing (especially via hydrosilylation and/or peroxide curing)), the thus obtained 3D printed object comprises a printed composition of polymerized siloxanes especially comprising in the range of 0.5-8 wt.%, more especially in the range of 1-5 wt.% acrylate groups, wherein the weight of the acrylate groups is defined as the weight of methacrylic acid. Here, the term "acrylate groups" especially refer to the acrylate groups comprised by the acrylate-based cross-links (between the polysiloxanes). The total weight of the composition relates to weight of the (cross-linked and/or cured) polysiloxanes. The composition may further include material not covalently linked to the polysiloxanes. Such material is not included in the total weight of the composition for the purpose of determining the acrylate groups. Examples of such materials may include one or more of a filler material, a preservative, a stabilizer, a pigment, a luminescent material, a catalyst, etc..

Especially, to obtain the acrylic cross-linking a photo initiator may be applied. Hence, in an embodiment the composition may further comprise a photo polymerization catalyst, such as irgacure, and the method may further comprise photo polymerizing the printed composition to provide said 3D printed object. Further, visible light or other radiation may be used to start and/or speed up the cross-linking. Hence, in a further embodiment the 3D printer may further comprise a radiation source configured to irradiate with radiation said printed composition, wherein the radiation is selected from the group consisting of UV radiation, visible radiation, and IR radiation, especially at least UV radiation.

Different types of polysiloxanes may be applied. This may e.g. depend upon the desired application. In an embodiment the composition comprises (meth)acryloxypropyl terminated poly(dimethyl) siloxanes and one or more of (a) poly(dimethylsiloxane-co-methylhydrosiloxanes and vinyl terminated poly(dimethyl siloxanes), and (b) poly(dimethylsiloxane-co-methylvinyl siloxanes). By the cross-linking via the acrylate groups, cross-links are formed. In general, substantial all acrylate groups may be used, such as at least 80 % of all acrylate groups may be used to cross-link the polysiloxanes. Hence, at least part of the total number of acrylate groups may be used to polymerize the polysiloxanes. For instance, (meth)acryloxypropyl terminated poly(dimethyl) siloxanes may have a Mn > 10,000 and/or a viscosity > 50 cSt. Further, for instance poly(dimethylsiloxane-co-

methylhydrosiloxanes may have a Mn>600 and/or a viscosity > 25cSt. Yet, for instance poly(dimethylsiloxane-co-methylvinyl siloxanes) may have a Mn > 10,000 and/or a viscosity > 400 cSt. Herein, "Mn" indicates the number average molecular weight, as known in the art. Molecular weights are in gram/mol.

Hence, in an embodiment radiation may be applied to cross-link the siloxanes via the acrylate groups, and e.g. heat may be used to (further) cure the composition by polysiloxane curing (as known in the art). As indicated above, the former bonding is herein indicated as "acrylate-based cross-link" and the latter is herein indicated as "siloxanes cross-link". Hence, in an embodiment the method comprises 3D printing said composition to provide said printed composition, wherein during or after or during and after printing the composition downstream from a printer nozzle of the 3D printer is irradiated with radiation and subjected to heat.

In yet a further aspect, the invention also provides a 3D printed object comprising polysiloxanes covalently linked via acrylate-based crosslinks. Especially, the 3D printed object is obtainable by the method as described herein (especially described above). Further, in an embodiment the polysiloxanes further comprise cross-links obtained by hydrosilylation reactions or peroxide initiated carbon bonds formation (i.e. "siloxanes cross-links").

As indicated above, the 3D printed object as described herein may e.g. be applied for optical applications. In a specific embodiment, at least a part of said polymerized polysiloxane is transmissive for visible light. In yet another specific embodiment, the 3D printed object comprises an optical component. The polysiloxane of the invention, such as the printed composition, more especially the (thus obtained) 3D printed object, may comprises polymerized polysiloxane comprising an acrylate group IR absorption at about 1720 cm^{-1}. The term "at about 1720 cm^{-1}" will be clear to an IR skilled person, but may e.g. indicate in the range of 1690-1750 cm^{-1}. Of course, the skilled person may use further support for proving the presence of the acrylate-based cross-links in these polysiloxanes. Further, as indicated above, the 3D printed object may especially comprise in the range of 0.5-8 wt.% acrylate groups, wherein the weight of the acrylate groups is defined as the weight of methacrylic acid.

