



- (51) **International Patent Classification:**
C08F 2/48 (2006.01) *C08L 33/08* (2006.01)
C08F 220/18 (2006.01)
- (21) **International Application Number:**
PCT/US2016/051515
- (22) **International Filing Date:**
13 September 2016 (13.09.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
62/218,224 14 September 2015 (14.09.2015) US
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- (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, KW, 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).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

- (54) **Title:** LIGHT-CURABLE ARTICLE OF MANUFACTURE WITH PORTIONS OF DIFFERING SOLUBILITY

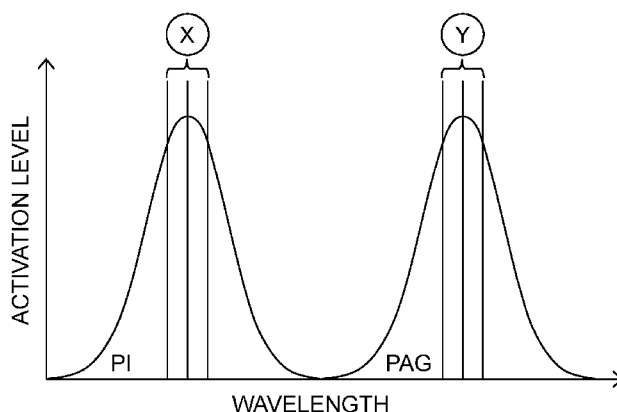


FIG. 1A

(57) **Abstract:** Provided herein is a polymerizable liquid composition useful for additive manufacturing, which composition may include: (i) a free radical photoinitiator; (ii) monomers and/or prepolymers (e.g., reactive diluents) that are polymerizable by exposure to actinic radiation or light, optionally wherein some or all of said monomers and/or prepolymers comprise one or more acid-labile or base-labile groups; (iii) a crosslinker comprising one or more acid-labile or base-labile groups; and (iv) a photoacid generator or a photobase generator, wherein said free radical photoinitiator and said photoacid generator or photobase generator are, or are selected to be, activated by light at different ranges of wavelengths or intensities. Methods of forming a three-dimensional object with the composition, and articles so formed are also provided. Methods of removing a portion of the article by dissolving in a polar or non-polar solvent are further provided.



LIGHT-CURABLE ARTICLE OF MANUFACTURE WITH PORTIONS OF DIFFERING SOLUBILITY

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RELATED APPLICATIONS

This application claims the benefit of United States Provisional Patent Application Serial No. 62/218,224 filed September 14, 2015, the disclosure of which is incorporated by reference herein in its entirety.

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BACKGROUND

It is well-known in polymer science that covalently crosslinked thermoset materials are insoluble in most any solvent, and, therefore, cannot be readily dissolved. Light-curable three-dimensional printing resins may also contain multifunctional reactive groups which act as covalent crosslinkers upon curing. Once cured, they form connection points to polymer chains resulting in a crosslinked resin that also cannot be readily dissolved.

Three-dimensional printed parts produced with resins often require the use of supports in order to print fine/delicate structures and overhangs. A significant amount of effort is then needed post-printing to remove the supports, by clipping or sawing, and to sand down the small bumps remaining after the support has been removed. This processing can be difficult if the part is made of a tough resin that is resistant to cutting and sanding, and/or has an intricate shape that makes it challenging to cut or sand.

There is, therefore, a need to produce three-dimensional printed objects having supports that can be more easily removed, such as by dissolving or melting.

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SUMMARY

Provided herein is a polymerizable liquid composition useful for additive manufacturing, which composition may include: (i) a free radical photoinitiator; (ii) monomers and/or prepolymers (e.g., reactive diluents) that are polymerizable by exposure to actinic radiation or light, optionally wherein some or all of said monomers and/or prepolymers comprise one or more acid-labile groups; (iii) a crosslinker comprising one or more acid-labile groups; and (iv) a photoacid generator, wherein said free radical photoinitiator and said photoacid generator are, or are selected to be, activated by light at different ranges of wavelengths or intensities.

In some embodiments, the different ranges of wavelengths or intensities may be selected such that there is a wavelength at which the free radical photoinitiator is activated and the

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photoacid generator is not activated (or not appreciably activated). In some embodiments, the free radical photoinitiator and the photoacid generator have spectra with a peak activation wavelength that is at least 5 or 10 nm apart from one another. In some embodiments, the free radical photoinitiator is activated at wavelengths 250-600 nm (or any subrange therein), and the photoacid generator is activated at wavelengths 250-375 (or any subrange therein).

In some embodiments, the composition comprises: (i) from 0.1 to 4 percent by weight of free radical photoinitiator; (ii) from 10 to 90 percent by weight of monomers and/or prepolymers; (iii) from 5 to 90 percent by weight of crosslinker; and (iv) from 0.1 to 4 percent by weight of photoacid generator.

Also provided is a polymerizable liquid composition useful for additive manufacturing, which composition may include: (i) a free radical photoinitiator; (ii) monomers and/or prepolymers (*e.g.*, reactive diluents) that are polymerizable by exposure to actinic radiation or light, optionally wherein some or all of said monomers and/or prepolymers comprise one or more base-labile groups; (iii) a crosslinker comprising one or more base-labile groups; and (iv) a photobase generator, wherein said free radical photoinitiator and said photobase generator are, or are selected to be, activated by light at different ranges of wavelengths or intensities.

In some embodiments, the different ranges of wavelengths or intensities may be selected such that there is a wavelength at which the free radical photoinitiator is activated and the photobase generator is not activated (or not appreciably activated). In some embodiments, the free radical photoinitiator and the photobase generator have spectra with a peak activation wavelength that is at least 5 or 10 nm apart from one another. In some embodiments, the free radical photoinitiator is activated at wavelengths 250-600 nm, and the photobase generator is activated at wavelengths 250-375.

In some embodiments, the composition comprises: (i) from 0.1 to 4 percent by weight of free radical photoinitiator; (ii) from 10 to 90 percent by weight of monomers and/or prepolymers; (iii) from 5 to 90 percent by weight of crosslinker; and (iv) from 0.1 to 4 percent by weight of photobase generator.

Further provided is a method of forming a three-dimensional object comprising an acidic region, which method may include some or all of the steps of: (a) providing the polymerizable liquid composition having a photoacid generator as taught herein; (b) polymerizing a build region of said polymerizable liquid composition to form a crosslinked polymer, wherein said polymerizing is carried out by irradiating said polymerizable liquid with light at a first wavelength or intensity; and (c) activating the photoacid generator by further irradiating a portion of the build region intended or selected to be acidic with light at a second wavelength or

intensity, whereby the photoacid generator produces acid in said portion of the crosslinked polymer to thereby form said acidic region, to thereby form said three-dimensional object comprising an acidic region.

5 In some embodiments, the first wavelength is produced by a first light source, and the second wavelength is produced by a second light source, each having an emission peak wavelength that is at least 5 or 10 nm apart from one another.

10 In some embodiments, the first wavelength and the second wavelength are produced by the same light source, being configured to produce a first or second emission peak wavelength that is at least 5 or 10 nm apart (*e.g.*, with UV filters and/or rapid lamp and/or mirror switching time).

In some embodiments, the forming is carried out by additive manufacturing (*e.g.*, bottom-up or top-down three-dimensional fabrication). In some embodiments, the forming is carried out by continuous liquid interface production (CLIP).

15 In some embodiments, the method also includes the step of: (d) heating the acidic region of the three-dimensional object to a temperature of from 40 degrees Celsius to 250 degrees Celsius (or any subrange therein), whereby acid of the acidic region reacts with the acid-labile groups to form reacted groups.

20 In some embodiments, the reacted groups comprise polar or non-polar moieties, said moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object.

In some embodiments, the reacted groups confer a different melting temperature (T_m) or glass transition temperature (T_g) to the acidic region.

25 Also provided is a method of forming a three-dimensional object comprising an acidic region, which method may include some or all of the steps of: (a) providing a carrier and a build plate, said build plate comprising a build surface with said build surface and said carrier defining a build region therebetween; (b) filling said build region with the polymerizable liquid composition comprising a photoacid generator (PAG) as taught herein, said polymerizable liquid composition contacting said build surface; (c) polymerizing said polymerizable liquid composition to form a crosslinked polymer, wherein said polymerizing is carried out by
30 irradiating said build region through said build plate with light at a first wavelength or intensity to activate the free radical photoinitiator, polymerize the photopolymerizable monomer to form a polymer, and crosslink the polymer with said crosslinker, thereby forming a crosslinked polymer in said build region; (d) activating the photoacid generator by further irradiating a portion of the build region intended to be acidic through said build plate with light at a second wavelength or

intensity, whereby the photoacid generator produces acid in said crosslinked polymer to thereby form said acidic region; and (e) advancing said carrier with said crosslinked polymer adhered thereto away from said build surface on said build plate to create a subsequent build region between said crosslinked polymer and said build surface; to thereby form said three-dimensional object comprising an acidic region.

In some embodiments, the method also includes the step of: (f) heating the acidic region of the three-dimensional object, whereby acid of the acidic region reacts with the acid-labile groups to form reacted groups.

In some embodiments, the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object.

In some embodiments, the reacted groups confer a different melting temperature (T_m) or glass transition temperature (T_g) to the acidic region.

Further provided is a method of forming a three-dimensional object comprising an acidic region, comprising some or all of the steps of: (a) providing a carrier and a build plate, said build plate comprising a semipermeable member, said semipermeable member comprising a build surface with said build surface and said carrier defining a build region therebetween, and with said build surface in fluid communication by way of the semipermeable member with a source of polymerization inhibitor; (b) filling said build region with the polymerizable liquid composition comprising a photoacid generator (PAG) as taught herein, said polymerizable liquid composition contacting said build surface; (c) polymerizing said polymerizable liquid composition to form a crosslinked polymer, wherein said polymerizing is carried out by irradiating said build region through said build plate with light at a first wavelength or intensity to activate the free radical photoinitiator, polymerize the photopolymerizable monomer to form a polymer, and crosslink the polymer with said crosslinker, thereby forming a crosslinked polymer in said build region, while forming or maintaining a liquid film release layer comprised of said polymerizable liquid composition formed between said crosslinked polymer and said build surface, the polymerization of which liquid film is inhibited by said polymerization inhibitor; (d) activating the photoacid generator by further irradiating a portion of the build region intended to be acidic through said build plate with light at a second wavelength or intensity, whereby the photoacid generator produces acid in said crosslinked polymer to thereby form said acidic region, while forming or maintaining a liquid film release layer comprised of said polymerizable liquid composition formed between said crosslinked polymer and said build surface, the polymerization of which liquid film is inhibited by said polymerization inhibitor; and (e) advancing said carrier with said

crosslinked polymer adhered thereto away from said build surface on said build plate to create a subsequent build region between said crosslinked polymer and said build surface; to thereby form a three-dimensional object comprising an acidic region.

5 In some embodiments, the method further includes the step of: (f) heating the three-dimensional object, whereby acid of the acidic region reacts with the acid-labile groups to form reacted groups.

In some embodiments, the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object.

10 In some embodiments, the reacted groups confer a different melting temperature (T_m) or glass transition temperature (T_g) to the acidic region.

Also provided are methods of forming a three-dimensional object as detailed above having a basic region rather than an acidic region, in which the composition includes a photobase generator in place of the photoacid generator.

15 Further provided is an article of manufacture produced by a method of three-dimensional fabrication as taught herein.

Still further provided is an article of three-dimensional additive manufacture, said article comprising a photopolymerized polymer with acid-labile groups and a photoacid generator, wherein said article comprises at least one, or a plurality of, acidic regions, and at least one, or a plurality of, non-acidic regions, wherein the regions are integrally formed with one another.

In some embodiments, the acidic regions are soluble in an aqueous solution, and the non-acidic regions are not soluble in the aqueous solution.

25 In some embodiments, the acidic regions comprise a support structure or a portion thereof. In some embodiments, the acidic regions comprise a raft or portion thereof. In some embodiments, the acidic regions comprise less than half of the total volume of the article.

Also provided is an article of three-dimensional additive manufacture, said article comprising a photopolymerized polymer having base-labile groups and a photobase generator, wherein said article comprises at least one, or a plurality of, basic regions, and at least one, or a plurality of, non-basic regions, wherein the regions are integrally formed with one another.

30 Further provided is a method of removing a portion of an article of three-dimensional additive manufacture, comprising: providing an article having at least one, or a plurality of, acidic regions; and heating the article, whereby acid of the acidic region reacts with the acid-labile groups to form reacted groups, wherein the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-acidic region of the three-

dimensional object; and then, dissolving the acidic region in a polar or non-polar solvent, thereby removing the portion of the article of three-dimensional additive manufacture.

Still further provided is a method of removing a portion of an article of three-dimensional additive manufacture, comprising: providing an article having at least one, or a plurality of, basic regions; and heating the article, wherein photobase of the basic region reacts with the base-labile groups to form reacted groups, wherein the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-basic region of the three-dimensional object; and then, dissolving the basic region in a polar or non-polar solvent, thereby removing the portion of the article of three-dimensional additive manufacture.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A-1G provide example graphs of a photoinitiator (PI) and photoacid generator (PAG) which are activated by light at different ranges of wavelengths or intensities. An example first light source X and second light source Y are provided, each having an emission spectrum represented by three vertical lines, the middle line representing the wavelength at maximum intensity, and the flanking lines representing the full width at half maximum intensity (FWHM).

FIG. 1A provides an example graph in which the PI and PAG have non-overlapping activation (absorbance) ranges.

FIG. 1B provides an example graph of PI and PAG having overlapping activation ranges.

FIG. 1C provides an example graph in which the PI and PAG have non-overlapping activation (absorbance) ranges, with the activation range of PAG is at a lower range of wavelengths than the activation range of PI.

FIG. 1D provides another example graph of PI and PAG having overlapping activation ranges.

FIG. 1E provides an example graph in which the PI and PAG have overlapping activation ranges, with the PI having a tail in the higher wavelengths.

FIG. 1F shows an example graph in which the activation range of the PAG is wholly within the activation range of the PI.

FIG. 1G shows another example graph in which the activation wavelength range of the PAG is wholly within the activation wavelength range of the PI.

FIG. 1H shows an example graph in which the PI and PAG have overlapping activation ranges, and the X light source used is centered at the peak activation of the PI.

FIG. 2 is a photograph of an example additive manufacturing product or article (10), a ball, which has a rounded surface that is manufactured with supports (12) and on a raft (13). The supports and raft are removed after fabrication.

FIGS. 3A-3B present a schematic of additive manufacturing of an article (10) using a dual LED light source for printing an object having a PAG-active acidic region (**FIG. 3A**), with subsequent dissolving of the PAG-active regions (**FIG. 3B**).

