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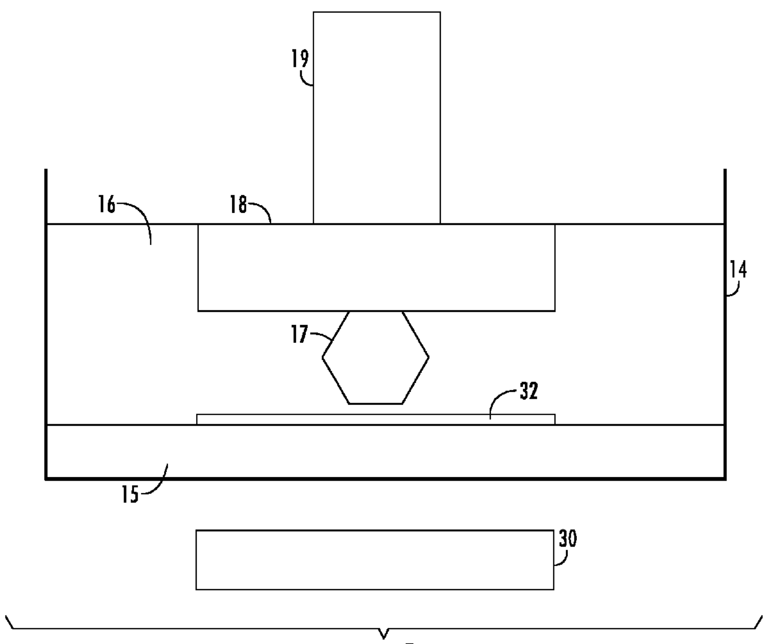


FIG. 1

**(57) Abstract**: A method and a system for the production of a three-dimensional object by additive manufacturing. The method is carried out continuously. The three-dimensional object (17) is produced from a liquid interface. The polymerizable liquid comprises magnetic particles dispersed therein, said magnetic particles comprising a polymerization initiator or a polymerization inhibitor.

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# ADDITIVE MANUFACTURING USING POLYMERIZATION INITIATORS OR INHIBITORS HAVING CONTROLLED MIGRATION

## Related Applications

This application claims the benefit of United States Provisional Patent Application Serial No. 62/132,189, filed March 12, 2015, the disclosure of which is incorporated by reference herein in its entirety.

## Field of the Invention

The present invention concerns methods and apparatus for the fabrication of solid three-dimensional objects from liquid materials.

## Background of the Invention

In conventional additive or three-dimensional fabrication techniques, construction of a three-dimensional object is performed in a step-wise or layer-by-layer manner. In particular, layer formation is performed through solidification of photo curable resin under the action of visible or UV light irradiation. Two techniques are known: one in which new layers are formed at the top surface of the growing object; the other in which new layers are formed at the bottom surface of the growing object.

If new layers are formed at the top surface of the growing object, then after each irradiation step the object under construction is lowered into the resin "pool," a new layer of resin is coated on top, and a new irradiation step takes place. An early example of such a technique is given in Hull, US Patent No. 5,236,637, at Figure 3. A disadvantage of such "top down" techniques is the need to submerge the growing object in a (potentially deep) pool of liquid resin and reconstitute a precise overlayer of liquid resin.

If new layers are formed at the bottom of the growing object, then after each irradiation step the object under construction must be separated from the bottom plate in the fabrication well. An early example of such a technique is given in Hull, US Patent No. 5,236,637, at Figure 4. While such "bottom up" techniques hold the potential to eliminate the need for a deep well in which the object is submerged by instead lifting the object out of a relatively shallow well or pool, a problem with such "bottom up" fabrication techniques, as commercially implemented, is that extreme care must be taken, and additional mechanical elements employed, when separating the solidified layer from the bottom plate due to physical and chemical interactions therebetween. For example, in US Patent No. 7,438,846, an elastic separation layer is used to achieve "non-destructive" separation of solidified material at the bottom construction plane.

Other approaches, such as the B9Creator™ 3-dimensional printer marketed by B9Creations of Deadwood, South Dakota, USA, employ a sliding build plate. *See, e.g.,* M. Joyce, US Patent App. 2013/0292862 and Y. Chen et al., US Patent App. 2013/0295212 (both Nov. 7, 2013); *see also* Y. Pan et al., *J. Manufacturing Sci. and Eng.* **134,** 051011-1 (Oct. 2012). Such approaches introduce a mechanical step that may complicate the apparatus, slow the method, and/or potentially distort the end product.

Continuous processes for producing a three-dimensional object are suggested at some length with respect to "top down" techniques in US Patent No. 7,892,474, but this reference does not explain how they may be implemented in "bottom up" systems in a manner non-destructive to the article being produced. Accordingly, there is a need for alternate methods and apparatus for three-dimensional fabrication that can obviate the need for mechanical separation steps in "bottom-up" fabrication.

## Summary of the Invention

Described herein are methods, systems and apparatus (including associated control methods, systems and apparatus), for the production of a three-dimensional object by additive manufacturing. In preferred (but not necessarily limiting) embodiments, the method is carried out continuously. In preferred (but not necessarily limiting) embodiments, the three-dimensional object is produced from a liquid interface. Hence they are sometimes referred to, for convenience and not for purposes of limitation, as "continuous liquid interphase printing" or "continuous liquid interface production" ("CLIP") herein (the two being used interchangeably).

In some preferred embodiments of CLIP, the filling, irradiating, and/or advancing steps are carried out while also concurrently: (i) continuously maintaining a dead zone (or persistent liquid interface) of polymerizable liquid in contact with said build surface, and (ii) continuously maintaining a gradient of polymerization zone (which may also be described as an active surface on the bottom of the growing three dimensional object, to which additional monomers may continue to polymerize) between said dead zone and said solid polymer and in contact with each thereof, said gradient of polymerization zone comprising said polymerizable liquid in partially cured form. Stated differently, in some preferred embodiments of CLIP, the three dimensional object, or at least some contiguous portion thereof, is formed or produced in situ. "In situ" as used herein has its meaning in the field of chemical engineering, and means "in place."