As indicated above, a 3D printer may especially be applied to execute the herein described method. Hence, in a further aspect the invention provides a 3D printer comprising a printer head for printing a composition comprising polymerizable compounds to a receiver item, the 3D printer further optionally comprising (i) a heating unit configured

to heat said printed composition, and (ii) a radiation source configured to irradiate with radiation said printed composition, wherein the radiation is selected from the group consisting of UV radiation, visible radiation, and IR radiation, the 3D printer further comprising a control unit configured to control the printer head, the heating unit and the radiation source. In general, the heating unit and the radiation source are different items, i.e. the source of radiation is not especially designed to provide the heat the printed composition. However, in embodiments the source of radiation may also be used for this purpose. In a specific embodiment, the radiation source comprises a laser, especially a UV laser. Such source may be used to locally irradiate the printed composition. The term "UV laser" also relates to a source of radiation including a laser and providing UV radiation (e.g. by frequency doubling, etc.). The heating unit may optionally comprise an IR laser. Such laser may be used to locally heat the (just) deposited polymerizable polysiloxane material. The 3D printer may amongst others be configured as inkjet 3D printer or as dispenser 3D printer.

The invention further provides a composition comprising polymerizable compounds, wherein the polymerizable compounds comprise polysiloxanes comprising polymerizable acrylate groups covalently linked to the polysiloxanes, wherein the composition 200 especially comprises in the range of 1-5wt.% acrylate groups 225, wherein the weight of the acrylate groups is defined as the weight of methacrylic acid. The weight is defined relative to the total weight of the composition (to be polymerized). The total weight of the composition relates to weight of the cross-linkable and/or curable polysiloxanes (see also above in relation to the printed composition).

Hence, amongst others the invention provides a (printable) mixture of silicones containing a photopolymerisable system for gelation during printing or dispensing and a thermal polymerizable system for further hardening. Further, the invention provides such mixture where the thermal polymerizable system essentially consist of a mixture of poly(dimethylsiloxane-co-methylvinylsiloxane) and a peroxide. Yet further, the invention provides such mixture where the thermal polymerizable system consist of a mixture of vinyl siloxane derived poly(dimethylsiloxane), poly(dimethylsiloxane-co-methylhydrosiloxane) and a platinum derived catalyst. Further, the invention provides such a mixture where the photopolymerisable system consist of a mixture of methacryloxypropyl terminated poly(dimethylsiloxane) and a photo initiator. The invention also provides 3-D produced structures using the mixtures. The invention may amongst others be applied in 3D inkjet printers and dispensers to enable 3D printing of transparent or coloured or scattering parts.

The term "3D printed object" refers to a three dimensional object obtained via 3D printing (which is an additive manufacturing process).

The terms "upstream" and "downstream" relate to an arrangement of items or features relative to the propagation of the composition from a composition generating means (here especially the nozzle of the 3D printer (head)), wherein relative to a first position within a flow of the composition from the composition generating means, a second position in the flow of the composition closer to the composition generating means is "upstream", and a third position within the flow of composition further away from the composition generating means is "downstream".

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying schematic drawings in which corresponding reference symbols indicate corresponding parts, and in which:

Fig.1 schematically depicts an embodiment of an example of a 3D printer;

Figs. 2a-2e schematically depict some aspects of the invention;

Fig. 3 shows an IR spectrum. The schematic drawings are not necessarily on scale.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Fig. 1 schematically depicts an embodiment of a 3D printer. Reference 500 indicates this 3D printer. Reference 530 indicates the functional unit configured to 3D print, especially FDM 3D printing; this reference may also indicate the 3D printing stage unit. Here, only the printer head for providing 3D printed material, such as a FDM 3D printer head is schematically depicted. Reference 501 indicates the printer head. The 3D printer of the present invention may especially include a plurality of printer heads, though other embodiments are also possible. Reference 502 indicates a printer nozzle. The 3D printer of the present invention may especially include a plurality of printer nozzles, though other embodiments are also possible. Reference 320 indicates a filament of printable 3D printable material (such as indicated above). For the sake of clarity, not all features of the 3D printer have been depicted, only those that are of especial relevance for the present invention. The 3D printer 500 is configured to generate a 3D item 100 by depositing on a receiver item 550 a plurality of filaments 320 wherein each filament 20 comprises 3D printable material,. The 3D printer 500 is configured to heat the filament material upstream of the printer nozzle 502.

This may e.g. be done with a device comprising one or more of an extrusion and/or heating function. Such device is indicated with reference 573, and is arranged upstream from the printer nozzle 502 (i.e. in time before the filament material leaves the printer nozzle 502). Reference 572 indicates a spool with material, especially in the form of a wire. The 3D printer 500 transforms this in a filament or fiber 320. Arranging filament by filament and filament on filament, a 3D item 100 may be formed. The invention is not limited to FDM and is also not limited to FDM 3D printers. For instance, the invention is especially related to embodiments of 3D printers having printer heads, wherein the 3D printers are configured as inkjet printer or dispensing printer.

Reference 1500 indicates a control unit, which may especially be configured to control the 3D printer 100. Further, the 3D printer may include other elements such as a heating unit 1100 and/or a source of radiation 1200. The source of radiation 1200 is especially configured to provide radiation 1201. The heating unit 1100 may be configured to (locally) heat the printed composition 201, here in the example e.g. the filaments 320 on the receiver item 550. Heat is indicated with reference 1101.This radiation 1201 may e.g. UV radiation to polymerize the polysiloxanes via the acrylate groups.