FIG. 4 shows a schematic of an example article (10) having PAG-active acidic regions at the point of contact of the supports (12). The supports are removed by dissolving the PAG-active regions.

FIG. 5 shows a schematic of an example article (10) having a "brick" of cured material where a shape is defined by the regions of inactive PAG and active PAG. Regions of active PAG in the support structure (12) are dissolved after thermal cure to produce the shaped article.

DETAILED DESCRIPTION

The present disclosure relates to compositions and methods useful for creating objects by additive manufacturing such as stereolithography and related processes such as Continuous Liquid Interface Production (CLIP), in which the objects have portions of differing solubility and/or melting or glass transition temperatures (*e.g.*, where the object is connected to supports).

The present invention is now described more fully hereinafter with reference to the accompanying drawings, in which embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the invention to those skilled in the art.

Like numbers refer to like elements throughout. In the figures, the thickness of certain lines, layers, components, elements or features may be exaggerated for clarity. Where used, broken lines illustrate optional features or operations unless specified otherwise.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a," "an" and "the" are intended to include plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements components and/or groups or combinations thereof, but do not preclude the presence or addition

of one or more other features, integers, steps, operations, elements, components and/or groups or combinations thereof.

Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the specification and claims and should not be interpreted in an idealized or overly formal sense unless expressly so defined herein. Well-known functions or constructions may not be described in detail for brevity and/or clarity.

It will be understood that when an element is referred to as being "on," "attached" to, "connected" to, "coupled" with, "contacting," etc., another element, it can be directly on, attached to, connected to, coupled with and/or contacting the other element or intervening elements can also be present. In contrast, when an element is referred to as being, for example, "directly on," "directly attached" to, "directly connected" to, "directly coupled" with or "directly contacting" another element, there are no intervening elements present. It will also be appreciated by those of skill in the art that references to a structure or feature that is disposed "adjacent" another feature can have portions that overlap or underlie the adjacent feature.

Spatially relative terms, such as "under," "below," "lower," "over," "upper" and the like, may be used herein for ease of description to describe an element's or feature's relationship to another element(s) or feature(s) as illustrated in the figures. It will be understood that the spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. For example, if the device in the figures is inverted, elements described as "under" or "beneath" other elements or features would then be oriented "over" the other elements or features. Thus the exemplary term "under" can encompass both an orientation of over and under. The device may otherwise be oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly. Similarly, the terms "upwardly," "downwardly," "vertical," "horizontal" and the like are used herein for the purpose of explanation only, unless specifically indicated otherwise.

It will be understood that, although the terms first, second, etc., may be used herein to describe various elements, components, regions, layers and/or sections, these elements, components, regions, layers and/or sections should not be limited by these terms. Rather, these terms are only used to distinguish one element, component, region, layer and/or section, from another element, component, region, layer and/or section. Thus, a first element, component, region, layer or section discussed herein could be termed a second element, component, region,

layer or section without departing from the teachings of the present invention. The sequence of operations (or steps) is not limited to the order presented in the claims or figures unless specifically indicated otherwise.

5 **1. Polymerizable liquid compositions.**

Polymerizable liquid compositions curable by actinic radiation (typically light, and in some embodiments ultraviolet (UV) light) are provided to enable the present invention. The liquid (sometimes referred to as "liquid resin," "ink," or simply "resin" herein) may include a polymerizable monomer, particularly photopolymerizable and/or free radical polymerizable
10 monomers, optionally prepolymers (*i.e.*, reacted monomers capable of further polymerization), a crosslinker and a suitable initiator such as a free radical initiator.

In some embodiments, the crosslinker and/or monomer has one or more acid-labile groups. In some embodiments, the crosslinker and/or monomer has one or more base-labile groups. Examples of liquid resins, monomers and initiators include, but are not limited to, those
15 set forth in U.S. Patent Nos. 8,232,043; 8,119,214; 7,935,476; 7,767,728; 7,649,029; WO 2012129968 A1; CN 102715751 A; JP 2012210408 A.

Photopolymerizable monomers. Examples of photopolymerizable monomers include, but are not limited to, acrylates, methacrylates, α -olefins, N-vinyls, acrylamides, methacrylamides, styrenics, epoxides, thiols, 1,3-dienes, vinyl halides, acrylonitriles, vinyl esters, maleimides,
20 vinyl ethers, etc. Combinations of such monomers may also be used. For example, thiol-containing monomers may be included and react with vinyl monomers/prepolymers during radical polymerization and become part of the polymer backbone. As noted above, in some embodiments, the monomer has one or more acid-labile groups or one or more base-labile groups. Such groups may form moieties having differing solubilities and/or melting temperatures
25 when cleaved by the acid or photobase, respectively.

In some embodiments, the photopolymerizable monomer may be a reactive diluent. Diluents as known in the art are compounds used to reduce viscosity in a resin composition. Reactive diluents undergo reaction to become part of the polymeric network. In some
30 embodiments, the reactive diluent may react at approximately the same rate as other reactive monomers and/or the reactive crosslinkers in the composition. Reactive diluents may include aliphatic reactive diluents, aromatic reactive diluents, and cycloaliphatic reactive diluents. Examples include, but are not limited to, isobornyl acrylate, isobornyl methacrylate, lauryl acrylate, lauryl methacrylate, 2-ethyl hexyl methacrylate, 2-ethyl hexyl acrylate, di(ethylene glycol) methyl ether methacrylate, phenoxyethyl methacrylate, hydroxyethyl acrylate,

hydroxyethyl methacrylate, dimethyl(aminoethyl) methacrylate, butyl acrylate, butyl methacrylate, cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, and tert-butylaminoethyl methacrylate.

Free radical photoinitiators. Free radical photoinitiators are known in the art. These
5 initiators absorb energy in varying ranges in the UV spectrum (100-450 nm), including UV A (320-400 nm), UV B (280-320 nm), UV C (200-280 nm), deep UV (100-200 nm) and near-visible UV (400-450 nm, also known as UV-VIS) and produce a free radical reactive species, which then initiates polymerization of the polymerizable monomers. *See, e.g.,* W. Arther Green, "Industrial Photoinitiators: A Technical Guide," CRC Press, 2010. In some embodiments, the free
10 radical photoinitiators are activated in the visible spectrum, *i.e.*, up to 600 or 700 nm.

Photoinitiators activated in various areas of the UV spectrum are known, and may include, but are not limited to, Type I photoinitiators such as hydroxyacetophenones (HAPs), benzil ketals (BKs), alkylaminoacetophenones (AAAPs), phosphine oxides (POs, such as TPO (diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide, *e.g.*, Darocure TPO, Irgacure TPO, Lucrin
15 TPO)), etc.; and Type II photoinitiators such as benzophenones, substituted benzophenones, anthraquinones, thioxanthenes, etc. Free radical photoinitiators may include, but are not limited to, alpha-hydroxyketones, phenylglyoxylates, benzyldimethyl-ketals, alpha-aminoketones, mono acyl phosphines (MAPOs), bis acyl phosphines (BAPOs), metallocenes, iodonium salts, combinations thereof, etc. *See Photoinitiators for UV Curing, Key Products Selection Guide*
20 *2003*, Ciba Specialty Chemicals Inc., Basel, Switzerland.

In some embodiments, the free radical photoinitiator is selected to have an absorption spectrum that is not coextensive with the absorption spectrum of the photoacid generator or photobase generator in the composition. In some embodiments, the free radical photoinitiator is activated in a higher-energy section of the UV spectrum (*i.e.*, shorter wavelengths), and the
25 photoacid generator or photobase generator is activated in a lower-energy section of the UV spectrum (*i.e.*, longer wavelengths). In some embodiments, the free radical photoinitiator is activated in a lower-energy section of the UV spectrum (*i.e.*, longer wavelengths), and the photoacid generator or photobase generator is activated in a higher-energy section of the UV spectrum (*i.e.*, shorter wavelengths).

30 For example, hydroxyacetophenones (HAPs) absorb at about 240-260 nm; *e.g.*, Darocur 1173 absorbs at about 244; Irgacure 907 absorbs at about 306 nm; and Irgacure 369 absorbs at about 325 nm. Benzophenone absorbs at about 254 nm; while substituted benzophenone Speedcure PBZ absorbs at about 288 nm; and Speedcure BMS absorbs at about 315 nm. *See also*

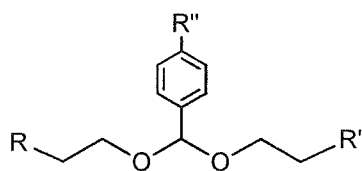
Photoinitiators for UV Curing, Key Products Selection Guide 2003, Ciba Specialty Chemicals Inc., Basel, Switzerland, providing absorption spectra for Irgacure and Darocure photoinitiators.

In some embodiments, the free radical photoinitiator is selected to have an activation intensity at one or more wavelengths that is not coextensive with the activation intensity of the photoacid generator or photobase generator in the composition. In some embodiments, the free radical photoinitiator is activated at a lower intensity than the photoacid generator. *See FIG. 1H.*

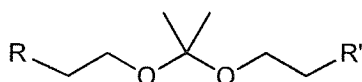
Crosslinkers. Crosslinkers as used herein refer to chemical compounds or portions thereof that serve to join two or more polymer chains through covalent attachment or non-covalent (*e.g.*, ionic) attraction. The crosslinkers may be provided as moieties reactive at one or more than one end (*e.g.*, containing unsaturated vinyl moieties), or may be provided as part of the polymerizable monomer chemical structure. As taught herein, the crosslinker and/or polymerizable monomer has acid-labile or base-labile group(s).

Acid-labile groups. In some embodiments, the polymerizable liquid composition comprises compounds with an acid-labile group suitable for acid-mediated cleavage in a crosslinker, and/or monomer or prepolymer. Such acid-labile groups may be selected by one of skill in the art in view of the overall predicted structure of the formed polymer, and may include groups such as orthoester, tertiary ester, acetal, ketal, hydrazone, imine, cis aconityl, trityl, silyl ester, carbamate, tert-butyloxycarbonyl, tosyl group, etc. *See, e.g.*, Binauld and Stenzel, "Acid-degradable polymers for drug delivery: a decade on innovation," *Chem. Commun.* 49: 2082-2102, 2013; U.S. Patent No. 7,993,749. In some embodiments, the acid-labile group may be cleavable as part of a chemical amplification.

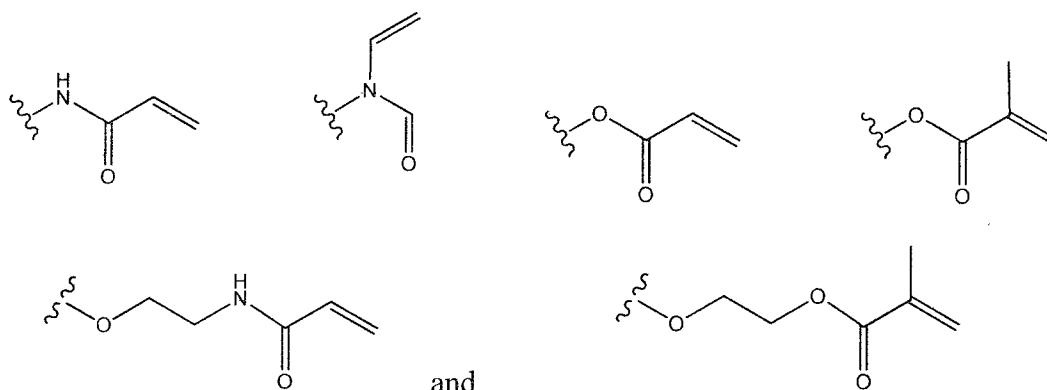
As an example, acid-labile acetal or ketal crosslinkers may have the formula:



OR



wherein R'' is OH, alkoxy, or polyether, and
wherein R and R' are the same or different, and are selected from the group consisting of:



Suitable acid-labile monomers may include tert-butyl methacrylate, tert-butyl acrylate, T-BoC protected hydroxystyrene, and other alcohol-containing methacrylate and acrylate monomers protected with T-BoC, etc.

Photoacid generators. To form an acid with which to carry out an acid-mediated cleavage of the acid-labile crosslinkers and/or monomers, in some embodiments a suitable (ionic or non-ionic) photoacid generator (PAG) is included in the polymerizable liquid composition. PAGs are known in the field of photolithography and can be activated by a particular spectrum of light wavelengths. These materials typically generate strong acids upon exposure to light of appropriate wavelengths.

Examples of PAGs include, but are not limited to, onium salts, sulfonium and iodonium salts, etc., such as diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenyl triflate, diphenyl p-toluenyl triflate, diphenyl p-isobutylphenyl triflate, diphenyl p-tert-butylphenyl triflate, triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate, dibutylnaphthylsulfonium triflate, etc., including mixtures thereof. *See, e.g.*, U.S. Patent Nos. 8,685,616; 7,824,839; 7,550,246; 7,534,844; 6,692,891; 5,374,500; and 5,017,461; *see also Photoacid Generator Selection Guide for the electronics industry and energy curable coatings* (BASF 2010).

Further examples of PAGs include, but are not limited to, arylketosulphinates, o-nitrobenzyl esters, naphthoquinonediazides, oximinosulphonates, trichloroacetophenones, trichloromethyl-S-triazines, etc.

In some embodiments, a polymerizable liquid composition as taught herein comprises from 1, 2 or 5 percent by weight to 20, 30, 40, 90 or 99 percent by weight of the photopolymerizable monomer or prepolymer and/or acid-labile crosslinker; and from 0.01, 0.05, 0.1, 0.5 or 1 percent by weight to 5, 8 or 10 percent by weight of the free radical photoinitiator.

In some embodiments, the polymerizable liquid composition comprises from 0.01, 0.05, 0.1, 0.5 or 1 percent by weight to 5, 8 or 10 percent by weight of the PAG, and may optionally include one or more additional components.

Base-labile groups. In some embodiments, the polymerizable liquid composition comprises a photobase-labile group suitable for photobase-mediated or amine-mediated cleavage in a crosslinker and/or monomer. Such base-labile groups may be selected by one of skill in the art in view of the overall predicted structure of the formed polymer. For example, the 9-fluorenylmethyloxycarbonyl (Fmoc) protecting group can be removed with an imine such as piperidine. Piperidine is a catalyst as it is re-generated at the end of the reaction, promoting chemical amplification. As another example, the carbamate group in a gamma-keto carbamate can cleave under the catalyzation of a primary amine. The original amine is re-generated at the end of the reaction. Some photogenerated amines may also be nucleophiles. A leaving group cleavable by an amine through nucleophilic substitution may be a base-labile group.