For example, where both the growing portion of the three-dimensional object and the build surface (typically with their intervening active surface or gradient of polymerization, and dead zone) are maintained in place during formation of at least a portion of the 3D object, or sufficiently in place to avoid the formation of fault lines or planes in the 3D object. For example, in some embodiments according to the invention, different portions of the 3D object, which are contiguous with one another in the final 3D object, can both be formed sequentially from or within a gradient of polymerization or active surface. Furthermore, a first portion of the 3D object can remain in the gradient of polymerization or contacting the active surface while a second portion, that is contiguous with the first portion, is formed in the gradient of polymerization. Accordingly, the 3D object can be remotely fabricated, grown or produced continuously from the gradient of polymerization or active surface (rather than fabricated in discrete layers). The dead zone and gradient of polymerization zone/active surface may be maintained through some or all of the formation of the object being made, for example (and in some embodiments) for a time of at least 5, 10, 20, or 30 seconds, and in some embodiments for a time of at least 1 or 2 minutes.

In some embodiments, the gradient of polymerization and/or dead zone is formed upon magnetic repulsion or attraction of a particle comprising polymerization inhibitor in the liquid resin.

Thus the present invention includes a method of forming a three-dimensional object, comprising:

providing a carrier and an optically transparent member having a build surface, the carrier and the build surface defining a build region therebetween;

filling the build region with a polymerizable liquid,

irradiating the build region through the optically transparent member to form a solid polymer from the polymerizable liquid while concurrently advancing the carrier away from the build surface to form the three-dimensional object from the solid polymer, while also concurrently: (i) continuously maintaining a dead zone of polymerizable liquid in contact with the build surface by electrochemically generating a polymerization inhibitor therein from a precursor of the polymerization inhibitor, and (ii) continuously maintaining a gradient of polymerization zone (*e.g.*, an active surface) between the dead zone and the solid polymer and in contact with each thereof, the gradient of polymerization zone comprising the polymerizable liquid in partially cured form.

In some embodiments of the foregoing, the dead zone of the polymerizable liquid is a zone in which no or an insufficient amount of polymerization initiator is present to initiate polymerization. Thus, the polymerizable liquid requires the initiator in order to polymerize, even in the presence of radiation.

In some embodiments, the gradient of polymerization and/or dead zone is formed upon magnetic attraction of a particle comprising initiator to the build zone or magnetic repulsion away from the dead zone.

In some embodiments of the foregoing, the dead zone of the polymerizable liquid is a zone in which a sufficient amount of polymerization inhibitor is present to inhibit polymerization. Thus, the polymerizable liquid requires removal of the inhibitor in order to polymerize, even in the presence of radiation.

A further aspect of the invention is an apparatus for forming a three-dimensional object from a polymerizable liquid, comprising:

(a) a support;

(b) a carrier operatively associated with the support on which carrier the three-dimensional object is formed;

(c) an optically transparent member having a build surface, with the build surface and the carrier defining a build region therebetween;

(d) a polymerizable liquid supply operatively associated with the build surface and configured to supply polymerizable liquid into the build region for solidification or polymerization, wherein said polymerizable liquid comprises magnetic particles dispersed therein, said magnetic particles comprising a polymerization initiator or a polymerization inhibitor;

(e) a radiation source configured to irradiate the build region through the optically transparent member to form a solid polymer from the polymerizable liquid;

(f) a controller operatively associated with the carrier and the radiation source for advancing the carrier away from the build surface to form the three-dimensional object from the solid polymer, while also concurrently: (i) continuously maintaining a dead zone of polymerizable liquid in contact with the build surface, and (ii) continuously maintaining a gradient of polymerization zone (*e.g.,* an active surface) between the dead zone and the solid polymer and in contact with each thereof, the gradient of polymerization zone comprising the polymerizable liquid in partially cured form; and

(g) a magnet operatively associated with the build region and configured to attract or repulse the magnetic particles comprising a polymerization initiator or a polymerization inhibitor in an amount sufficient to maintain the dead zone.

Additional aspects, non-limiting examples and specific embodiments of the present invention are explained in greater detail in the drawings herein and the specification set forth below. The disclosure of all United States Patent references cited herein are to be incorporated herein by reference in their entirety.

## Brief Description of the Drawings

**FIG. 1** is a schematic illustration of a three-dimensional printer apparatus according to some embodiments of the invention, where the apparatus includes a magnet **30** positioned beneath the window **15** and configured to repel magnetic particles comprising a photo-initiator in the polymerizable liquid (resin) **16** to form a dead zone **32** next to the window **15**. In an alternative embodiment, the magnet **30** is configured to attract magnetic particles comprising a polymerization inhibitor in the resin, again forming a dead zone **32** next to the window **15**.

**FIG. 2** is a perspective view of one embodiment of an apparatus that may be used in accordance with the present invention.

**FIG. 3** is a schematic illustration of an embodiment that may be used in the invention, where an optically transparent magnet **30** is placed on top of the window **15**.

## Detailed Description of Illustrative Embodiments

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.

As used herein, the term "and/or" includes any and all possible combinations or one or more of the associated listed items, as well as the lack of combinations when interpreted in the alternative ("or").

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.

**1. Polymerizable liquids.**

Any suitable polymerizable liquid can be used to enable the present invention. The liquid (sometimes also referred to as "liquid resin" "ink," or simply "resin" herein) can include a monomer, particularly photopolymerizable and/or free radical polymerizable monomers, and a suitable initiator such as a free radical initiator, and combinations thereof. Examples include, but are not limited to, acrylics, methacrylics, acrylamides, styrenics, olefins, halogenated olefins, cyclic alkenes, maleic anhydride, alkenes, alkynes, carbon monoxide, functionalized oligomers, multifunctional cute site monomers, functionalized PEGs, etc., including combinations thereof. Examples of liquid resins, monomers and initiators include but are not limited to those set forth in US 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.

***Acid catalyzed polymerizable liquids.*** While in some embodiments as noted above the polymerizable liquid comprises a free radical polymerizable liquid (in which case an inhibitor may be oxygen as described below), in other embodiments the polymerizable liquid comprises an acid catalyzed, or cationically polymerized, polymerizable liquid. In such embodiments the polymerizable liquid comprises monomers and/or particles containing groups suitable for acid catalysis, such as epoxide groups, vinyl ether groups, carboxy groups (*e.g.*, a fatty acid such as lauric acid), etc. Thus suitable monomers include olefins such as methoxyethene, 4-methoxystyrene, styrene, 2-methylprop-1-ene, 1,3-butadiene, etc.; heterocycloic monomers (including lactones, lactams, and cyclic amines) such as oxirane, thietane, tetrahydrofuran, oxazoline, 1,3, dioxepane, oxetan-2-one, etc., and combinations thereof. A suitable (generally ionic or non-ionic) photoacid generator (PAG) is included in the acid catalyzed polymerizable liquid, examples of which 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 hexafluororphosphate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate, dibutylnaphthylsulfonium triflate, *etc.*, including mixtures thereof. *See, e.g.*, US Patent Nos. 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).