Fig. 2a schematically depict a composition 200 comprising polymerizable compounds 210. By 3D printing this composition 200, a printed composition 201 may be provided. As indicated above, the polymerizable compounds 210 may comprise polysiloxanes 220 comprising polymerizable acrylate groups 225, see Fig. 2b, covalently linked to the polysiloxanes 220. By polymerizing at least part of the total number of acrylate groups 225 of the printed composition 201 a 3D printed object 100 with polymerized polysiloxanes 230 may be provided. Fig. 2b by way of example shows in a possible first reaction scheme the functionalizing of a siloxanes 220 with the acrylate group 225, and in a second reaction scheme the cross-linking to form the acrylate-based cross-link (also indicated with reference 225).

Here, by way of example in Fig. 2a a 3D object 100, by way of example a lens, is depicted, of which part 235, especially essentially all is transmissive, more especially transparent for light. Reference 235 indicates the acrylate groups before polymerization, as well as the acrylate-based groups after polymerization, covalently linking two polysiloxane molecules 220.

The polysiloxanes 220 may also comprise curable polysiloxanes 220, e.g. via vinyl groups. These siloxane cross-links or (their) cross-link precursors are indicated with

reference 245, see also Fig. 2c. This figures shows a acrylate-based group crosslink (ref. 225) and a siloxane cross-link 245. Both are covalently linked to the polysiloxane 220.

The reactions are shown in more detail in Fig. 2d, with reaction scheme I indicating the cross-linking via the acrylate group 225. As indicated above, the polysiloxanes 220 comprise curable polysiloxanes 220 curably by one or more of (a) a hydrosilylation reaction (II) and (b) a peroxide curing (III).

Fig. 2e shows in fact the reaction product of scheme I (of Fig. 2d), i.e. $(C_2R_2R_3)C_3R_4R_5R_6)C_4C_1OOR_1$, with R_1 being the polysiloxane and R_2, R_3, R_4, R_5, and R_6 independently being selected from for instance the group consisting of H, an alkyl, an alkenyl, an alkynyl, an ether, an ester, a polysiloxane, etc., with especially at least one (especially of R_2 and R_3), and even more especially only one, being a polysiloxane. C_4 indicated the carbon atom to which OOR_1, C_3 and C_2 are covalently bound (i.e. in the case of methacrylic acid, the carbon atom to which COOH, CH_3 and CH_2 are covalently bound). The acrylate group is especially indicated in Fig. 2e. The weight of such group is calculates as if R1-R6 were H.

EXPERIMENTAL

In a first example, a mixture of the following components was made:

2 parts poly(dimethylsiloxane-co-methylhydrosiloxane) (ABCR 109380).

8 parts vinyl terminated poly(dimethylsiloxane) (ABCR 109356)

5 parts methacryloxypropyl terminated poly(dimethylsiloxane) (ABCR 130235).

400 ppm photo initiator (Ciba irgacure 651)

0.3 ppm 1,1,3,3-tetramethyl-1,3-divinyldisiloxane, platinum complex (ABCR 1466970).

The concentration of the platinum hydrosilylation complex was chosen such that solidification of the mixture at 150°C occurred within a few minutes but the mixture was stable for several days at room temperature.

When a small amount of the mixture was dispensed on a glass plate in the presence of UV light (360 nm) under N_2 it gelated and the form of the dispensed trace was retained. After heating the sample for a few minutes at 150°C a rubbery material was obtained.

The same type of rubbery material was obtained if the mixture was heated without pre- photopolymerization or when the dimethacrylate and photoinitiator had been omitted. This shows that the methacrylate, irgacure and its reaction products do not interfere with the thermal hydrosilylation reaction.

If we decrease the amount of diacrylate below 2.5 parts, gelation does not occur easily thus about 2.5 part is the lower limit. The amount of methacrylate for this limit can be calculated as follows: Dimethacrylate: Mn=4680; 33/100 part of dimethacrylate means: 0.33/Mn=0.33/4680=7.1E-5 mole/gram. The polymer contains two endgroup thus C(methacrylate)= 1.4E-4 methacrylate groups/gram. If we recalculate to methacrylic acid (Fw=86) we obtain: 1.4E-4*86=0.012 gram/gram silicone (thus minimum weight percentage methacrylic groups of about 1.2%).

In a second example, a mixture of the following components was made:
2 parts: poly(dimethylsiloxane-co-methylvinylsiloxane) (ABCR 116647).
1 part : methacryloxypropyl terminated poly(dimethylsiloxane) (ABCR 130235).
2000 ppm photo initiator (Ciba irgacure 651)
2000 ppm benzoyl peroxide

When a small amount of the mixture was dispensed on a glass plate in the presence of UV light (360 nm) under N_2 it gelated and the form of the dispensed trace was retained. After heating the sample for 10 minutes at 150°C, under N_2, a rubbery material was obtained.