Photobase generators. To form a photobase with which to carry out a base-mediated cleavage of base-labile crosslinkers and/or monomers, in some embodiments a suitable (ionic or non-ionic) photobase generator (PBG) is included in the polymerizable liquid composition. PBGs are known and can be activated by a particular spectrum of light wavelengths. These materials typically generate strong photobases upon exposure to UV light of appropriate wavelengths.

Examples of PBGs include, but are not limited to, aminoketones, alkylaminoacetophenones, diazabicyclononene, 2-nitrobenzyl protected carbamates, dimethoxybenzyl protected carbamates, O-carbamoyl acetophenone oximes, α -keto carbamate, *o*-Acyloximes, ammonium salts, amineimide derivatives, sulfamide derivatives, formamide derivatives, Cobalt (III) amine complexes, etc.

In some embodiments, the polymerizable liquid composition comprises from 1, 2 or 5 percent by weight to 20, 30, 40, 90 or 99 percent by weight of the photopolymerizable monomer or prepolymer and/or base-labile crosslinker; and from 0.01, 0.05, 0.1, 0.5 or 1 percent by weight to 5, 8 or 10 percent by weight of the free radical photoinitiator. In some embodiments, the polymerizable liquid composition comprises from 0.01, 0.05, 0.1, 0.5 or 1 percent by weight to 5, 8 or 10 percent by weight of the PBG, and may optionally include one or more additional components.

Additional resin ingredients. The liquid resin can have solid particles suspended or dispersed therein. Any suitable solid particle can be used, depending upon the end product being fabricated. The particles can be metallic, organic/polymeric, inorganic, or composites or

mixtures thereof. The particles can be nonconductive, semi-conductive, or conductive (including metallic and non-metallic or polymer conductors); and the particles can be magnetic, ferromagnetic, paramagnetic, or nonmagnetic. The particles can be of any suitable shape, including spherical, elliptical, cylindrical, etc. The particles can comprise an active agent or detectable compound as described below, though these may also be provided dissolved solubilized in the liquid resin as also discussed below. For example, magnetic or paramagnetic particles or nanoparticles can be employed.

Additional resin ingredients may also include pigments, dyes, active compounds or pharmaceutical compounds, detectable compounds (e.g., fluorescent, phosphorescent, radioactive), etc., again depending upon the particular purpose of the product being fabricated. Examples of such additional ingredients include, but are not limited to, proteins, peptides, nucleic acids (DNA, RNA) such as siRNA, sugars, small organic compounds (drugs and drug-like compounds), cells, etc., including combinations thereof.

Inhibitors of polymerization. In some embodiments, 3D printing by Continuous Liquid Interface Production (CLIP) makes use of polymerization inhibitors, which may be in the form of a liquid or a gas. In some embodiments, gas inhibitors are preferred. The specific inhibitor will depend upon the monomer being polymerized and the polymerization reaction. For free radical polymerization monomers, the inhibitor can conveniently be oxygen, which can be provided in the form of a gas such as air, a gas enriched in oxygen (optionally but in some embodiments preferably containing additional inert gases to reduce combustibility thereof), or in some embodiments pure oxygen gas.

In some embodiments, the acid-labile groups or base-labile groups form polar (i.e., water soluble) or non-polar groups upon acid cleavage. This, in turn, may provide a solubility difference of the acid-catalyzed or nucleophile-catalyzed portions of the printed articles versus non-acid catalyzed or nucleophile-catalyzed portions.

2. Methods.

Polymerizable liquid compositions comprising a photoacid generator or photobase generator as taught herein are useful in additive manufacturing to create an article having portions of different solubility and/or melting temperature (T_m) or glass transition temperature (T_g). For example, the formed object may have a portion in which the photoacid generator is active, by irradiating this portion of the object upon manufacture with an appropriate wavelength to activate the photoacid generator, whereupon the photoacid generator produces acid. This

portion in which the photoacid generator is activated and has produced acid may be referred to herein as an "acidic" region.

In some embodiments, upon heating the manufactured object, the acid of the acidic region will react with acid-labile groups in the crosslinked connections and/or main polymeric chains of the polymerized object, resulting in breaks in the polymer's chemical structure that renders those regions more easily dissolved and/or melted. In some embodiments, reacted acid-labile groups form moieties that create a difference in solubility of the acidic region(s) as compared to the non-acidic region(s) of the object (*e.g.*, in aqueous solution, organic solvent, etc.). In some embodiments, the acid-labile groups, upon cleaving, may regenerate or generate additional free protons (H^+) that go onto to catalyze the further cleaving of other acid-labile groups in a chemical amplification.

In a similar manner, polymerizable liquid compositions comprising a photobase generator as taught herein are useful in additive manufacturing to create an article having portions of different solubility. For example, the formed object may have a portion in which the photobase generator is active, by irradiating this portion of the object upon manufacture with an appropriate wavelength to activate the photobase generator, whereupon the photobase generator produces a photobase, amine or other nucleophile. This portion in which the photobase generator is activated and has produced nucleophiles may be referred to herein as a "basic" region.

In some embodiments, upon heating the manufactured object, the base of the basic region will react with base-labile groups in the crosslinked connections and/or main polymeric chains of the polymerized object, resulting in breaks in the polymer's chemical structure that renders those regions more easily dissolved and/or melted. In some embodiments, reacted base-labile groups form moieties that create a difference in solubility of the basic region(s) as compared to the non-basic region(s) of the object (*e.g.*, in aqueous solution, organic solvent, etc.). In some embodiments, the base-labile groups, upon cleaving, may regenerate or generate additional nucleophiles that go onto to catalyze the further cleaving of other base-labile groups in a chemical amplification.

In some embodiments, the portions of different solubility and/or melting temperature (T_m) or glass transition temperature (T_g) of the object are support structures or a portion thereof (*e.g.*, the portion of the support structure that is directly connected to the rest of the object).

In some embodiments, the object is formed from a polymerizable liquid composition as described above by additive manufacturing, typically bottom-up or top-down additive manufacturing. Such methods are known and described in, for example, U.S. Patent No. 5,236,637 to Hull, U.S. Patent No. 7,438,846 to John, U.S. Patent No. 8,110,135 to El-Siblani,

and U.S. Patent Application Publication Nos. 2013/0292862 to Joyce and 2013/0295212 to Chen et al. The disclosures of these patents and applications are incorporated by reference herein to the extent consistent with the descriptions herein.

In general, bottom-up three-dimensional (3D) fabrication may be carried out by:

- 5 (a) providing a carrier and an optically transparent member having a build surface, said carrier and said build surface defining a build region therebetween;
- (b) filling said build region with a polymerizable liquid;
- (c) polymerizing said polymerizable liquid composition to form a solid polymer, wherein said polymerizing is carried out by irradiating said build region through said build plate with
10 light to activate a free radical photoinitiator and polymerize the photopolymerizable monomer to form a polymer, thereby forming a solid polymer in said build region; and
- (d) advancing said carrier with said solid polymer adhered thereto away from said build surface on said build plate to create a subsequent build region between said solid polymer and said build surface.

15 In some embodiments, the article is formed by continuous liquid interface production (CLIP). CLIP is known and described in, for example, PCT Application Nos. PCT/US2014/015486 (also published as US 2015/0102532); PCT/US2014/015506 (also published as US 2015/0097315), PCT/US2014/015497 (also published as US 2015/0097316), and in J. Tumbleston, D. Shirvanyants, N. Ermoshkin et al., Continuous liquid interface
20 production of 3D Objects, *Science* **347**, 1349-1352 (published online 16 March 2015). In some embodiments, CLIP employs features of a bottom-up three dimensional fabrication as described above, but the irradiating and/or said advancing steps are carried out while also concurrently: (i) continuously maintaining a dead zone of polymerizable liquid in contact with said build surface, and (ii) continuously maintaining a gradient of polymerization zone (such as an active surface)
25 between said dead zone and said solid polymer and in contact with each thereof, said gradient of polymerization zone comprising said first component in partially cured form. In some embodiments of CLIP, the optically transparent member comprises a semipermeable member (e.g., a fluoropolymer), and said continuously maintaining a dead zone is carried out by feeding an inhibitor of polymerization through said optically transparent member, thereby creating a
30 gradient of inhibitor in said dead zone and optionally in at least a portion of said gradient of polymerization zone.

While the dead zone and the gradient of polymerization zone do not have a strict boundary therebetween (in those locations where the two meet), the thickness of the gradient of polymerization zone is in some embodiments at least as great as the thickness of the dead zone.

Thus, in some embodiments, the dead zone has a thickness of from 0.01, 0.1, 1, 2, or 10 microns up to 100, 200 or 400 microns, or more, and/or the gradient of polymerization zone and the dead zone together have a thickness of from 1 or 2 microns up to 400, 600, or 1000 microns, or more. Thus the gradient of polymerization zone may be thick or thin depending on the particular process conditions at that time. Where the gradient of polymerization zone is thin, it may also be described as an active surface on the bottom of the growing three-dimensional object, with which monomers can react and continue to form growing polymer chains therewith. In some embodiments, the gradient of polymerization zone, or active surface, is maintained (while polymerizing steps continue) for a time of at least 5, 10, 15, 20 or 30 seconds, up to 5, 10, 15 or 20 minutes or more, or until completion of the three-dimensional product.

The method may further comprise the step of disrupting the gradient of polymerization zone for a time sufficient to form a cleavage line in the three-dimensional object (*e.g.*, at a predetermined desired location for intentional cleavage, or at a location in the object where prevention of cleavage or reduction of cleavage is non-critical), and then reinstating the gradient of polymerization zone (*e.g.*, by pausing, and resuming, the advancing step, increasing, then decreasing, the intensity of irradiation, and combinations thereof).

CLIP may be carried out in different operating modes (that is, different manners of advancing the carrier and build surface away from one another), including continuous, intermittent, reciprocal, and combinations thereof.

Thus, in some embodiments, the advancing step is carried out continuously, at a uniform or variable rate, with either constant or intermittent illumination or exposure of the build area to the light source.

In other embodiments, the advancing step is carried out sequentially in uniform increments (*e.g.*, of from 0.1 or 1 microns, up to 10 or 100 microns, or more) for each step or increment. In some embodiments, the advancing step is carried out sequentially in variable increments (*e.g.*, each increment ranging from 0.1 or 1 microns, up to 10 or 100 microns, or more) for each step or increment. The size of the increment, along with the rate of advancing, will depend in part upon factors such as temperature, pressure, structure of the article being produced (*e.g.*, size, density, complexity, configuration, etc.), etc.

In some embodiments, the rate of advance (whether carried out sequentially or continuously) is from about 0.1, 1, or 10 microns per second, up to about 100, 1,000, or 10,000 microns per second, again depending on factors such as temperature, pressure, structure of the article being produced, intensity of radiation, etc.

In still other embodiments, the carrier is vertically reciprocated with respect to the build surface to enhance or speed the refilling of the build region with the polymerizable liquid. In some embodiments, the vertically reciprocating step, which comprises an upstroke and a downstroke, is carried out with the distance of travel of the upstroke being greater than the distance of travel of the downstroke, to thereby concurrently carry out the advancing step (that is, driving the carrier away from the build plate in the z-plane) in part or in whole.

In some embodiments, the methods comprise polymerizing a build region of said polymerizable liquid composition to form a crosslinked polymer, wherein said polymerizing is carried out by irradiating said polymerizable liquid with light having a first wavelength or intensity; and activating a photoacid generator by further irradiating a portion of the build region intended to be acidic with light having a second wavelength or intensity, whereby the photoacid generator produces acid in said portion of the crosslinked polymer to thereby form an acidic region.

The first wavelength or intensity may be one in which the photopolymerization of the monomers and/or prepolymers and crosslinkers by the photoinitiator are active, but in which the photoacid generator is not activate. The second wavelength or intensity may be one in which the photoacid generator is activated (which may or may not also be a wavelength in which the photopolymerization is active). In this manner, only a portion of the polymerized object will have an active photoacid generator.

FIGS. 1A-1G provide example graphs of a photoinitiator (PI) and photoacid generator (PAG) which are activated by light at different ranges of wavelengths or intensities. To illustrate activation, an example first light source X and second light source Y are provided, each having an emission spectrum represented by three vertical lines, the middle line representing the wavelength at maximum intensity, and the flanking lines representing the full width at half maximum intensity (FWHM).

In **FIG.1A**, the PI and PAG have non-overlapping activation (absorbance) ranges. To activate the PI but not PAG (or not appreciably), only light source X is applied. To activate both PI and PAG, both light source X and light source Y are applied. For example, light source X may be applied in the entire area of polymerization, while Y is applied only in the region intended to have PAG activation (*e.g.*, with a focused projector).

FIG. 1B provides an example graph of PI and PAG having overlapping activation ranges. In this instance, the X light source used is shifted down in wavelength range in order to have X activate PI but not PAG (or not appreciably). To activate both PI and PAG, both light source X and light source Y are applied. Light source Y is at the peak of activation for the PAG but also

overlaps the PI activation. This is acceptable since the PI is also activated in the PAG-active region. To activate the PI but not PAG (or not appreciably), only light source X is applied.

In **FIG. 1C**, the PI and PAG have non-overlapping activation (absorbance) ranges, with the activation range of PAG is at a lower range of wavelengths than the activation range of PI.

5 To activate the PI but not PAG (or not appreciably), only light source Y is applied. To activate both PI and PAG, both light source X and light source Y are applied.

FIG. 1D provides another example graph of PI and PAG having overlapping activation ranges. In this instance, the X light source used is shifted down in wavelength range in order to have X activate PI but not PAG (or not appreciably). Light source Y is also shifted to lower
10 wavelengths to be able to activate both PI and PAG without the need to also apply light source X in the PAG-active region.

In **FIG. 1E**, the PI and PAG have overlapping activation ranges, with the PI having a tail in the higher wavelengths. In this instance, the X light source used is shifted up in wavelength in order to have X activate PI but not PAG (or not appreciably), and shifted up in intensity to
15 account for the lower absorbance of the PI at the lower wavelengths. Light source Y is not shifted in this example, but it could be also shifted up, if desired, similar to **FIG.1D** to be able to activate both PI and PAG without the need to also apply light source X in the PAG-active region.

FIG. 1F shows an example graph in which the activation range of the PAG is wholly within the activation range of the PI. The X light source used is shifted down in wavelength in
20 order to have X activate PI but not PAG (or not appreciably). Light source Y can activate both PI and PAG without the need to shift from the PAG activation peak.

FIG. 1G shows another example graph in which the activation wavelength range of the PAG is wholly within the activation wavelength range of the PI. The X light source used is shifted up in wavelength in order to have X activate PI but not PAG (or not appreciably), and can
25 be increased in intensity to account for the lower absorbance of the PI at the higher wavelengths. Light source Y can activate both PI and PAG without the need to shift from the PAG activation peak.