***Hydrogels.*** In some embodiments suitable resins includes photocurable hydrogels like poly(ethylene glycols) (PEG) and gelatins. PEG hydrogels have been used to deliver a variety of biologicals, including Growth factors; however, a great challenge facing PEG hydrogels crosslinked by chain growth polymerizations is the potential for irreversible protein damage. Conditions to maximize release of the biologicals from photopolymerized PEG diacrylate hydrogels can be enhanced by inclusion of affinity binding peptide sequences in the monomer resin solutions, prior to photopolymerization allowing sustained delivery. Gelatin is a biopolymer frequently used in food, cosmetic, pharmaceutical and photographic industries. It is obtained by thermal denaturation or chemical and physical degradation of collagen. There are three kinds of gelatin, including those found in animals, fish and humans. Gelatin from the skin of cold water fish is considered safe to use in pharmaceutical applications. UV or visible light can be used to crosslink appropriately modified gelatin. Methods for crosslinking gelatin include cure derivatives from dyes such as Rose Bengal.

***Photocurable silicone resins.*** A suitable resin includes photocurable silicones. UV cure silicone rubber, such as Siliopren™ UV Cure Silicone Rubber can be used as can LOCTITE™ Cure Silicone adhesives sealants. Applications include optical instruments, medical and surgical equipment, exterior lighting and enclosures, electrical connectors / sensors, fiber optics and gaskets.

***Biodegradable resins.*** Biodegradable resins are particularly important for implantable devices to deliver drugs or for temporary performance applications, like biodegradable screws and stents (US patents 7,919,162; 6,932,930). Biodegradable copolymers of lactic acid and glycolic acid (PLGA) can be dissolved in PEG dimethacrylate to yield a transparent resin suitable for use. Polycaprolactone and PLGA oligomers can be functionalized with acrylic or methacrylic groups to allow them to be effective resins for use.

***Photocurable polyurethanes.*** A particularly useful resin is photocurable polyurethanes. A photopolymerizable polyurethane composition comprising (1) a polyurethane based on an aliphatic diisocyanate, poly(hexamethylene isophthalate glycol) and, optionally, 1,4-butanediol; (2) a polyfunctional acrylic ester; (3) a photoinitiator; and (4) an anti-oxidant, can be formulated so that it provides a hard, abrasion-resistant, and stain-resistant material (US Patent 4,337,130). Photocurable thermoplastic polyurethane elastomers incorporate photoreactive diacetylene diols as chain extenders.

***High performance resins.*** In some embodiments, high performance resins are used. Such high performance resins may sometimes require the use of heating to melt and/or reduce the viscosity thereof, as noted above and discussed further below. Examples of such resins include, but are not limited to, resins for those materials sometimes referred to as liquid crystalline polymers of esters, ester-imide, and ester-amide oligomers, as described in US Patents Nos. 7,507,784; 6,939,940. Since such resins are sometimes employed as high-temperature thermoset resins, in the present invention they further comprise a suitable photoinitiator such as benzophenone, anthraquinone, amd fluoroenone initiators (including derivatives thereof), to initiate cross-linking on irradiation, as discussed further below.

***Additional example resins.*** Particularly useful resins for dental applications include EnvisionTEC's Clear Guide, EnvisionTEC's E-Denstone Material. Particularly useful resins for hearing aid industries include EnvisionTEC's e-Shell 300 Series of resins. Particularly useful resins include EnvisionTEC's HTM140IV High Temperature Mold Material for use directly with vulcanized rubber in molding / casting applications. A particularly useful material for making tough and stiff parts includes EnvisionTEC's RC31 resin. A particularly useful resin for investment casting applications includes EnvisionTEC's Easy Cast EC500 resin.

***Additional resin ingredients.*** The liquid resin or polymerizable material 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). In some embodiments, the particles are 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. The resin or polymerizable material may contain a dispersing agent, such as an ionic surfactant, a non-ionic surfactant, a block copolymer, or the like.

The liquid resin can have additional ingredients solubilized therein, including 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), etc., including combinations thereof.

***Initiators of polymerization.*** Initiators or polymerization initiators for use in the present invention are attached or otherwise incorporated into magnetic particles, which are generally in the form of a solid or liquid. The specific initiator will depend upon the monomer being polymerized and the polymerization reaction. In some embodiments, the initiator is an acid, such as those describe above. *See, e.g.*, Dadashi-Silab et al., "Magnetic iron oxide nanoparticles as long wavelength photoinitiators for free radical polymerization," *Polym. Chem.* DOI: 10.1039/c4py01658k (2015).

***Inhibitors of polymerization.*** Inhibitors or polymerization inhibitors for use in the present invention are attached or otherwise incorporated into magnetic particles, which are generally in the form of a solid or liquid. The specific inhibitor will depend upon the monomer being polymerized and the polymerization reaction. In some embodiments, such as where the monomer is polymerized by photoacid generator initiator, the inhibitor can be a base such as ammonia, trace amines (*e.g.* methyl amine, ethyl amine, di and trialkyl amines such as dimethyl amine, diethyl amine, trimethyl amine, triethyl amine, etc.), or carbon dioxide, including mixtures or combinations thereof. In some embodiments, where the polymerization inhibitor is oxygen, oxygen generating particles can be used.

***Magnetic particles.*** Magnetic particles for use in the present invention include paramagnetic particles (*e.g.*, iron oxide particles) and ferromagnetic particles (*e.g.*, chromium dioxide particles), and may be any suitable size or shape. In some embodiments, the particles are nanoparticles. In some embodiments, the particles are formed from a paramagnetic or ferromagnetic coating of a particle (*e.g.*, polystyrene core), which core and/or coating have attached or otherwise incorporated therein a polymerization inhibitor or a polymerization initiator. *See, e.g.*, US Patent No. 5,629,092 to Gay et al.; US Patent No. 4,554,089 to Umemura et al.