The same type of rubbery material was obtained if the mixture was heated without pre- photopolymerization or when the dimethacrylate and photoinitiator had been omitted. This shows that the methacrylate, irgacure and its reaction products do not interfere with the peroxide crosslinking reaction.

When the dimethacrylate was omitted, some gelation was observed upon irradiation, however, the form of the dispensed trace could not be retained.

Poly(acrylate) groups, irgacure, benzoyl peroxide and remnants of these initiators are detectable by infrared spectroscopy (FTIR–ATR Ge crystal). Fig. 3 shows that the poly(methacrylate) signal in an IR spectrum around 1720 cm^{-1} in the mixture with the lower limit of methacrylate groups (see above) can be observed easily. It was recorded after photopoymerisation and thermal curing. This signal is absent in the IR spectra of "normal" silicones.

The term "substantially" herein, such as in "substantially consists", will be understood by the person skilled in the art. The term "substantially" may also include embodiments with "entirely", "completely", "all", etc. Hence, in embodiments the adjective substantially may also be removed. Where applicable, the term "substantially" may also relate to 90% or higher, such as 95% or higher, especially 99% or higher, even more especially 99.5% or higher, including 100%. The term "comprise" includes also

embodiments wherein the term “comprises” means “consists of”. The term “and/or” especially relates to one or more of the items mentioned before and after “and/or”. For instance, a phrase “item 1 and/or item 2” and similar phrases may relate to one or more of item 1 and item 2. The term "comprising" may in an embodiment refer to "consisting of" but may in another embodiment also refer to "containing at least the defined species and optionally one or more other species".

Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

The devices herein are amongst others described during operation. As will be clear to the person skilled in the art, the invention is not limited to methods of operation or devices in operation.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. Use of the verb "to comprise" and its conjugations does not exclude the presence of elements or steps other than those stated in a claim. The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. The invention may be implemented by means of hardware comprising several distinct elements, and by means of a suitably programmed computer. In the device claim enumerating several means, several of these means may be embodied by one and the same item of hardware. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

The invention further applies to a device comprising one or more of the characterizing features described in the description and/or shown in the attached drawings. The invention further pertains to a method or process comprising one or more of the characterizing features described in the description and/or shown in the attached drawings.

The various aspects discussed in this patent can be combined in order to provide additional advantages. Furthermore, some of the features can form the basis for one or more divisional applications.

CLAIMS:

1. A method for producing a 3D printed object (100), the method comprising the steps of:

- providing a composition (200) comprising a curable polysiloxane (220), the curable polysiloxane (220) comprising polymerizable acrylate groups (225) covalently linked to the curable polysiloxane (220) and the curable polysiloxane (220) being curable by one or more of (a) a hydrosilylation reaction and (b) a peroxide curing, the composition (200) further comprising a photo polymerization catalyst and one or more of (a1) a hydrosilylation catalyst and (b1) a peroxide catalyst,
- 3D printing, using a 3D printer (500), the composition (200) to provide a printed composition (201),
- photo polymerizing at least part of the total number of acrylate groups (225) of the printed composition (201) to provide said 3D printed object (100) with polymerized polysiloxanes (230), and
- providing heat to the printed composition (201) to solidify said 3D printed object (100) under thermally induced reactions of hydrosilylation or peroxide initiated crosslinking.

2. The method according to claim 1, wherein the 3D printer (500) further comprises a heating unit (1100) configured to heat said printed composition (201).

3. The method according to any one of the preceding claims, wherein the composition (200) comprises in the range of 1-5wt.% acrylate groups (225), wherein the weight of the acrylate groups (225) is defined as the weight of methacrylic acid.

4. The method according to any one of the preceding claims, wherein the 3D printer (500) further comprises a radiation source (1200) configured to irradiate with radiation (1201) said printed composition (201), wherein the radiation (1201) is selected from the group consisting of UV radiation, visible radiation, and IR radiation.

5. The method according to any one of the preceding claims, wherein said composition (200) comprises methacryloxypropyl terminated poly(dimethyl) siloxanes and one or more of (a) poly(dimethylsiloxane-co-methylhydrosiloxane and vinyl terminated poly(dimethyl siloxanes), and (b) a poly(dimethylsiloxane-co-methylvinyl siloxanes).

6. The method according to any one of the preceding, wherein the method comprises 3D printing said composition (200) to provide said printed composition (201), wherein during or after or during and after printing the composition (200,201) downstream from a printer nozzle (502) of the 3D printer (500) is irradiated with radiation (1201) and subjected to heat.

7. A 3D printed object (100) comprising a polymerized polysiloxane (230), wherein the polymerized polysiloxane (230) comprises polysiloxanes (220) that are covalently linked via acrylate-based crosslinks, and wherein the polysiloxanes (220) further comprise siloxanes cross-links.