In **FIG. 1H**, the PI and PAG have overlapping activation ranges, and the X light source used is centered at the peak activation of the PI. Thus, at a lower intensity, PI is activated but
30 PAG is not appreciably activated. However, upon increasing the intensity of X, both PI and PAG are activated.

In some embodiments, light of both the first and second wavelengths or intensities is applied to the PAG-activated portion of the object being polymerized. Light of the first wavelength or intensity may be applied to the PAG-activated portion of the object concurrently,

prior to or after the light of the second wavelength or intensity. In some embodiments, the second wavelength or intensity is sufficient to activate the photopolymerization as well as the PAG, and thus only the second wavelength or intensity need be applied to the PAG-activated portion of the object to activate both the photoinitiator (PI) and the PAG.

5 In some embodiments, light of the first wavelength or intensity is produced by a first light source, and light of the second wavelength or intensity is produced by (or added to the first light source by) a second light source. The first light source may illuminate the PAG-activated portion of the object concurrently, prior to or after the second light source.

10 In some embodiments, the first wavelength is applied at the same depth in the resin as the second wavelength. In some embodiments, the first wavelength is applied at different depth(s) than the second wavelength.

The photobase generators may be incorporated and activated in a similar manner to form basic regions as that described above for the photoacid generators.

15 Once the three-dimensional object is formed, it may be removed from the carrier, optionally washed, and then heated and/or microwave irradiated sufficiently to further cure the resin and/or react the acid-labile or base-labile groups of the acidic or basic region, respectively.

20 In some embodiments, the heating step is carried out at a temperature greater than ambient temperature. For example, the object may be heated to a temperature of about 40°C to about 250°C, or a temperature of about 50 or 60°C, to 70, 80, 90, 100, 110, 120, 130, 140, 150, 175, 200, 225, or 250 °C with the duration of each heating depending on the size, shape, and/or thickness of the object or portion thereof being heated.

25 In some embodiments, upon heating the three-dimensional object, acid of the acidic region reacts with the acid-labile groups to form reacted groups. In some embodiments, the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object.

FIGS. 3A-3B present a schematic of additive manufacturing of an article (10) having a PAG-active acidic region (**FIG. 3A**), with subsequent dissolving of the PAG-active regions (**FIG. 3B**).

30 In some embodiments, after baking, the three-dimensional object with portions of differing solubility is then exposed to an aqueous or non-aqueous solution suitable for dissolving the portion having the acid-reacted groups. In some embodiments, the baking and exposure to the solution may be conveniently combined into a concurrent step (*e.g.*, baking the three-dimensional object while submerged in the solution).

3. Products.

The resins and methods described above are particularly useful for making three-dimensional articles with rafts and/or that have overhangs or otherwise are in need of support(s) during the fabrication process, and/or desired to have portions of differing solubility/melting temperatures to allow selective ablation/dissolving/melting. Products that may be produced by the methods and resins described herein include, but are not limited to, large-scale models or prototypes, small custom products, miniature or microminiature products or devices, etc. Examples include, but are not limited to, mechanical parts, medical devices and implantable medical devices such as stents, drug delivery depots, functional structures, microneedle arrays, fibers and rods such as waveguides, micromechanical devices, microfluidic devices, etc.

A "raft," as known in the art, is an extra layer or portion, often wider than the article being fabricated, connected to the carrier that serves to increase the adhesion of the manufactured article to the carrier.

Supports useful in fabricating an article with fine/delicate structures, rounded or cantilevered sections and overhangs are known, and include, but are not limited to, pillars, lattices or blocks situated thereunder and intended to be removed after fabrication. For example, **FIG. 2** is a photograph of an example additive manufacturing product (10), a ball, which has a rounded surface that is manufactured with supports (12) and on a raft (13). The supports are removed after fabrication.

FIG. 4 shows a schematic of an example article having PAG-active acidic regions at the point of contact of the supports (12) with the printed object (10). As taught herein, the supports can be removed by dissolving the PAG-active regions.

FIG. 5 shows a schematic of an example article (10) having a "brick" of cured material where a shape is defined by the regions of inactive PAG and active PAG. Regions of active PAG in the support structure (12) can be dissolved after thermal cure to produce the shaped article.

In some embodiments, the acidic or basic regions comprise less than 20, 30, 40 or 50% of the total volume of the manufactured article. In some embodiments, the acidic and non-acidic regions, or basic and non-basic regions, are integrally formed with one another during fabrication. In some embodiments, the article is unitary (that is, formed of a single polymerizable liquid); in some embodiments, the article is a composite (that is, formed of two or more different polymerizable liquids). In some embodiments, the article is a unitary member, meaning it is seamless and/or is not formed by the joining of two or more component pieces.

In some embodiments, a portion of the article is solubilized/melted in order to free a caged or trapped internal element (*e.g.*, gear, impeller, valve, gate, piston, etc. in a housing; ball

in a ball, etc.). In some embodiments, the internal element is rigidly connected to the housing in a pre-aligned manner for ease of post-fabrication assembly or operation, *e.g.*, pre-aligned for insertion of a shaft therethrough in the housing, followed by solubilization/melting of the rigid support.

5

4. Apparatus for Additive Manufacturing.

Various types of apparatuses are known in the art of additive manufacturing that make use of a light source to effect polymerization. In some embodiments, the apparatus includes one, two, or three or more light sources such as lamps capable of transmitting one or more
10 wavelengths of light in the UV, near-visible or visible spectrum. In some embodiments, the light may be filtered to alter the output spectrum, if desired.

In some embodiments, the apparatus may comprise a controller configured to control transmission of the first and/or second wavelengths and/or intensities of light as appropriate to create PAG-active and PAG-inactive regions (or PBG-active and PBG-inactive regions) of the
15 formed polymeric object. In some embodiments, PAG-active and PAG-inactive regions may occur in the same frame or slice, or same layer, of the object in the z-plane.

In some embodiments, the lamp may emit wavelengths in the i-line region (*e.g.*, 365 nm). In some embodiments, the lamp may emit wavelengths in the h-line region (*e.g.*, 405 nm). In some embodiments, the lamp may emit wavelengths in the g-line region (*e.g.*, 436 nm).

20 In some embodiments, the lamp may comprise a light emitting diode (LED). LED lamps may emit at discrete peak wavelengths throughout the UV spectrum, such as at 436 nm, 405 nm, 395 nm, 390 nm or 365 nm. *See also* U.S. Patent Application Publication 2012/0251841 to Southwell et al. In some embodiments, the lamp may be an LED UV lamp having a peak wavelength at 365 nm, 385 nm, or 405 nm (*e.g.*, Nichia Corporation UV LED, U365, U385,
25 U405, Cat. No. 140826).

In some embodiments, the peak wavelength has a spectrum half width (*i.e.*, full width at half maximum intensity (FWHM)) of from 2 or 5 to 8, 9, 10, 11, 12 or 15 nm.

In some embodiments, the lamp may comprise a laser. For example, the laser may be a helium-cadmium (325 nm), nitrogen (337 nm), krypton ion (337 nm), argon ion (363 nm, 488
30 nm and 514 nm), neodymium-YAG (532 nm), or helium-neon (633 nm) laser.

In some embodiments, the light source may comprise a tunable UV light system, such as that in U.S. Patent No. 3,947,688 to Massey; U.S. Patent No. 5,745,284 to Goldberg et al.; U.S. Patent No. 6,876,689 to Walling et al.; U.S. Patent No. 7,848,381 to Barnes et al.; or U.S. 2002/0054613 to Jin Kang.

In some embodiments, the lamp may comprise a mercury lamp such as a medium-pressure mercury (MPM) lamp ("H" lamp), which typically emits UV wavelengths of about 254 nm, about 313 nm, about 365 nm (i-line), about 405 nm (h-line), and about 436 nm (g-line).

In some embodiments, the lamp may be an arc lamp such as a mercury arc lamp, xenon arc lamp or mercury-xenon arc lamp.

In some embodiments, the lamp may comprise an electrodeless UV lamp. *See* U.S. Patent No. 4,501,993.

In some embodiments, the lamp may comprise a doped lamp, such as with iron, lead, tin and/or gallium, such as a D lamp (doped with iron) or V lamp (doped with gallium).

In some embodiments, the lamp may comprise a low-pressure mercury lamp, which typically emits short wave UV such as about 254 nm.

In some embodiments, the lamp may comprise an excimer lamp, which typically emits short wave UV such as about 308 nm.

Embodiments of the present invention are explained in greater detail in the following non-limiting examples.

EXAMPLES

With reference to **FIG. 3A**, "PAG active" and "PAG inactive" regions can be generated in the same plane of fabrication by first exposing the X wavelength for PAG inactive (insoluble) regions, and exposing the X+Y wavelengths for PAG active (soluble) regions, before advancing the part to the next planar frame. After printing, a post-exposure baking step is performed, followed by washing/soaking in an appropriate solvent until the supports are removed. *See* **FIG. 3B**.

In some embodiments, only very small connection points of supports to the part receive the exposure of both X&Y wavelengths (*i.e.*, are PAG active). *See* **FIG. 4**. In this embodiment, it is not necessary to dissolve the entire support for removal.

Photo-base generator-active (PBG-active) regions and base-labile moieties may be used in a similar manner.

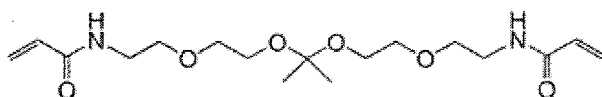
With reference to **FIG. 5**, in some embodiments, one could fabricate a "brick" of cured material where all regions are exposed and the part is defined by the regions of X vs. X+Y exposure. Similarly, this soluble structure could be a lattice or other patterned region.

Composition Example 1

A composition containing the following is prepared:

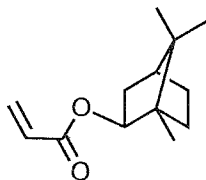
10 wt% of the acid-sensitive ketal crosslinker shown below:

5



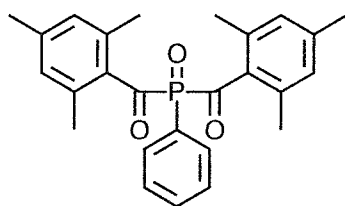
85 - 88 wt% of the monomer shown below (isobornyl acrylate):

10



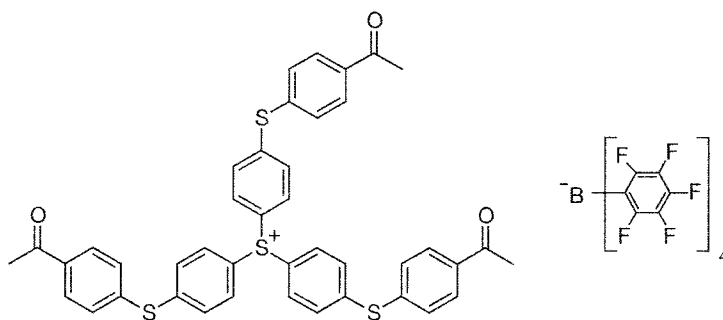
1 wt% of the free radical photoinitiator below (Irgacure 819), which is active at 365 - 405nm wavelengths:

15



20

1 - 4 wt% of the photoacid generator shown below (Irgacure 290 TPC), which is active at 365nm but not with 405nm wavelength.



25

The above formulation is mixed and placed into a 3D printer equipped with a dual-LED system having a 365nm and 405nm LED. When only the 365nm light is on, or when both the 365nm and 405nm LEDs are on, both the PAG and the free radical initiator will be active, thus forming cross-linked material containing acid ("acidic region"). When only the 405nm light is

on, the PAG will remain inactive, but the free radical initiator will be active, thus forming a cross-linked material without activated PAG.

The part is printed, residual resin is washed away using a suitable solvent (*e.g.*, isopropanol), the part is dried and put into an oven set at 100 °C. During the heating, the acid generated from the PAG degrades the crosslinker in the acidic regions that had been exposed to 365nm light, thus forming soluble polymer chains. The crosslinker in the regions exposed to only 405nm light remains intact, and, therefore, that region remains insoluble. The part is removed from the oven and placed in an isopropanol bath. The soluble portions of the part are dissolved away, leaving only the insoluble portions of the part.

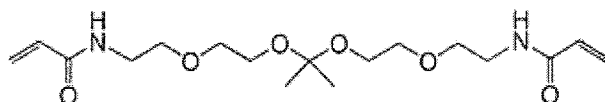
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Composition Example 2

A composition containing the following is prepared:

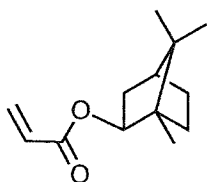
10 wt% of the acid-sensitive ketal crosslinker shown below:

15



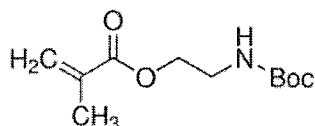
10 - 80 wt% of the monomer/reactive diluent shown below (isobornyl acrylate):

20



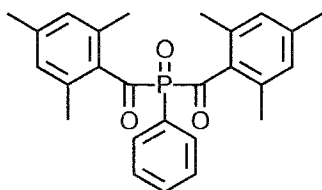
10 - 80% of the acid-sensitive monomer shown below (2-Boc-aminoethyl methacrylate):

25

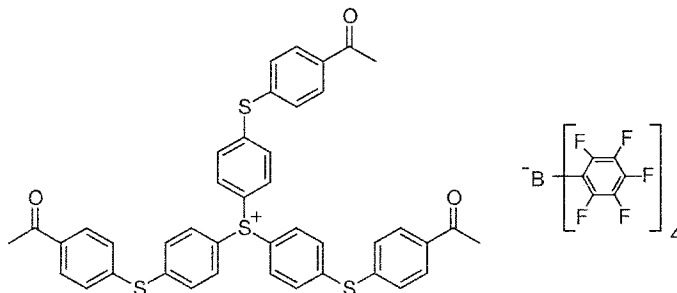


1 wt% of the free radical photoinitiator below (Irgacure 819), which is active at wavelengths 365 - 405nm:

30



1 – 4 wt% of the photoacid generator shown below (Irgacure 290 TPC), which is active as 365nm wavelength, but not at 405nm.



5

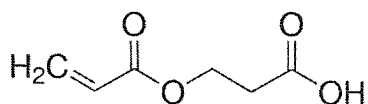
The above formulation is mixed and placed into a printer equipped with a dual-LED system having a 365nm and 405nm LED. When only the 365nm light is on, or when both the 365nm and 405nm LEDs are on, both the PAG and the free radical initiator will be active, thus forming cross-linked material containing acid ("acidic region"). When only the 405nm light is on, the PAG will remain inactive, but the free radical initiator will be active, thus forming a cross-linked material without the PAG-generated acid. Additionally, the 2-Boc-amino ethyl methacrylate is cleaved in the active PAG regions to yield a free amine. The presence of the free amine can impart water solubility to the polymer in these exposed regions.