***Polymerizable liquids carrying live cells.*** In some embodiments, the polymerizable liquid may carry live cells as "particles" therein. Such polymerizable liquids are generally aqueous, and may be oxygenated, and may be considered as "emulsions" where the live cells are the discrete phase. Suitable live cells may be plant cells (*e.g.*, monocot, dicot), animal cells (*e.g.*, mammalian, avian, amphibian, reptile cells), microbial cells (*e.g.*, prokaryote, eukaryote, protozoal, etc.), etc. The cells may be of differentiated cells from or corresponding to any type of tissue (*e.g.*, blood, cartilage, bone, muscle, endocrine gland, exocrine gland, epithelial, endothelial, etc.), or may be undifferentiated cells such as stem cells or progenitor cells. In such embodiments the polymerizable liquid can be one that forms a hydrogel, including but not limited to those described in US Patent Nos. 7,651,683; 7,651,682; 7,556,490; 6,602,975; 5,836,313; etc.

## 2. Apparatus.

Features and aspects of the methods and apparatus described herein can be implemented in like manner as described in DeSimone et al., PCT Application Publication No. WO

2014/126837, published August 21, 2014 (and see also PCT Application Pub. Nos. WO 2014/126830 and WO 2014/126834, and US Patent Application Publication No. US 2014/0361463) (the disclosures of all of which are incorporated by reference herein in their entirety). Examples of such features and aspects include, but are not limited to, carriers, carrier drives, radiation sources/light engines, supporting frames, controllers and the like, along with descriptions and examples of the three-dimensional products made.

In general, a liquid resin reservoir, tubing, pumps, liquid level sensors and/or valves can be included to replenish the pool of liquid resin in the build chamber though in some embodiments a simple gravity feed or siphon tube may be employed. Drives/actuators for the carrier or linear stage, along with associated wiring, can be included in accordance with known techniques. The drives/actuators, radiation source, and in some embodiments pumps and liquid level sensors can all be operatively associated with a suitable controller, again in accordance with known techniques.

In general, when configured for placement in the apparatus, the carrier defines a "build region" on the build surface, within the total area of the build surface. Because lateral "throw" (*e.g.*, in the X and/or Y directions) is not required in the present invention to break adhesion between successive layers, as in the Joyce and Chen devices noted previously, the area of the build region within the build surface may be maximized (or conversely, the area of the build surface not devoted to the build region may be minimized). Hence in some embodiments, the total surface area of the build region can occupy at least fifty, sixty, seventy, eighty, or ninety percent of the total surface area of the build surface.

The various components can be mounted on a support or frame assembly. While the particular design of the support or frame assembly is not critical and can assume numerous configurations, it may generally comprise a base to which the radiation source is securely or rigidly attached, a vertical member which the linear stage is operatively associated, and a horizontal table to which a walls removably or securely attached (or on which the wall is placed), and with the build plate fixed, either permanently or removably, to form the build chamber as described above.

***Windows/build surfaces.*** The choice of material for the optically transparent member (*i.e.*, the "window") is not critical, so long as it is sufficiently optically transparent at to the radiation at the relevant wavelengths to allow sufficient actinic radiation (*e.g.*, light such as ultraviolet light) to pass therethrough and polymerize the polymerizable liquid and form the three dimensional object. The portions of the window material (and/or magnet) that contact the polymerizable liquid are preferably substantially inert with respect to the constituents of the polymerizable liquid. In general, the window may be flexible or inflexible, porous or non-porous, and may be formed of an inorganic material (*e.g.,* glass, silica), an organic polymer (*e.g.,* perflouropolymer, silicone, polydimethylsiloxane, etc.), or a composite thereof.

***Magnet.*** Attractive or repulsive movement of the magnetic particles as taught herein may be accomplished with a magnet. Such magnet may be a permanent magnet, an electromagnet, for example comprising conductive coils (*e.g.*, Helmholtz coils, solenoid, etc.), or any other magnetic field generating device. As will be understood, the choice of magnet and placement thereof will depend in part on the particular configuration of the apparatus, the particular magnetic particles used, and/or the particular polymerization initiator or inhibitor used. The magnet may be fixed or movable, and may be positioned, *e.g.*, beneath or above the window, on or in the carrier, in or partially included in the build region, at least partially surrounding the build region, etc. When positioned in or on the window, the magnet may be formed of a material that is optically transparent to the radiation source used for polymerization, or, if formed of a material that is not transparent, formed in sufficiently fine or narrow elements, with intervening gaps or spaces (*e.g.,* in the form of a mesh or screen), so that radiation or light transmission through the electrode array is not unduly disrupted.

In some embodiments, the magnet and optically transparent window may be combined in the same component, comprising an optically transparent magnetic material. Optically transparent magnetic materials are known, and often are iron (Fe) containing materials, such as iron oxides. *See, e.g.*, Dagani, "New Material is Optically Transparent, Magnetic at Room Temperature," *Chem. Eng. News* 70(29): 20-21 (1992), describing nanocrystals of $\gamma$-FeO having these properties; *see also* Ziolo et al., "Matrix-Mediated Synthesis of Nanocrystalline ggr-$Fe_2O_3$: A New Optically Transparent Magnetic Material," *Science* 257(5067):219-23 (1992) (comparing small particle form of gamma-$Fe_2O_3$ with $FeBO_3$ and $FeF_3$ transparent magnets); Elizabeth Pennisi, "Nanotechnology yields transparent magnet," Science News 11 July 1992 (iron oxice particles 2-10 minometers across); Philip Ball, "See-through magnets get hard," Nature News 24 June 2003 (aerogel made of small particles of silica having fine grains of magnetic particles of meodymium, iron and boron ($Nd_2Fe_{14}B$)); Louzguine-Luzgin et al., "Optically transparent magnetic and electrically conductive Fe-Cr-Zr ultra-thin films," *physica status solidi (a)*, 211(5):999-1004 (2014) (transparent magnetic thin films having a nominal composition of $Fe_{75}Cr_{15}Zr_{10}$ and containing nanocrystalline BCC Fe particles homogeneously embedded in a metallic glassy matrix); Ohkoshi et al., "Nanometer-size hard magnetic ferrite exhibiting high optical-transparency and nonlinear optical-magnetoelectric effect," *Scientific Reports*, 5, Article No. 14414 (2015) (magnetic ferrite particles composed of $\varepsilon$-$Fe_2O_3$).