8. The 3D printed object (100) according to claim 7, wherein at least a part (235) of said polymerized polysiloxane (230) is transmissive for visible light, and wherein the 3D printed object (100) comprises an optical component.

9. The 3D printed object (100) according to any one of claims 7 and 8, wherein the polymerized polysiloxane (230) comprises an acrylate group showing IR absorption at about 1720 cm^{-1}, and wherein the polymerized siloxane (230) comprises in the range of 1-5 wt.% acrylate groups (225), the weight of the acrylate groups (225) being defined as the weight of methacrylic acid.

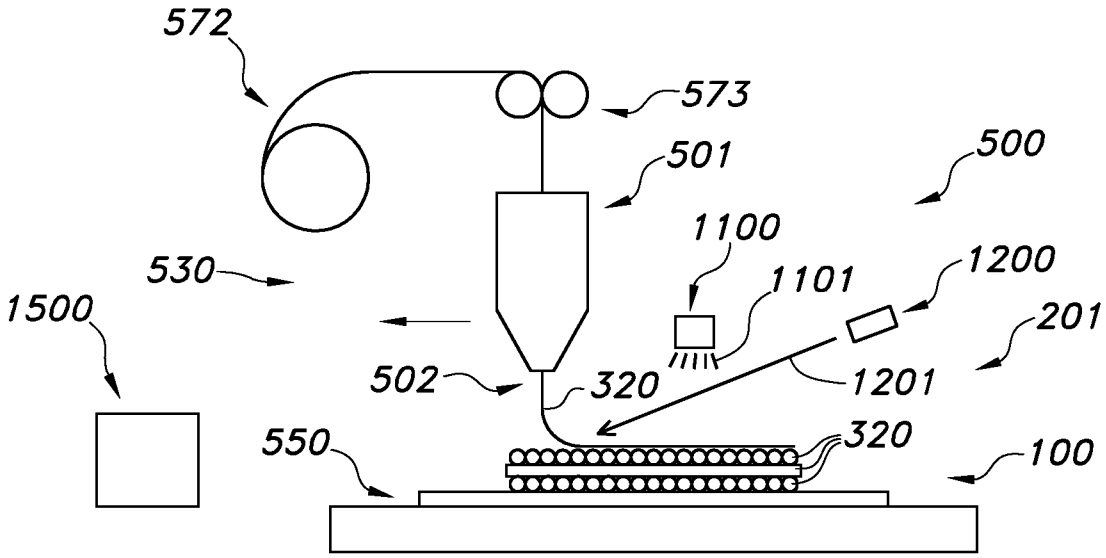

572
573
501
500
1100
530
1101
1200
1500
201
502
320
1201
320
550
100

FIG. 1

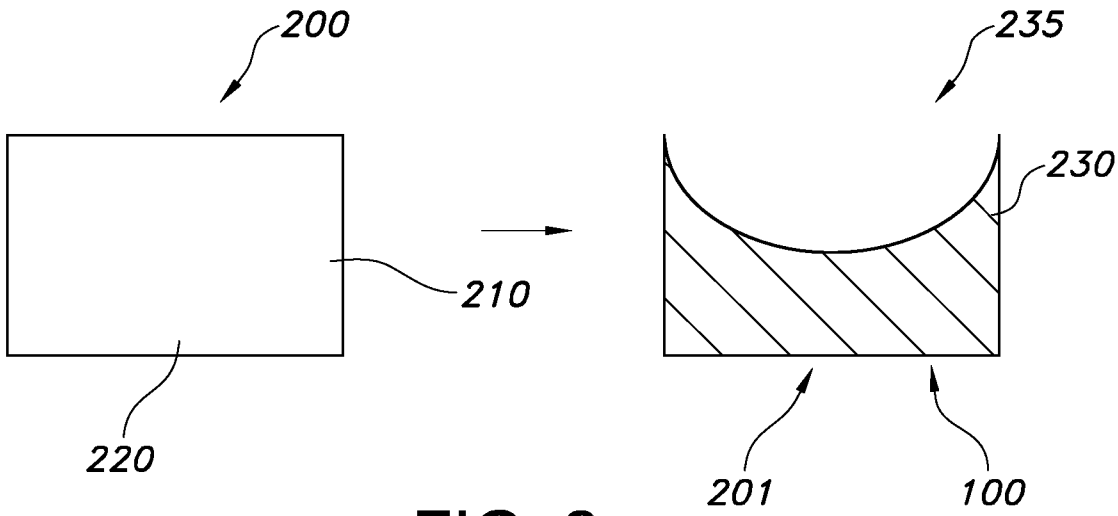

200
235
230
210
220
201
100

FIG. 2a

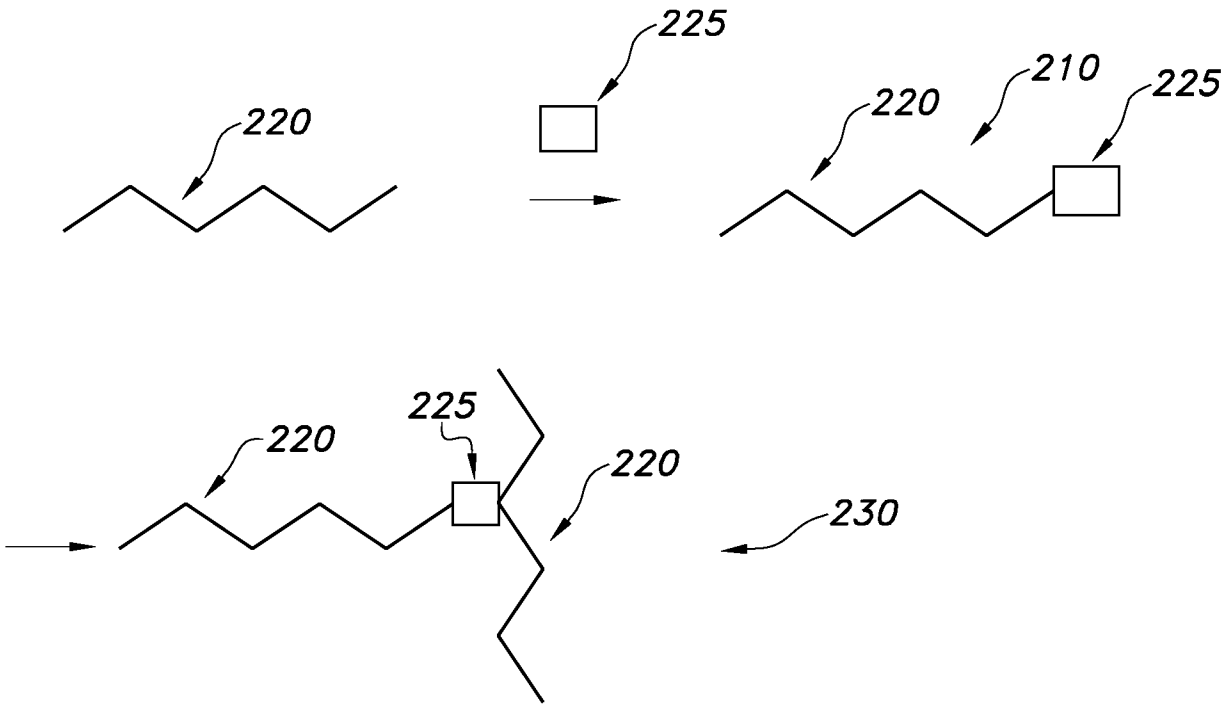


FIG. 2b

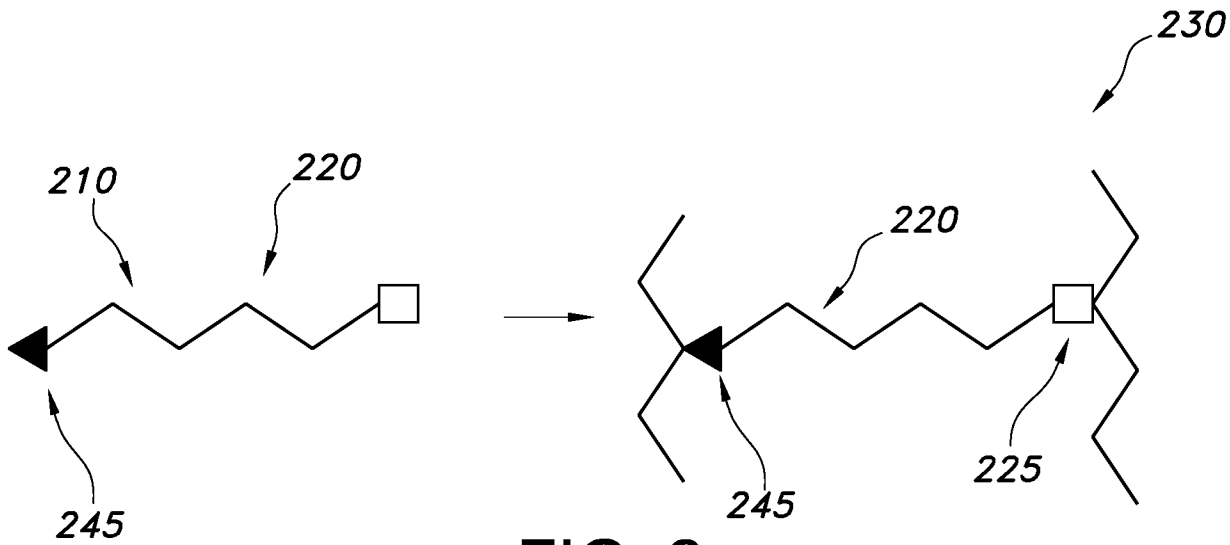


FIG. 2c

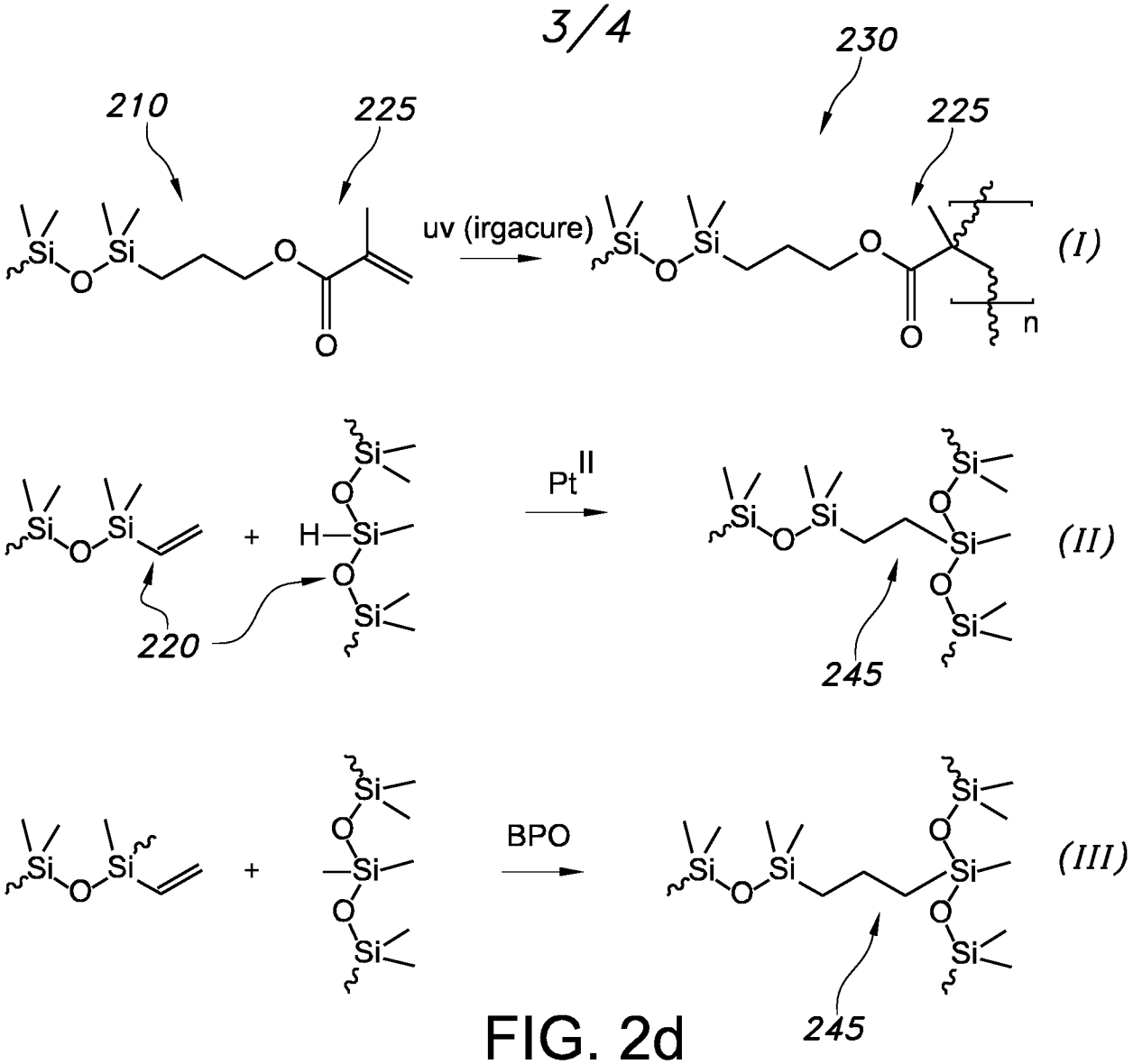

210
225
230
225
uv (irgacure)
(I)
n
Pt II
(II)
220
245
BPO
(III)
245

FIG. 2d

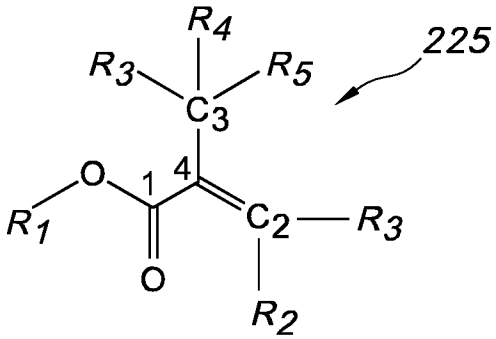

R4
R3
R5
225
C3
O
1
4
R1
C2
R3
O
R2

FIG. 2e

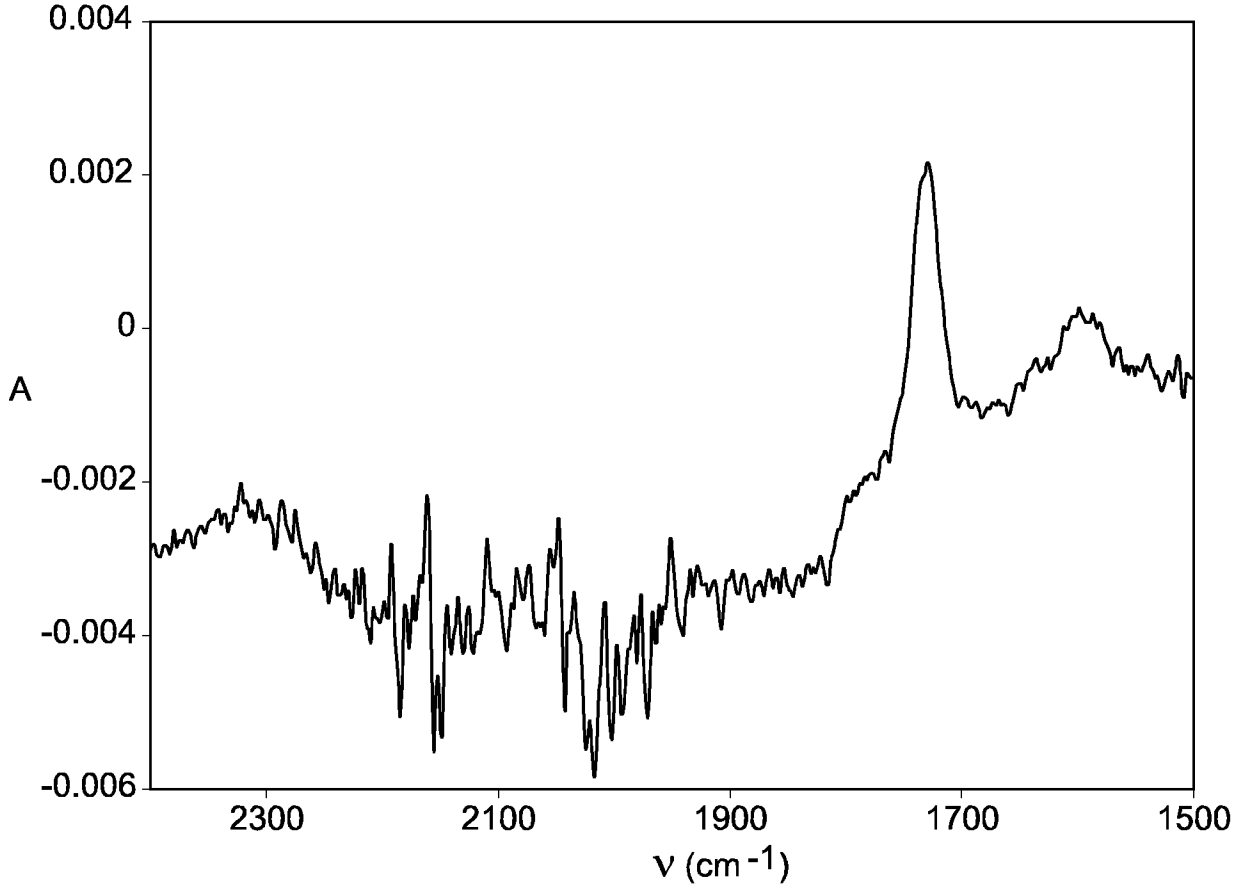


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/052826

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F220/08 B29C67/00 C08F230/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/037606 A1 (FRAUNHOFER GES FORSCHUNG [DE]; HANNOVER LASER ZENTRUM [DE]; HOUBERTZ-K) 8 May 2003 (2003-05-08) claims 1,12; example 1 -----	1-6,8,9
Y	JOSEF KUMPFMUELLER ET AL: "Two-photon-induced Microfabrication of Flexible Optical Waveguides", JOURNAL OF LASER MICRO/NANOENGINEERING, vol. 6, no. 3, 1 December 2011 (2011-12-01), pages 195-198, XP055129252, DOI: 10.2961/jlmn.2011.03.0004 page 196, paragraph 2.1 -----	1-6,8,9

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 May 2016	24/05/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Friederich, Pierre

3

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	INFUEHR ET AL: "Functional polymers by two-photon 3D lithography", APPLIED SURFACE SCIENCE, vol. 254, 10 August 2007 (2007-08-10), pages 836-840, XP002757437,	7
Y	paragraph [0002]	1-6,8,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/052826

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03037606 A1	08-05-2003	DE 10152878 A1	15-05-2003
		EP 1499490 A1	26-01-2005
		WO 03037606 A1	08-05-2003