The part is printed, residual resin is washed away using a suitable solvent (*e.g.*, isopropanol), the part is dried and put into an oven set at 100 °C. During the heating stage, the acid degrades the crosslinker in the acidic regions that had exposed to 365nm light, thus forming soluble polymer chains. The crosslinker in the regions exposed to only 405nm light remains intact, and, therefore, that region remains insoluble. The part is removed from the oven and placed in an isopropanol or aqueous bath. The soluble portions of the part are dissolved away, leaving only the insoluble portions of the part.

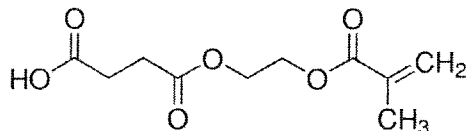
Dissolution Study with Homopolymers

Homopolymers of the following monomers were prepared by bulk UV polymerization initiated by Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (PPO) and cured into homopolymer films:

2-carboxylethyl acrylate (CEA)



2-hydroxyethyl methacrylate succinate (HEMAS)



Films were submersed into NaOH solution (0.5 N), and their dissolution rates were measured by thickness reduction.

Dissolution rate for CEA homopolymer = 0.27 mm/min

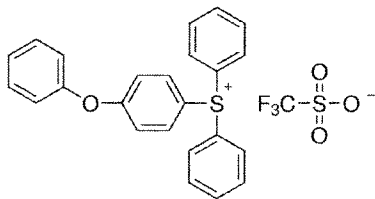
Dissolution rate for HEMAS homopolymer = 0.1 mm/min

The results indicate that if every single side group is water soluble in an uncrosslinked polymer, the dissolution rate of the entire polymer in aqueous base is considerable.

Dissolution Study of Partially Deprotected Poly(tert-butyl methacrylate)

Formulation:

Poly(tert-butyl methacrylate) 18% in propylene glycol methyl ether acetate (PGMEA) with 0.5% PAG ((4-Phenoxyphenyl)diphenylsulfonium triflate)



Experiment:

Spin coat the above solution on a glass slide

Bake entire film @ 120°C for 1 min to bake off the residual solvent

Expose half the film to Dymax 5000-EC flood lamp (mercury lamp with broad band light source) for 90 sec

Bake entire film @ 120°C for 5 min

Develop by immersing in 0.5 N NaOH solution

Results: The film was delaminated in the developer and curled up, making it difficult to estimate the thickness. However, the unexposed region remained intact whereas the exposed film gradually dissolved in the developers (0.5 NaOH solution) after 1 hour.

The results indicate that the selective exposure of one portion of the polymer film to light that activates the PAG results in reaction and production of groups soluble in aqueous solution on the exposed portion of the polymer upon baking.

Another study was performed, starting with monomer, with the following formulation:

COMPONENT	LOADING
tert-butyl methacrylate (Monomer)	50%
TPO (diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide) (PI)	0.5%
(4-Phenoxyphenyl)diphenylsulfonium triflate (PAG)	1%
PGMEA (Solvent)	48.5%

10 Experiment

Irradiate composition with 385 nm LED light for 30 min to polymerize TBMA (observed viscosity increase)

Spin coat into film followed by baking @ 120°C for 1 min to remove solvent

Expose half of the film to Dymax 5000-EC flood lamp for 3 min

15 Bake @ 120C for 5 min

Develop in 0.5 N NaOH

Measure thickness using a Mitutoyo height gauge

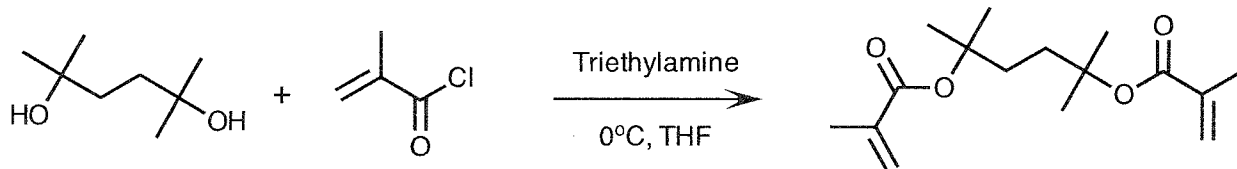
20 Results were as follows:

Develop time	unexposed region	exposed region
t = 0	6.5 μm	6.5 μm
t = 30 min	6.5 μm	1.5 μm

The results indicate that the selective exposure of one portion of the polymerized film to light that activates the incorporated PAG results in reaction and production of groups soluble in aqueous solution on the exposed portion of the polymer upon baking.

5 Dissolution Study of Polymer with Crosslinker having acid-labile groups

A resin was formed with an acid cleavable crosslinker, 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA), to cure into a solid polymer. The di-functional crosslinker was successfully synthesized.



10

Tested formulations all exhibited swelling after acid-catalyzed cleavage of the ester, indicating cleavage of a portion of the crosslinkers, but did not completely dissolve. The formulation can be tuned to achieve dissolving in aqueous base by, *e.g.*, adding carboxyl pendant monomers into the network, using less crosslinker, etc.

15

The foregoing is illustrative of the present invention, and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

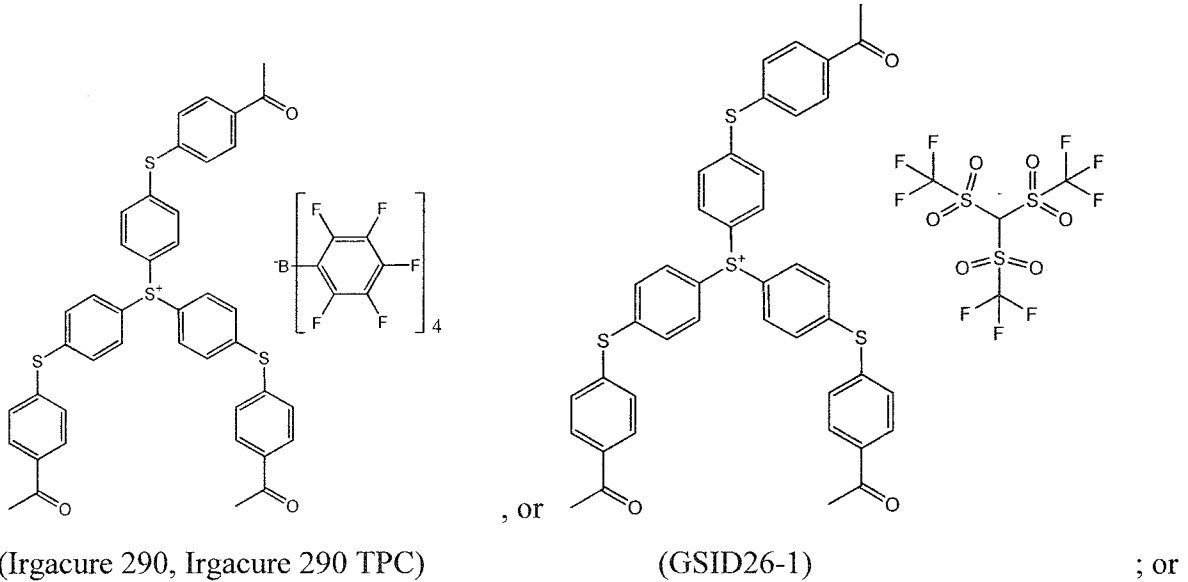
20

That which is claimed is:

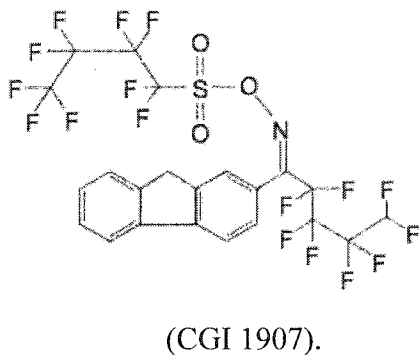
1. A polymerizable liquid composition useful for additive manufacturing, comprising:
 - (i) a free radical photoinitiator;
 - (ii) monomers and/or prepolymers (*e.g.*, reactive diluents) that are polymerizable by exposure to actinic radiation or light, optionally wherein some or all of said monomers and/or prepolymers comprise one or more acid-labile groups;
 - (iii) a crosslinker comprising one or more acid-labile groups; and
 - (iv) a photoacid generator,wherein said free radical photoinitiator and said photoacid generator are activated by light at different ranges of wavelengths or intensities.
2. The composition of claim 1, wherein said different ranges of wavelengths or intensities are selected such that there is a wavelength at which the free radical photoinitiator is activated and the photoacid generator is not activated.
3. The composition of claim 1 or claim 2, wherein said free radical photoinitiator has an absorbance spectrum with a peak activation wavelength that is at least 5 or 10 nm apart from a peak activation wavelength in an absorbance spectrum of said photoacid generator.
4. The composition of any one of claims 1-3, wherein said monomers and/or prepolymers comprise unsaturated vinyl groups and/or thiol groups.
5. The composition of any one of claims 1-4, wherein said acid-labile crosslinker comprises unsaturated vinyl groups and/or thiol groups.
6. The composition of any one of claims 1-5, wherein said one or more acid-labile groups comprise an orthoester, tertiary ester, acetal, ketal, hydrazone, imine, cis aconyl, trityl, silyl ester, carbamate, tert-butyloxycarbonyl, or tosyl group.
7. The composition of any one of claims 1-6, wherein said free radical photoinitiator is activated at wavelengths 250-600 nm, or any subrange therein, and said photoacid generator is activated at wavelengths 250-375 nm, or any subrange therein.

8. The composition of any one of claims 1-7, wherein said free radical photoinitiator is 2,4,6-trimethyl benzoyl (Irgacure 819), 2-Benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (Irgacure 369); or diphenyl (2,4,6-trimethylbenzoyl)- phosphine oxide (Darocure TPO).

9. The composition of any one of claims 1-8, wherein said photoacid generator is an ionic photoacid generator, such as:



a non-ionic photoacid generator, such as:



10. The composition of any one of claims 1-9, wherein said composition comprises:
- (i) from 0.1 to 4 percent by weight of said free radical photoinitiator;
 - (ii) from 10 to 90 percent by weight of said monomers and/or prepolymers;
 - (iii) from 5 to 90 percent by weight of said crosslinker; and
 - (iv) from 0.1 to 4 percent by weight of said photoacid generator.

11. A polymerizable liquid composition useful for additive manufacturing, comprising:
- (i) a free radical photoinitiator;
 - (ii) monomers and/or prepolymers (*e.g.*, reactive diluents) that are polymerizable by exposure to actinic radiation or light, optionally wherein some or all of said monomers and/or prepolymers comprise one or more base-labile groups;
 - (iii) a crosslinker comprising one or more base-labile groups; and
 - (iv) a photobase generator,
- wherein said free radical photoinitiator and said photobase generator are activated by light at different ranges of wavelengths or intensities.
12. The composition of claim 11, wherein said different ranges of wavelengths or intensities are selected such that there is a wavelength at which the free radical photoinitiator is activated and the photobase generator is not activated.
13. The composition of claim 11 or claim 12, wherein said free radical photoinitiator has an absorbance spectrum with a peak activation wavelength that is at least 5 or 10 nm apart from a peak activation wavelength in an absorbance spectrum of said photobase generator.
14. The composition of any one of claims 11-13, wherein said monomers and/or prepolymers comprise unsaturated vinyl groups and/or thiol groups.
15. The composition of any one of claims 11-14, wherein said base-labile crosslinker comprises unsaturated vinyl groups and/or thiol groups.
16. The composition of any one of claims 11-15, wherein said free radical photoinitiator is activated at wavelengths 250-600 nm, or any subrange therein, and said photoacid generator is activated at wavelengths 250-375 nm, or any subrange therein.
17. The composition of any one of claims 11-16, wherein said free radical photoinitiator is 2,4,6-trimethyl benzoyl (Irgacure 819), 2-Benzyl-2-(dimethylamino)-1-[4- (4-morpholinyl) phenyl]-1-butanone (Irgacure 369); or diphenyl (2,4,6-trimethylbenzoyl)- phosphine oxide (Darocure TPO).

18. The composition of any one of claims 11-17, wherein said photobase generator is ortho-nitrobenzyl carbamate.
19. The composition of any one of claims 11-18, wherein said composition comprises:
- (i) from 0.1 to 4 percent by weight of said free radical photoinitiator;
 - (ii) from 10 to 90 percent by weight of said monomers and/or prepolymers;
 - (iii) from 5 to 90 percent by weight of said crosslinker; and
 - (iv) from 0.1 to 4 percent by weight of said photobase generator.
20. A method of forming a three-dimensional object comprising an acidic region, comprising the steps of:
- (a) providing the polymerizable liquid composition of any one of claims 1-10;
 - (b) polymerizing a build region of said polymerizable liquid composition to form a crosslinked polymer, wherein said polymerizing is carried out by irradiating said polymerizable liquid with light at a first wavelength or intensity; and
 - (c) activating the photoacid generator by further irradiating a portion of the build region intended or selected to be acidic with light at a second wavelength or intensity, whereby the photoacid generator produces acid in said portion of the crosslinked polymer to thereby form said acidic region,
- to thereby form said three-dimensional object comprising an acidic region.
21. The method of claim 20, wherein said first wavelength or intensity is produced by a first light source, and said second wavelength or intensity is produced by a second light source, said first light source having an emission peak wavelength that is at least 5 or 10 nm apart from an emission peak wavelength of the second light source.
22. The method of claim 20, wherein said first wavelength or intensity and said second wavelength or intensity is produced by the same light source configured to produce a first or second emission peak wavelength that is at least 5 or 10 nm apart (*e.g.*, with UV filters and/or rapid lamp and/or mirror switching time).
23. The method of any one of claims 20-22, wherein said forming is carried out by additive manufacturing (*e.g.*, bottom-up or top-down three-dimensional fabrication).