***Example embodiments.*** Non-limiting examples of the present invention are given in **FIGS 1-3.**

As set forth in **FIG. 1**, an apparatus for carrying out a method of the invention may comprise a radiation source **11** (not shown, but see FIG. 2), an optically transparent window **15**, a carrier **18** connected to a build stage **19**, and a magnet **30**. The window **15** may be a composite of elements as noted above. A supply of resin **16** containing magnetically active photoinitiator may be included in a reservoir on top of the window. A growing three-dimensional object **17** is shown positioned between the carrier **18** and the window **15**, with a dead zone **32** substantially free of the magnetically repelled photo-initiator at the bottom of the growing three-dimensional object. In an alternative embodiment, the magnet **30** is configured to attract magnetic particles comprising a polymerization inhibitor in the resin, again forming a dead zone **32** next to the window **15**. The magnet **30** may be situated under or otherwise generate a magnetic field in the build chamber. Alternatively, the magnet **30** may be an optically transparent magnet situated beneath, on top, or incorporated into, the window **15**.

A non-limiting embodiment of an apparatus of the invention is also shown in **FIG. 2**. It comprises a radiation source **11** such as a digital light processor (DLP) providing electromagnetic radiation **12** which through reflective mirror **13** illuminates a build chamber defined by wall **14** and a window **15** forming the bottom of the build chamber, which build chamber is filled with polymerizable liquid **16.** The top of the object under construction **17** is attached to a carrier **18.** The carrier **18** is driven in the vertical direction by linear stage **19**. These elements may be operably connected by suitable supports (**20**, **21**, **22**, **23**). Drives/actuators for the carrier or linear stage, along with associated wiring, can be included in accordance with known techniques (not shown for clarity).

**FIG. 3** schematically illustrates an embodiment with the magnet **30** being an optically transparent magnet situated on top of the window **15**. A liquid resin reservoir **40** and tubing **41** connecting the resin reservoir **40** to the build chamber is used to supply the resin **16**. Pumps, liquid level sensors and/or valves can be included to replenish the pool of liquid resin **16** in the build chamber (not shown for clarity), though in some embodiments a simple gravity feed may be employed. The drives/actuators, radiation source, and in some embodiments pumps and liquid level sensors can all be operatively associated with a suitable controller, again in accordance with known techniques.

***Radiation source.*** Any suitable radiation source (or combination of sources) can be used, depending upon the particular polymerizable liquid employed, including electron beam and ionizing radiation sources. In a preferred embodiment the radiation source is an actinic radiation source, such as one or more light sources, and in particular one or more ultraviolet light sources. Any suitable light source can be used, such as incandescent lights, fluorescent lights, phosphorescent or luminescent lights, a laser, light-emitting diode, etc., including arrays thereof. The light source preferably includes a pattern-forming element operatively associated with a controller, as noted above. In some embodiments, the light source or pattern forming element comprises a digital (or deformable) micromirror device (DMD) with digital light processing (DLP), a spatial modulator (SLM), or a microelectromechanical system (MEMS) mirror array, a mask (aka a reticle), a silhouette, or a combination thereof. See US Patent No. 7,902,526. Preferably the light source comprises a spatial light modulation array such as a liquid crystal light valve array or micromirror array or DMD (*e.g.,* with an operatively associated digital light processor, typically in turn under the control of a suitable controller), configured to carry out exposure or irradiation of the polymerizable liquid without a mask, *e.g.*, by maskless photolithography. *See, e.g.*, US Patent Nos. 6,312,134; 6,248,509; 6,238,852; and 5,691,541.

***Flat panel window and radiation source combinations.*** In some of the illustrated embodiments, the radiation source is not shown. However, it will be understood that the radiation source may be below and detached from the window (*See* DeSimone et al., PCT Application Publication No. WO 2014/126837, published August 21, 2014; and *see also* PCT Application Pub. Nos. WO 2014/126830 and WO 2014/126834, and US Patent Application Publication No. US 2014/0361463) (the disclosures of all of which are incorporated by reference herein in their entirety) or directly abut or contact the window, such as an array of light emitting diodes (*e.g.,* ultraviolet or visible light emitting diodes), with the LED array and the window together forming a flat panel.

In some embodiments, as discussed further below, there may be movement in the X and/or Y directions concurrently with movement in the Z direction, with the movement in the X and/or Y direction hence occurring during polymerization of the polymerizable liquid (this is in contrast to the movement described in Y. Chen et al., or M. Joyce, *supra*, which is movement between prior and subsequent polymerization steps for the purpose of replenishing polymerizable liquid). In the present invention such movement may be carried out for purposes such as reducing "burn in" or fouling in a particular zone of the build surface.

Because an advantage of some embodiments of the present invention is that the size of the build surface on the semipermeable member (*i.e.,* the build plate or window) may be reduced due to the absence of a requirement for extensive lateral "throw" as in the Joyce or Chen devices noted above, in the methods, systems and apparatus of the present invention lateral movement (including movement in the X and/or Y direction or combination thereof) of the carrier and object (if such lateral movement is present) is preferably not more than, or less than, 80, 70, 60, 50, 40, 30, 20, or even 10 percent of the width (in the direction of that lateral movement) of the build region.

While in some embodiments the carrier is mounted on an elevator to advance up and away from a stationary build plate, on other embodiments the converse arrangement may be used: That is, the carrier may be fixed and the build plate lowered to thereby advance the carrier away therefrom. Numerous different mechanical configurations will be apparent to those skilled in the art to achieve the same result.

Depending on the choice of material from which the carrier is fabricated, and the choice of polymer or resin from which the article is made, adhesion of the article to the carrier may sometimes be insufficient to retain the article on the carrier through to completion of the finished article or "build." For example, an aluminum carrier may have lower adhesion than a poly(vinyl chloride) (or "PVC") carrier. Hence one solution is to employ a carrier comprising a PVC on the surface to which the article being fabricated is polymerized. If this promotes too great an adhesion to conveniently separate the finished part from the carrier, then any of a variety of techniques can be used to further secure the article to a less adhesive carrier, including but not limited to the application of adhesive tape such as "Greener Masking Tape for Basic Painting #2025 High adhesion" to further secure the article to the carrier during fabrication.

***Controller and process control.*** The methods and apparatus of the invention can include process steps and apparatus features to implement process control, including feedback and feed-forward control, to, for example, enhance the speed and/or reliability of the method.