24. The method of any one of claims 20-23, wherein said forming is carried out by continuous liquid interface production (CLIP).
25. The method of any one of claims 20-24, further comprising the step of:
- (d) heating the acidic region of the three-dimensional object to a temperature of from 40 degrees Celsius to 250 degrees Celsius, whereby acid of the acidic region reacts with the acid-labile groups to form reacted groups.
26. The method of claim 25, wherein the reacted groups comprise polar or non-polar moieties, said moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object.
27. A method of forming a three-dimensional object comprising an acidic region, comprising the steps of:
- (a) providing a carrier and a build plate, said build plate comprising a build surface with said build surface and said carrier defining a build region therebetween;
 - (b) filling said build region with the polymerizable liquid composition of any one of claims 1-10, said polymerizable liquid composition contacting said build surface;
 - (c) polymerizing said polymerizable liquid composition to form a crosslinked polymer, wherein said polymerizing is carried out by irradiating said build region through said build plate with a light at a first wavelength or intensity to activate the free radical photoinitiator, polymerize the photopolymerizable monomer to form a polymer, and crosslink the polymer with said crosslinker, thereby forming a crosslinked polymer in said build region;
 - (d) activating the photoacid generator by further irradiating a portion of the build region intended to be acidic through said build plate with light at a second wavelength or intensity, whereby the photoacid generator produces acid in said crosslinked polymer to thereby form said acidic region; and
 - (e) advancing said carrier with said crosslinked polymer adhered thereto away from said build surface on said build plate to create a subsequent build region between said crosslinked polymer and said build surface;
to thereby form said three-dimensional object comprising an acidic region.
28. The method of claim 27, further comprising the step of:

(f) heating the acidic region of the three-dimensional object, whereby acid of the acidic region reacts with the acid-labile groups to form reacted groups.

29. The method of claim 28, wherein the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object.

30. A method of forming a three-dimensional object comprising an acidic region, comprising the steps of:

(a) providing a carrier and a build plate, said build plate comprising a semipermeable member, said semipermeable member comprising a build surface with said build surface and said carrier defining a build region therebetween, and with said build surface in fluid communication by way of the semipermeable member with a source of polymerization inhibitor;

(b) filling said build region with the polymerizable liquid composition of any one of claims 1-10, said polymerizable liquid composition contacting said build surface;

(c) polymerizing said polymerizable liquid composition to form a crosslinked polymer, wherein said polymerizing is carried out by irradiating said build region through said build plate with light at a first wavelength or intensity to activate the free radical photoinitiator, polymerize the photopolymerizable monomer to form a polymer, and crosslink the polymer with said crosslinker, thereby forming the crosslinked polymer in said build region, while forming or maintaining a liquid film release layer comprised of said polymerizable liquid composition formed between said crosslinked polymer and said build surface, the polymerization of which liquid film is inhibited by said polymerization inhibitor;

(d) activating the photoacid generator by further irradiating a portion of the build region intended to be acidic through said build plate with light at a second wavelength or intensity, whereby the photoacid generator produces acid in said crosslinked polymer to thereby form said acidic region, while forming or maintaining a liquid film release layer comprised of said polymerizable liquid composition formed between said crosslinked polymer and said build surface, the polymerization of which liquid film is inhibited by said polymerization inhibitor;
and

(e) advancing said carrier with said crosslinked polymer adhered thereto away from said build surface on said build plate to create a subsequent build region between said crosslinked polymer and said build surface;

to thereby form a three-dimensional object comprising an acidic region.

31. The method of claim 30, further comprising the step of:
- (f) heating the three-dimensional object, whereby acid of the acidic region reacts with the acid-labile groups to form reacted groups.
32. The method of claim 31, wherein the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object.
33. An article of manufacture produced by a method of any one of claims 20-32.
34. An article of three-dimensional additive manufacture, said article comprising a photopolymerized polymer with acid-labile groups, and a photoacid generator, wherein said article comprises at least one, or a plurality of, acidic regions, and at least one, or a plurality of, non-acidic regions, wherein the regions are integrally formed with one another and/or the article is a unitary member.
35. The article of claim 34, wherein said acidic regions are soluble in an aqueous solution, and said non-acidic regions are not soluble in the aqueous solution.
36. The article of claim 34 or claim 35, wherein said acidic regions comprise a support structure or a portion thereof.
37. The article of any one of claims 34-36, wherein said acidic regions comprise a raft or a portion thereof.
38. The article of any one of claims 34-37, wherein said acidic regions comprise less than half of the total volume of said article.
39. A method of removing a portion of an article of three-dimensional additive manufacture, comprising:
- providing the article of any one of claims 34-38;

heating the article, whereby acid of the acidic region reacts with acid-labile groups to form reacted groups, wherein the reacted groups comprise polar or non-polar moieties conferring a difference in solubility as compared to a non-acidic region of the three-dimensional object; and dissolving the acidic region in a polar or non-polar solvent, thereby removing the portion of the article of three-dimensional additive manufacture.

40. The method of claim 39, wherein the heating is to a temperature of from 40 degrees Celsius to 250 degrees Celsius.
41. The method of claim 39 or claim 40, wherein said solvent is water, an aqueous solution, or an organic solvent.
42. The method of any one of claims 39-41, wherein said dissolving is performed after said heating.
43. The method of any one of claims 39-41, wherein said heating and said dissolving are performed concurrently.

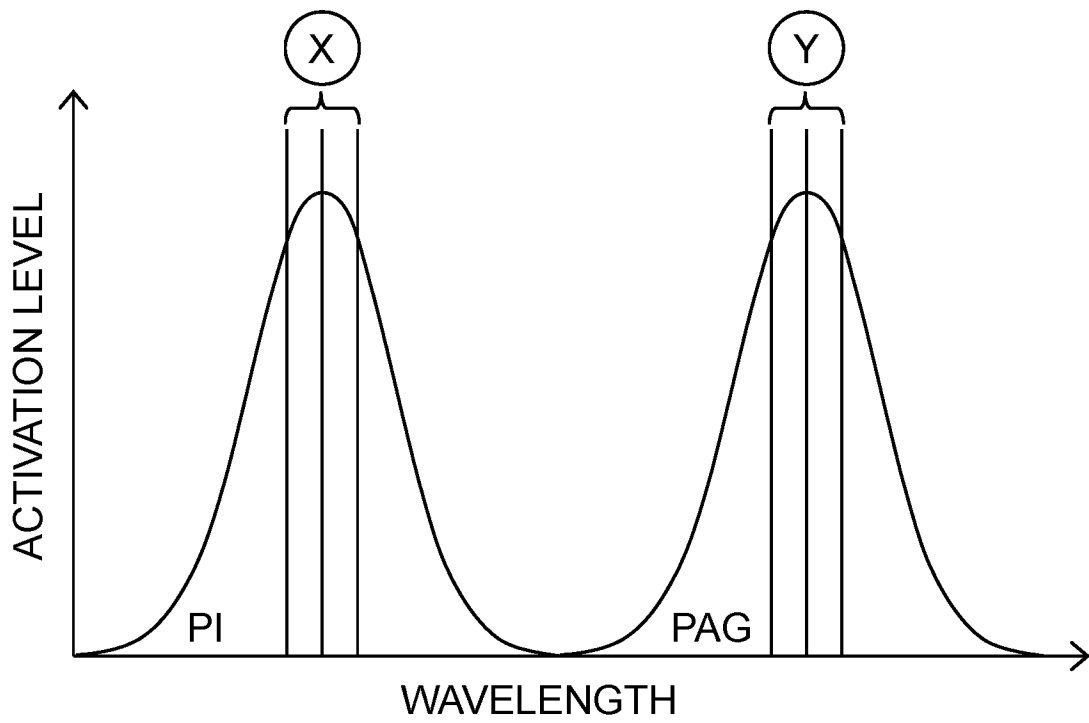


FIG. 1A

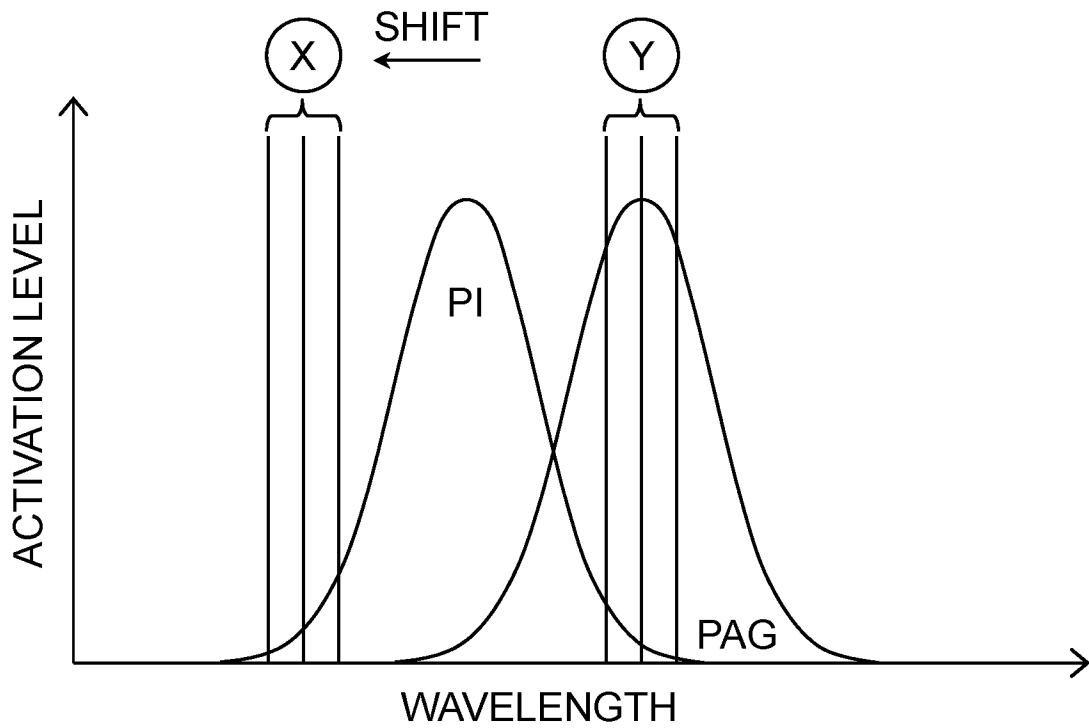


FIG. 1B

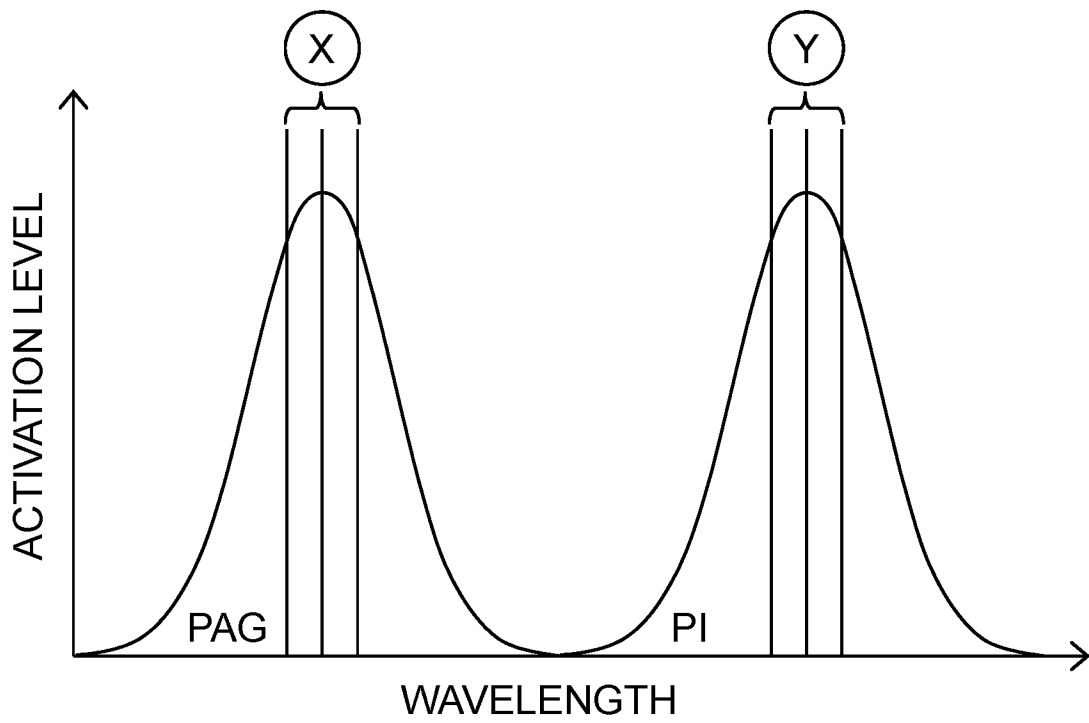


FIG. 1C

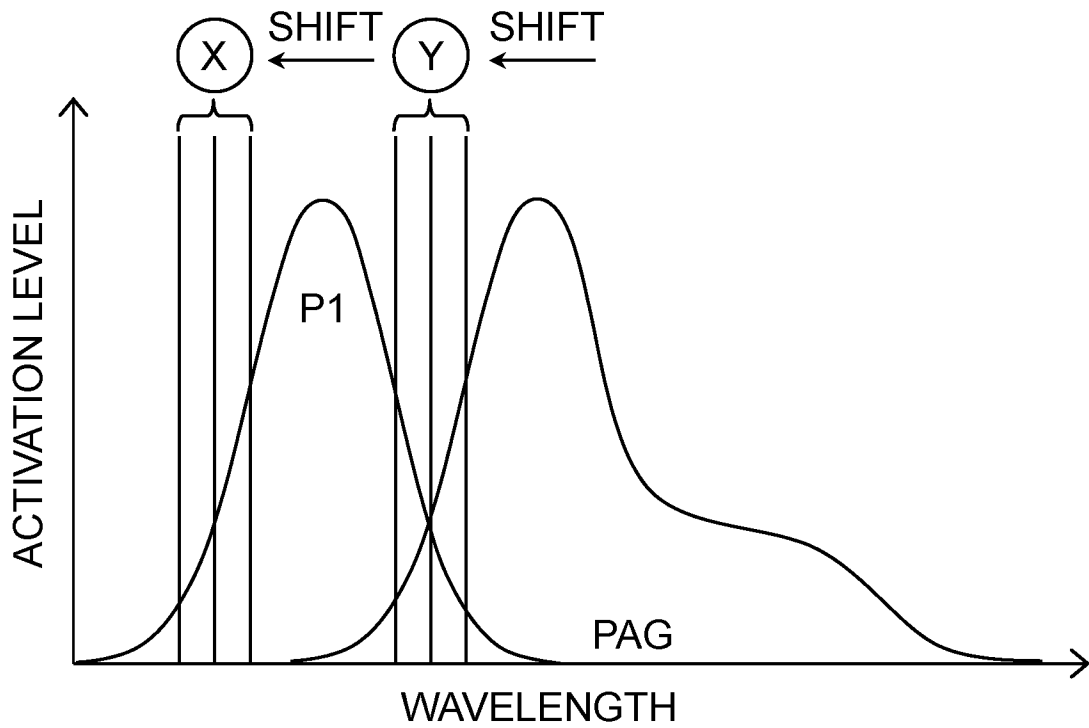


FIG. 1D

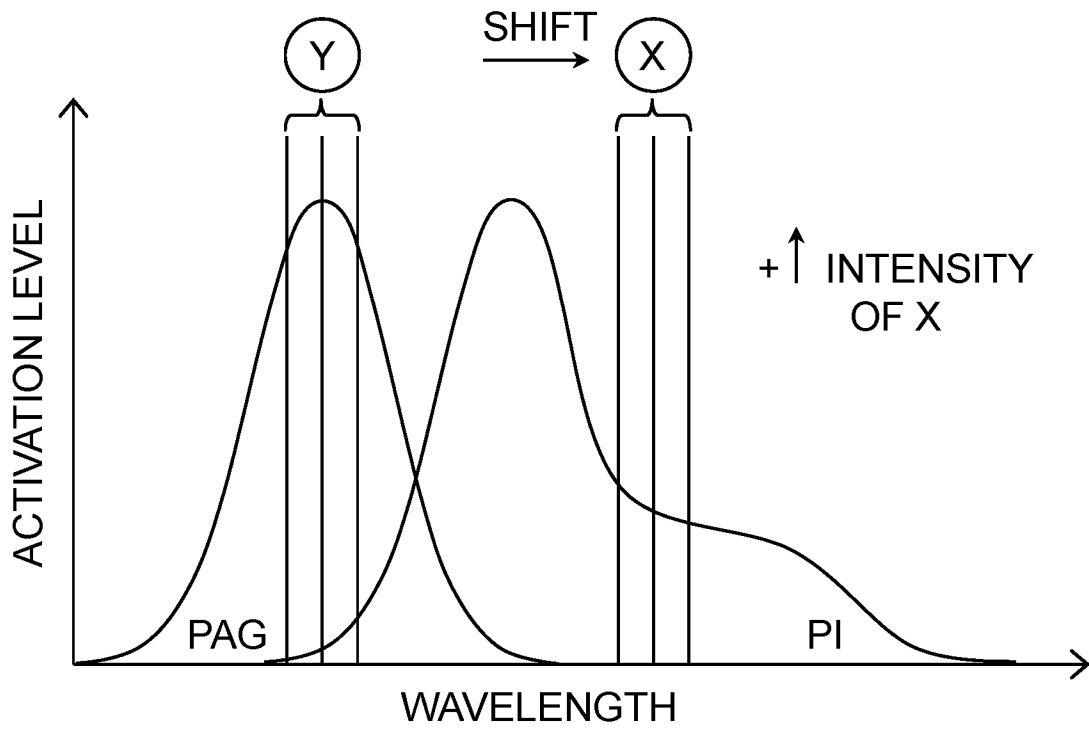


FIG. 1E

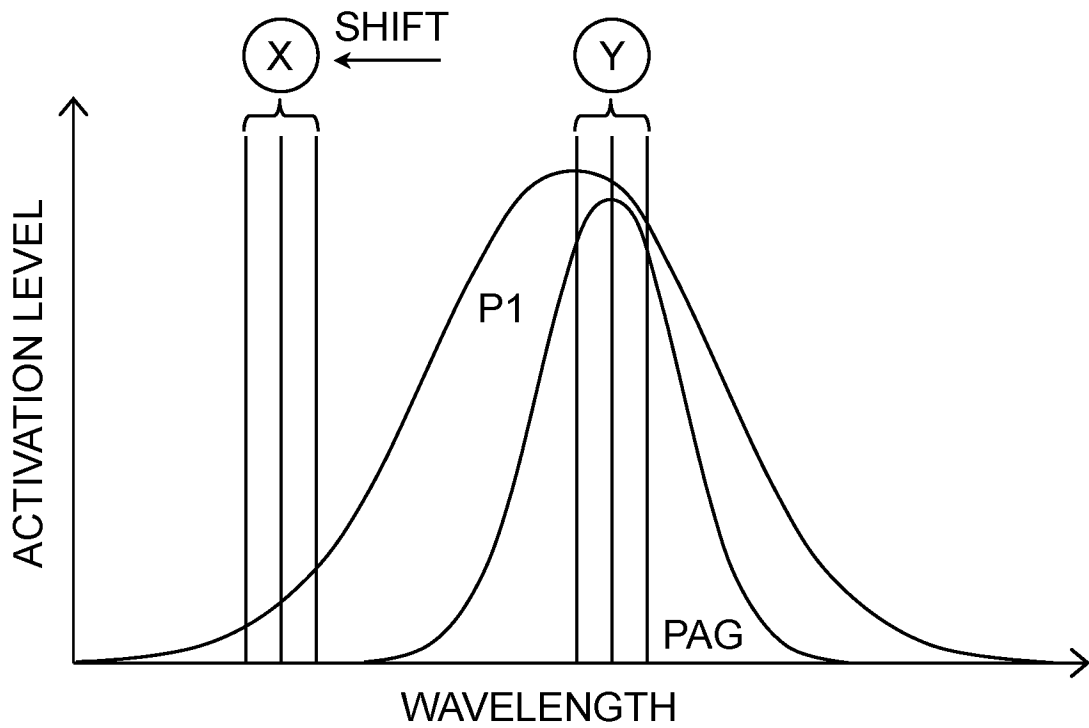


FIG. 1F

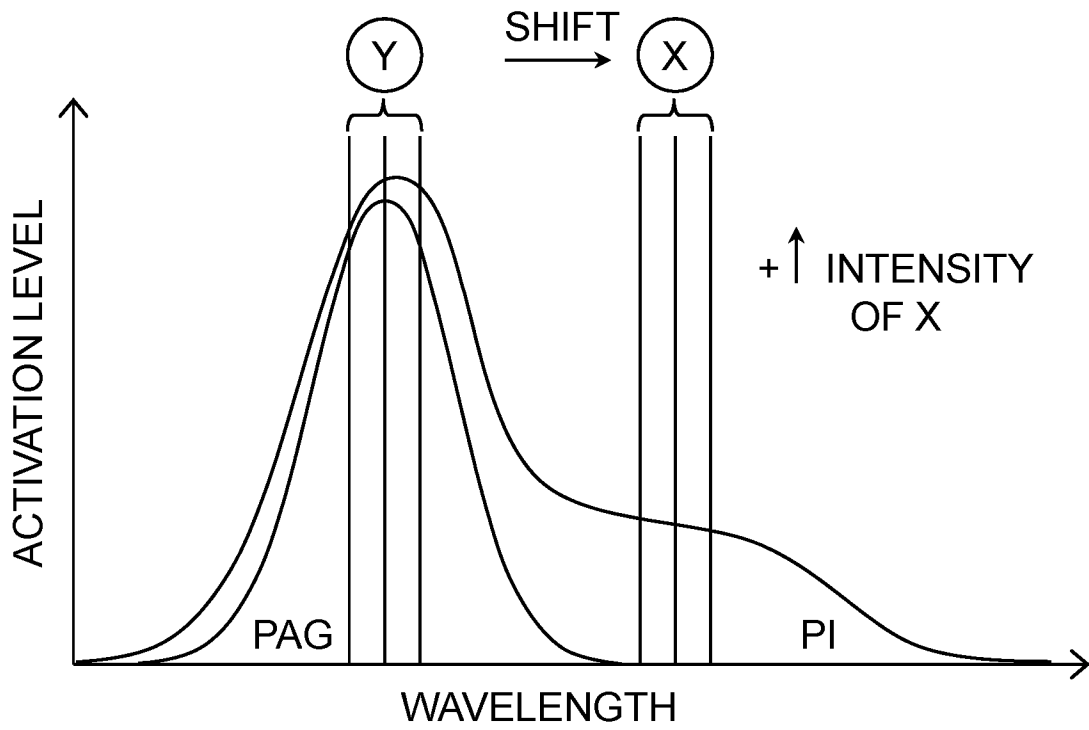


FIG. 1G

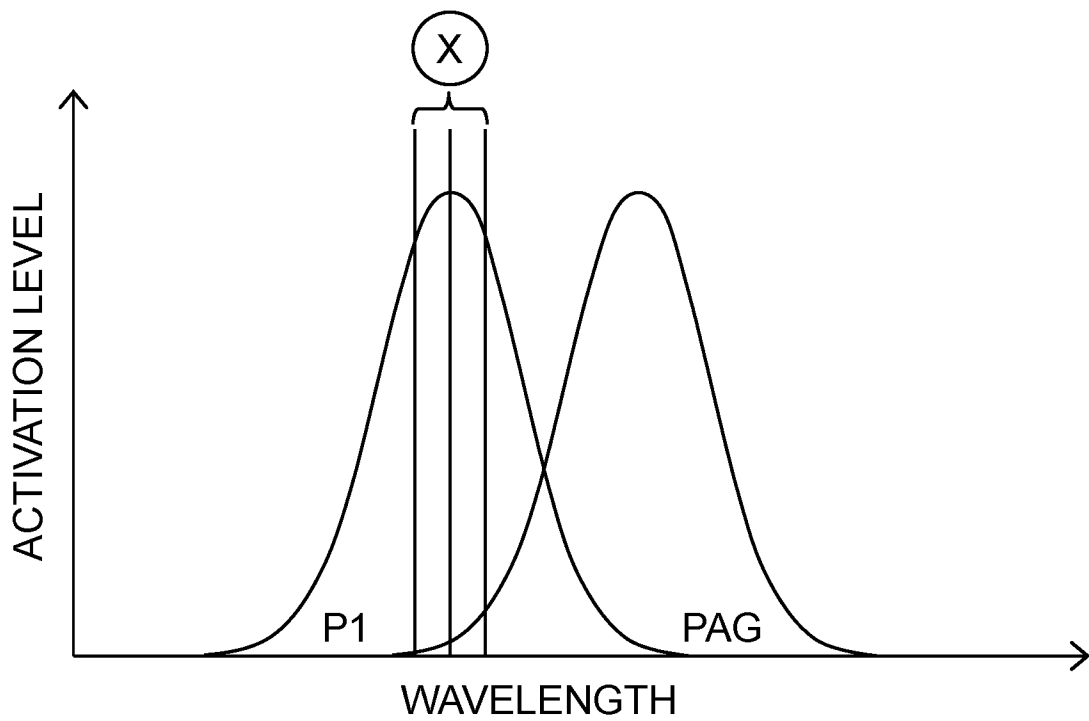


FIG. 1H

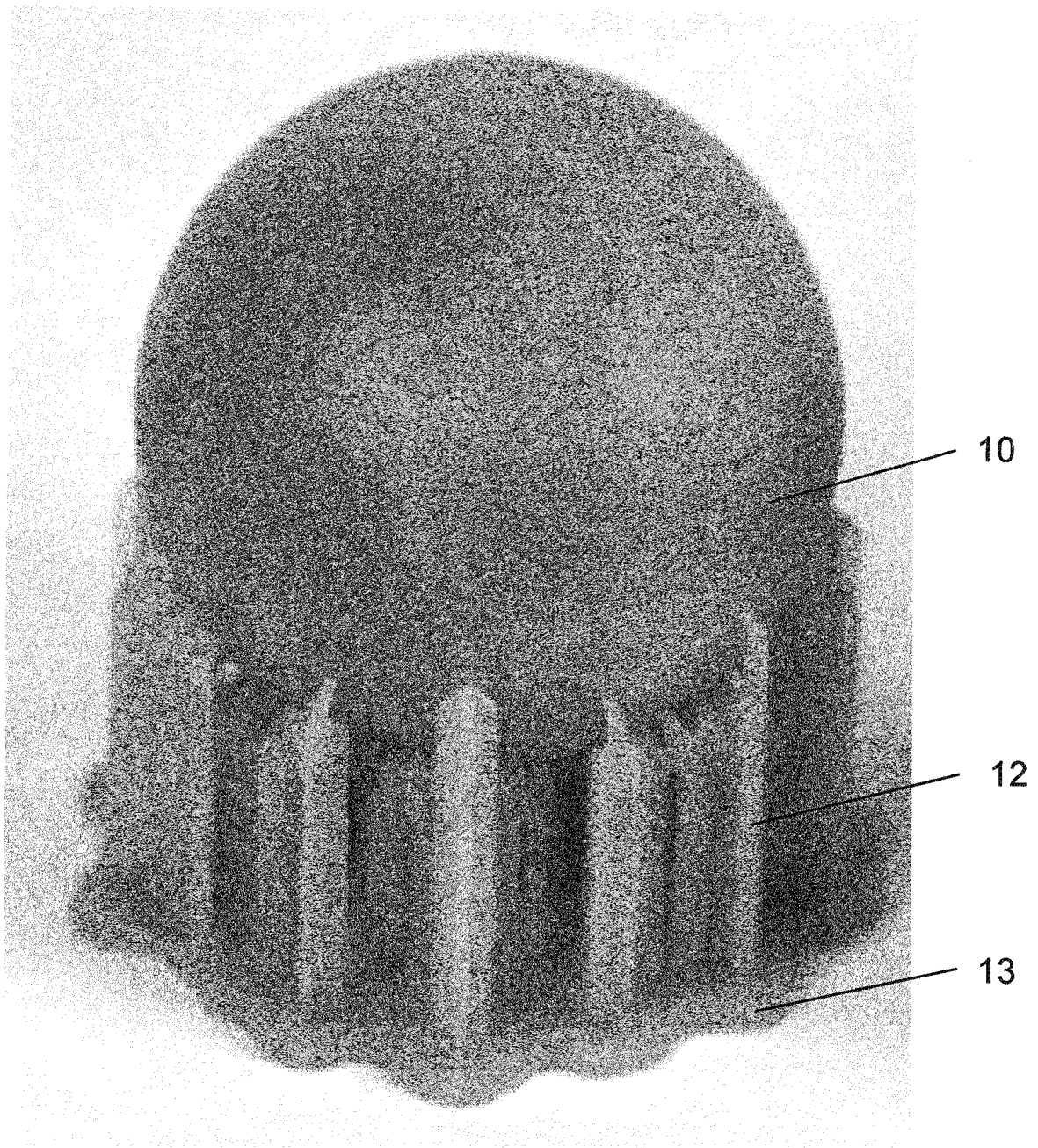


FIG. 2

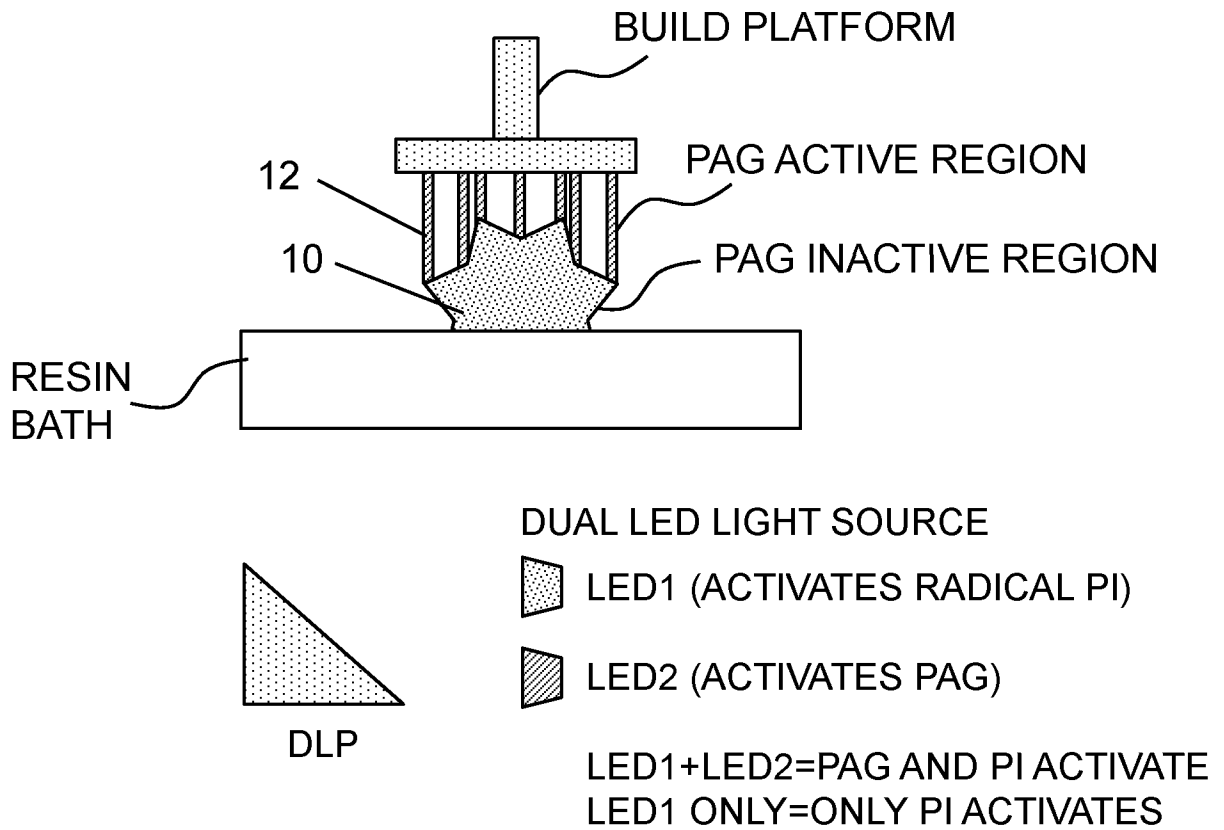


FIG. 3A

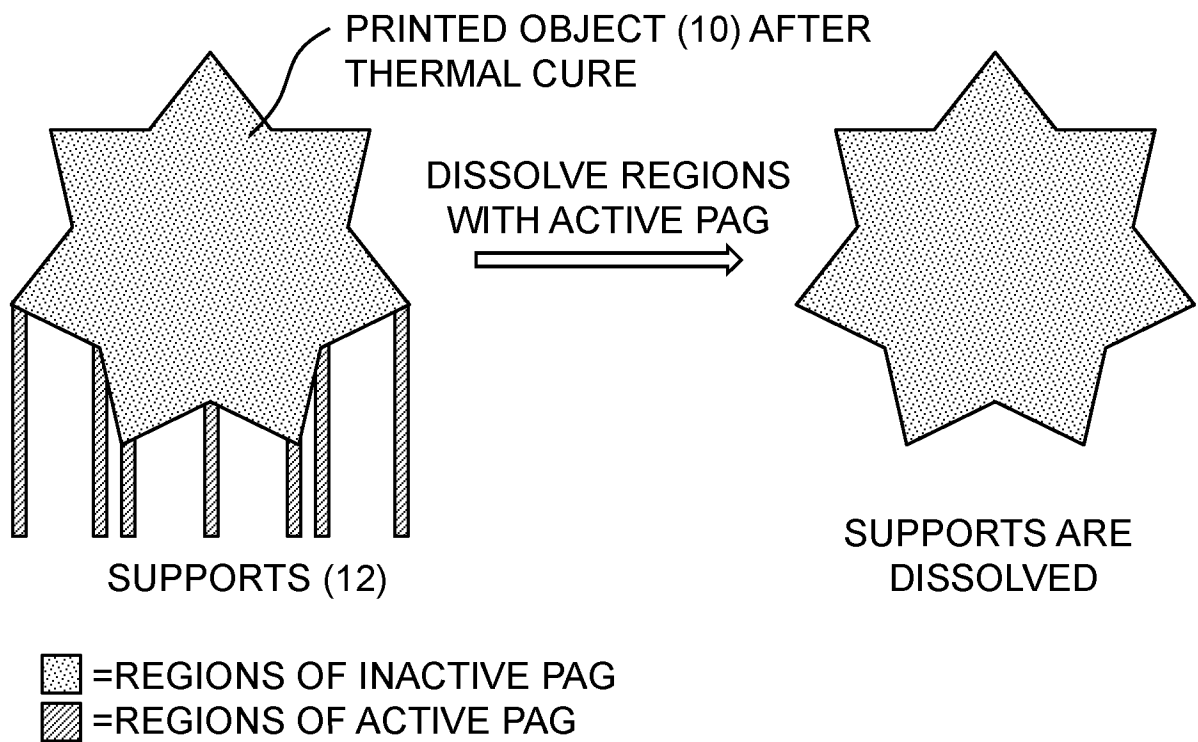


FIG. 3B

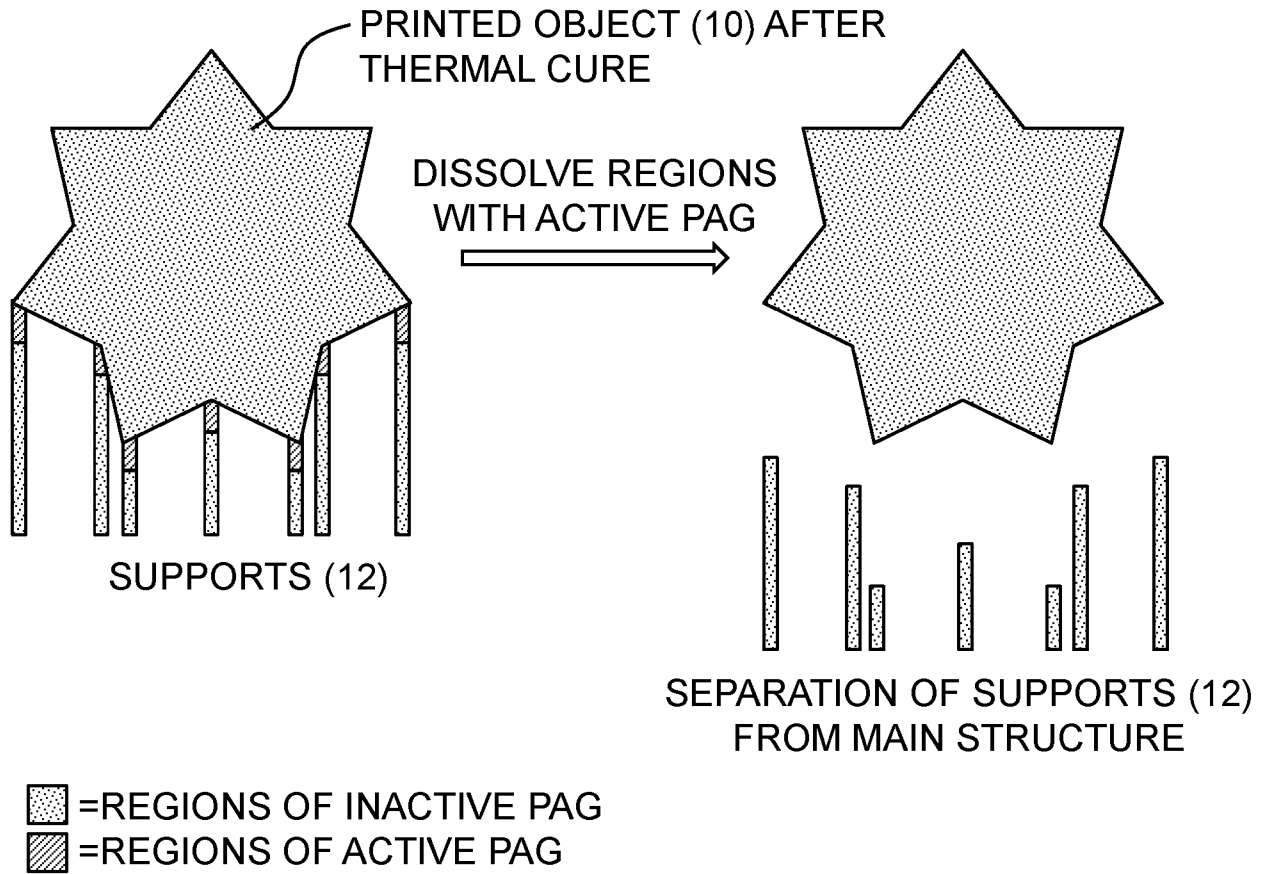


FIG. 4

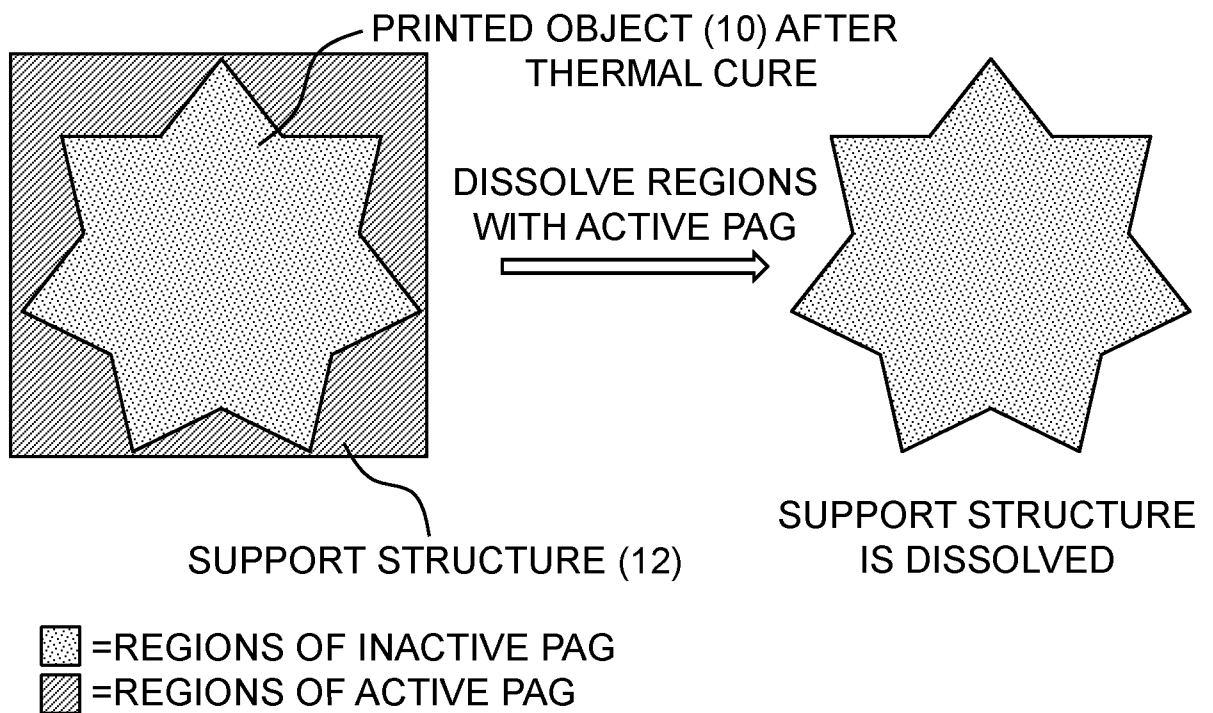


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/051515

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F2/48 C08F220/18 C08L33/08
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 C08L C09D
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.
X	US 2007/231735 A1 (PAWLOWSKI GEORG [US] ET AL) 4 October 2007 (2007-10-04) paragraphs [0009] - [0010], [0026], [0034], [0035], [0043]; claims 1-12 paragraph [0052] - paragraph [0056] -----	1-10, 20-43
X	US 2013/196153 A1 (WEIKEL ARLIN L [US] ET AL) 1 August 2013 (2013-08-01) paragraphs [0026] - [0028], [0033], [0036] - [0049], [0067]; claims 1-20 -----	1-7,9, 10,20, 22-26
Y	US 7 815 835 B2 (STAMPFL JURGEN [AT] ET AL) 19 October 2010 (2010-10-19) column 2, line 60 - column 3, line 6 column 3, line 56 - column 4, line 44 column 5, line 10 - line 24 column 7, line 12 - line 53; claims 1-17 ----- -/--	1-10, 20-43

Further documents are listed in the continuation of Box C.

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 18 November 2016	Date of mailing of the international search report 25/01/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Giani, Elena