A controller for use in carrying out the present invention may be implemented as hardware circuitry, software, or a combination thereof. In one embodiment, the controller is a general purpose computer that runs software, operatively associated with monitors, drives, pumps, and other components through suitable interface hardware and/or software. Suitable software for the control of a three-dimensional printing or fabrication method and apparatus as described herein includes, but is not limited to, the ReplicatorG open source 3d printing program, 3DPrint™ controller software from 3D systems, Slic3r, Skeinforge, KISSlicer, Repetier-Host, PrintRun, Cura, etc., including combinations thereof.

Process parameters to directly or indirectly monitor, continuously or intermittently, during the process (*e.g.*, during one, some or all of said filling, irradiating and advancing steps) include, but are not limited to, irradiation intensity, temperature of carrier, polymerizable liquid in the build zone, temperature of growing product, temperature of build plate, pressure, speed of advance, pressure, force (*e.g.*, exerted on the build plate through the carrier and product being fabricated), strain (*e.g.*, exerted on the carrier by the growing product being fabricated), thickness of release layer, etc.

Known parameters that may be used in feedback and/or feed-forward control systems include, but are not limited to, expected consumption of polymerizable liquid (*e.g.*, from the known geometry or volume of the article being fabricated), degradation temperature of the polymer being formed from the polymerizable liquid, etc.

Process conditions to directly or indirectly control, continuously or step-wise, in response to a monitored parameter, and/or known parameters (*e.g.*, during any or all of the process steps noted above), include, but are not limited to, rate of supply of polymerizable liquid, temperature, pressure, rate or speed of advance of carrier, intensity of irradiation, duration of irradiation (*e.g.* for each "slice"), etc.

For example, the temperature of the polymerizable liquid in the build zone, or the temperature of the build plate, can be monitored, directly or indirectly with an appropriate thermocouple, non-contact temperature sensor (*e.g.*, an infrared temperature sensor), or other suitable temperature sensor, to determine whether the temperature exceeds the degradation temperature of the polymerized product. If so, a process parameter may be adjusted through a controller to reduce the temperature in the build zone and/or of the build plate. Suitable process parameters for such adjustment may include: decreasing temperature with a cooler, decreasing the rate of advance of the carrier, decreasing intensity of the irradiation, decreasing duration of radiation exposure, etc.

In addition, the intensity of the irradiation source (*e.g.*, an ultraviolet light source such as a mercury lamp) may be monitored with a photodetector to detect a decrease of intensity from the irriadiation source (*e.g.*, through routine degredation thereof during use). If detected, a process parameter may be adjusted through a controller to accommodate the loss of intensity. Suitable process parameters for such adjustment may include: increasing temperature with a heater, decreasing the rate of advance of the carrier, increasing power to the light source, etc.

As another example, control of temperature and/or pressure to enhance fabrication time may be achieved with heaters and coolers (individually, or in combination with one another and separately responsive to a controller), and/or with a pressure supply (*e.g.*, pump, pressure vessel, valves and combinations thereof) and/or a pressure release mechanism such as a controllable valve (individually, or in combination with one another and separately responsive to a controller).

In some embodiments the controller is configured to maintain the gradient of polymerization zone or active surface described herein throughout the fabrication of some or all of the final product (*e.g.*, by control of the magnetic field applied in the build zone). The specific configuration (*e.g.,* times, rate or speed of advancing, radiation intensity, temperature, etc.) will depend upon factors such as the nature of the specific polymerizable liquid and the product being created. Configuration to maintain the gradient of polymerization zone may be carried out empirically, by entering a set of process parameters or instructions previously determined, or determined through a series of test runs or "trial and error"; configuration may be provided through pre-determined instructions; configuration may be achieved by suitable monitoring and feedback (as discussed above), combinations thereof, or in any other suitable manner.

In some embodiments, a method and apparatus as described above may be controlled by a software program running in a general purpose computer with suitable interface hardware between that computer and the apparatus described above. Numerous alternatives are commercially available. For example, a Parallax Propeller Microcontroller, Sparkfun EasyDriver stepper motor driver, Luxeon Single LED Driver, Parallax USB to Serial converter, and Texas Instruments LightCrafter DLP systems may be used.

**3. Methods.**

The three-dimensional object is preferably formed from resins 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, US Patent Nos. 5,391,072 and 5,529,473 to Lawton, U.S. Patent No. 7,438,846 to John, US Patent No. 7,892,474 to Shkolnik, U.S. Patent No. 8,110,135 to El-Siblani, U.S. Patent Application Publication Nos. 2013/0292862 to Joyce and 2013/0295212 to Chen et al., and PCT Application Publicaiton No. WO 2015/164234 to Robeson et al. The disclosures of these patents and applications are incorporated by reference herein in their entirety.

In general, top-down three-dimensional fabrication is carried out by:

*(a)* providing a polymerizable liquid reservoir having a polymerizable liquid fill level and a carrier positioned in the reservoir, the carrier and the fill level defining a build region therebetween;

*(b)* filling the build region with a polymerizable liquid (*i.e.,* the resin); and then

*(c)* irradiating the build region with light to form a solid polymer scaffold from the first component and also advancing (typically lowering) the carrier away from the build surface to form a three-dimensional object.

A wiper blade, doctor blade, or optically transparent (rigid or flexible) window, may optionally be provided at the fill level to facilitate leveling of the polymerizable liquid, in accordance with known techniques. In the case of an optically transparent window, the window provides a build surface against which the three dimensional intermediate is formed, analogous to the build surface in bottom-up three dimensional fabrication as discussed below.

In general, bottom-up three dimensional fabrication is carried out by:

*(a)* providing a carrier and an optically transparent member having a build surface, the carrier and the build surface defining a build region therebetween;

*(b)* filling the build region with a polymerizable liquid (*i.e.*, the resin); and then

*(c)* irradiating the build region with light through said optically transparent member to form the three-dimensional object.

In some embodiments of bottom up or top down three dimensional fabrication as implemented in the context of the present invention, the build surface is stationary during the formation of the three dimensional intermediate; in other embodiments of bottom-up three dimensional fabrication as implemented in the context of the present invention, the build surface is tilted, slid, flexed and/or peeled, and/or otherwise translocated or released from the growing three dimensional intermediate, usually repeatedly, during formation of the three dimensional intermediate.

In some embodiments of bottom up or top down three dimensional fabrication as carried out in the context of the present invention, the polymerizable liquid (or resin) is maintained in liquid contact with both the growing three dimensional object and the build surface during both the filling and irradiating steps, during fabrication of some of, a major portion of, or all of the three-dimensional object.

In some embodiments of bottom-up or top-down three-dimensional fabrication as carried out in the context of the present invention, the growing three-dimensional object is fabricated in a layerless manner (*e.g.*, through multiple exposures or "slices" of patterned actinic radiation or light) during at least a portion of the formation of the three-dimensional object.

In some embodiments of bottom-up or top-down three-dimensional fabrication as carried out in the context of the present invention, the growing three dimensional object is fabricated in a layer-by-layer manner (*e.g.*, through multiple exposures or "slices" of patterned actinic radiation or light), during at least a portion of the formation of the three-dimensional object.

In some embodiments of bottom-up or top-down three-dimensional fabrication employing a rigid or flexible optically transparent window, a lubricant or immiscible liquid may be provided between the window and the polymerizable liquid (*e.g.*, a fluorinated fluid or oil such as a perfluoropolyether oil).

From the foregoing it will be appreciated that, in some embodiments of bottom-up or top-down three-dimensional fabrication as carried out in the context of the present invention, the growing three dimensional object is fabricated in a layerless manner during the formation of at least one portion thereof, and that same growing three-dimensional object is fabricated in a layer-by-layer manner during the formation of at least one other portion thereof. Thus, operating mode may be changed once, or on multiple occasions, between layerless fabrication and layer-by-layer fabrication, as desired by operating conditions such as part geometry.

In preferred embodiments, the intermediate is formed by continuous liquid interface production (CLIP). CLIP is known and described in, for example, PCT Applications Nos. PCT/US2014/015486 (published as US Patent No. 9,211,678 on December 15, 2015); PCT/US2014/015506 (also published as US Patent No. 9,205,601 on December 8, 2015), PCT/US2014/015497 (also published as US Patent No 9,216,546 on Dec. 22, 2015), and in J. Tumbleston, D. Shirvanyants, N. Ermoshkin et al., Continuous liquid interface 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 the irradiating and/or said advancing steps are carried out while also concurrently maintaining a stable or persistent liquid interface between the growing object and the build surface or window, such as by: (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) between the dead zone and the solid polymer and in contact with each thereof, the gradient of polymerization zone comprising the first component in partially cured form. In some embodiments of CLIP, the optically transparent member comprises a semipermeable member (e.g., a fluoropolymer), and the continuously maintaining a dead zone is carried out by feeding an inhibitor of polymerization through the optically transparent member, thereby creating a gradient of inhibitor in the dead zone and optionally in at least a portion of the gradient of polymerization zone.

In some embodiments, the stable liquid interface may be achieved by other techniques, such as by providing an immiscible liquid as the build surface between the polymerizable liquid and the optically transparent member, by feeding a lubricant to the build surface (*e.g.*, through an optically transparent member which is semipermeable thereto, and/or serves as a reservoir thereof), etc.

As noted above, the present invention includes a method of forming a three-dimensional object, comprising:

providing a carrier and an optically transparent member having a build surface, the carrier and the build surface defining a build region therebetween;

filling the build region with a polymerizable liquid, wherein said polymerizable liquid comprises magnetic particles dispersed therein, said magnetic particles comprising a polymerization initiator or a polymerization inhibitor; and

irradiating the build region through the optically transparent member to form a solid polymer from the polymerizable liquid while concurrently advancing the carrier away from the build surface to form the three-dimensional object from the solid polymer, while also concurrently:

(i) continuously maintaining a dead zone of polymerizable liquid in contact with the build surface by magnetically attracting or repulsing the magnetic particles comprising a polymerization initiator or polymerization inhibitor, and

(ii) continuously maintaining a gradient of polymerization zone (*e.g.*, an active surface) between the dead zone and the solid polymer and in contact with each thereof, the gradient of polymerization zone comprising the polymerizable liquid in partially cured form.

In some embodiments of the foregoing, the method further comprises providing a magnet operatively associated with the build region and configured to attract or repulse magnetic particles comprising a polymerization initiator or a polymerization inhibitor in an amount sufficient to maintain the dead zone.

A further aspect of the invention is an apparatus for forming a three-dimensional object from a polymerizable liquid, comprising:

(a) a support;

(b) a carrier operatively associated with the support on which carrier the three-dimensional object is formed;

(c) an optically transparent member having a build surface, with the build surface and the carrier defining a build region therebetween;

(d) a polymerizable liquid supply operatively associated with the build surface and configured to supply polymerizable liquid into the build region for solidification or polymerization, wherein said polymerizable liquid comprises magnetic particles dispersed therein, said magnetic particles comprising a polymerization initiator or a polymerization inhibitor;

(e) a radiation source configured to irradiate the build region through the optically transparent member to form a solid polymer from the polymerizable liquid;

(f) a controller operatively associated with the carrier and the radiation source for advancing the carrier away from the build surface to form the three-dimensional object from the solid polymer, while also concurrently: (i) continuously maintaining a dead zone of polymerizable liquid in contact with the build surface, and (ii) continuously maintaining a gradient of polymerization zone (*e.g.,* an active surface) between the dead zone and the solid polymer and in contact with each thereof, the gradient of polymerization zone comprising the polymerizable liquid in partially cured form; and

(g) a magnet operatively associated with the build region and configured to attract or repulse magnetic particles comprising a polymerization initiator or a polymerization inhibitor in an amount sufficient to maintain the dead zone.

In some embodiments, the irradiating step is carried out by maskless photolithography.

In some embodiments, the method further comprises the step of disrupting the gradient of polymerization zone for a time sufficient to form a cleavage line in the three-dimensional object.

In some embodiments, the method further comprises heating the polymerizable liquid to reduce the viscosity thereof in the build region.

In some embodiments, the carrier has at least one channel formed therein, and the filling step is carried out by passing or forcing the polymerizable liquid into the build region through the at least one channel (*e.g., (i)* directly through the growing three-dimensional object, such as in the case of a hollow object, *(ii)* through feed conduits fabricated concurrently but separately from the growing three-dimensional object, or *(iii)* a combination thereof).

In some embodiments, the irradiating step is carried out with actinic radiation.

In some embodiments, the total surface area of the build region occupies at least seventy percent of the total surface area of the build surface; and/or lateral movement of the carrier and object in any direction is not more than thirty percent of the width of the build region in the corresponding direction.