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/051515

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/022709 A1 (JIN XIAOMING [US] ET AL) 28 January 2010 (2010-01-28) paragraph [0011]; claim 1 -----	1-10, 20-43

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/051515

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-10, 20-43

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-10, 20-43

polymerizable composition comprising a photoacid generator

2. claims: 11-19

polymerizable composition comprising a photobase generator

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/051515

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2007231735	A1	04-10-2007	CN 101410756 A	15-04-2009
			EP 2016464 A2	21-01-2009
			JP 5076092 B2	21-11-2012
			JP 2009531730 A	03-09-2009
			KR 20080104387 A	02-12-2008
			KR 20140043504 A	09-04-2014
			MY 144195 A	15-08-2011
			TW 200801808 A	01-01-2008
			US 2007231735 A1	04-10-2007
			WO 2007110773 A2	04-10-2007

US 2013196153	A1	01-08-2013	CN 103596992 A	19-02-2014
			EP 2723787 A1	30-04-2014
			JP 2014518929 A	07-08-2014
			KR 20140033450 A	18-03-2014
			US 2012301715 A1	29-11-2012
			US 2013196153 A1	01-08-2013
			WO 2012161997 A1	29-11-2012

US 7815835	B2	19-10-2010	AT 414602 T	15-12-2008
			AT 502110 A1	15-01-2007
			CN 101213070 A	02-07-2008
			EP 1907192 A1	09-04-2008
			ES 2317543 T3	16-04-2009
			JP 4861413 B2	25-01-2012
			JP 2008544879 A	11-12-2008
			US 2009224438 A1	10-09-2009
			WO 2007002965 A1	11-01-2007

US 2010022709	A1	28-01-2010	CA 2654814 A1	21-12-2007
			JP 2009540058 A	19-11-2009
			JP 2014218680 A	20-11-2014
			US 2008076853 A1	27-03-2008
			US 2010022709 A1	28-01-2010
			WO 2007146239 A2	21-12-2007