In some 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.)

In other embodiments of the invention, the advancing step is carried out continuously, at a uniform or variable rate.

In some embodiments, the cumulative rate of advance (whether carried out sequentially or continuously) is from about 0.1 1, or 10 microns per second, up to about to 100, 1,000, or

10,000 microns per second, again depending again depending on factors such as temperature, pressure, structure of the article being produced, intensity of radiation, etc.

As noted above, the irradiating step is in some embodiments carried out with patterned irradiation. The patterned irradiation may be a fixed pattern or may be a variable pattern created by a pattern generator (*e.g.*, a DLP) as discussed above, depending upon the particular item being fabricated.

When the patterned irradiation is a variable pattern rather than a pattern that is held constant over time, then each irradiating step may be any suitable time or duration depending on factors such as the intensity of the irradiation, the presence or absence of dyes in the polymerizable material, the rate of growth, etc. Thus in some embodiments each irradiating step can be from 0.001, 0.01, 0.1, 1 or 10 microseconds, up to 1, 10, or 100 minutes, or more, in duration. The interval between each irradiating step is in some embodiments preferably as brief as possible, *e.g.*, from 0.001, 0.01, 0.1, or 1 microseconds up to 0.1, 1, or 10 seconds.

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

In an embodiment of the present invention, the carrier is vertically reciprocated with respect to the build surface (that is, the two are vertically reciprocated with respect to one another) 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 dimension) in part or in whole.

In some embodiments, the speed of the upstroke gradually accelerates (that is, there is provided a gradual start and/or gradual acceleration of the upstroke, over a period of at least 20, 30, 40, or 50 percent of the total time of the upstroke, until the conclusion of the upstroke, or the change of direction which represents the beginning of the downstroke. Stated differently, the upstroke begins, or starts, gently or gradually.

In some embodiments, the speed of the downstroke gradually decelerates (that is, there is provided a gradual termination and/or gradual deceleration of the downstroke, over a period of at least 20, 30, 40, or 50 percent of the total time of the downstroke. Stated differently, the downstroke concludes, or ends, gently or gradually.

While in some embodiments there is an abrupt end, or abrupt deceleration, of the upstroke, and an abrupt beginning or deceleration of the downstroke (*e.g.,* a rapid change in vector or direction of travel from upstroke to downstroke), it will be appreciated that gradual transitions may be introduced here as well (*e.g.,* through introduction of a "plateau" or pause in travel between the upstroke and downstroke). It will also be appreciated that, while each reciprocating step may be consist of a single upstroke and downstroke, the reciprocation step may comprise a plurality of 2, 3, 4 or 5 or more linked set of reciprocations, which may e the same or different in frequent and/or amplitude.

In some embodiments, the vertically reciprocating step is carried out over a total time of from 0.01 or 0.1 seconds up to 1 or 10 seconds (*e.g.,* per cycle of an upstroke and a downstroke).

In some embodiments, the upstroke distance of travel is from 0.02 or 0.2 millimeters (or 20 or 200 microns) to 1 or 10 millimeters (or 1000 to 10,000 microns). The distance of travel of the downstroke may be the same as, or less than, the distance of travel of the upstroke, where a lesser distance of travel for the downstroke serves to achieve the advancing of the carrier away from the build surface as the three-dimensional object is gradually formed. Where a reciprocation step comprises multiple linked reciprocations, the sum distance of travel of all upstrokes in that set is preferably greater than the sum distance of travel of all downstrokes in that set, to achieve the advancing of the carrier away from the build surface as the three-dimensional object is gradually formed.

Preferably the vertically reciprocating step, and particularly the upstroke thereof, does not cause the formation of gas bubbles or a gas pocket in the build region, but instead the build region remains filled with the polymerizable liquid throughout the reciprocation steps, and the gradient of polymerization zone or region remains in contact with the "dead zone" and with the growing object being fabricated throughout the reciprocation steps. As will be appreciated, a purpose of the reciprocation is to speed or enhance the refilling of the build region, particularly where larger build regions are to be refilled with polymerizable liquid, as compared to the speed at which the build region could be refilled without the reciprocation step.

In some embodiments, the advancing step is carried out intermittently at a rate of 1, 2, 5 or 10 individual advances per minute up to 300, 600, or 1000 individual advances per minute, each followed by a pause during which an irradiating step is carried out. It will be appreciated that one or more reciprocation steps (*e.g.*, upstroke plus downstroke) may be carried out within each advancing step. Stated differently, the reciprocating steps may be nested within the advancing steps.

In some embodiments, the individual advances are carried out over an average distance of travel for each advance of from 10 or 50 microns to 100 or 200 microns (optionally including the total distance of travel for each vertically reciprocating step, *e.g.*, the sum of the upstroke distance minus the downstroke distance).

Apparatus for carrying out the invention in which the reciprocation steps described herein are implemented substantially as described above, with the drive associated with the carrier, and/or with an additional drive operatively associated with the transparent member, and with the controller operatively associated with either or both thereof and configured to reciprocate the carrier and transparent member with respect to one another as described above.

In the alternative, vertical reciprocation may be carried out by configuring the build surface (and corresponding build plate or transparent member) so that it may have a limited range of movement up and down in the vertical or "Z" dimension, while the carrier advances (*e.g.*, continuously or step-wise) away from the build plate in the vertical or "Z" dimension. In some embodiments, such limited range of movement may be passively imparted, such as with upward motion achieved by partial adhesion of the build plate to the growing object through a viscous polymerizable liquid, followed by downward motion achieved by the weight, resiliency, etc. of the build plate (optionally including springs, buffers, shock absorbers or the like, configured to influence either upward or downward motion of the build plate and build surface).

In another embodiment, such motion of the build surface may be actively achieved, by operatively associating a separate drive system with the build plate, which drive system is also operatively associated with the controller, to separately achieve vertical reciprocation. In still another embodiment, vertical reciprocation may be carried out by configuring the build plate, and/or the build surface, so that it flexes upward and downward, with the upward motion thereof being achieved by partial adhesion of the build surface to the growing object through a viscous polymerizable liquid, followed by downward motion achieved by the inherent stiffness of the build surface biasing it or causing it to return to a prior position.

It will be appreciated that illumination or irradiation steps, when intermittent, may be carried out in a manner synchronized with vertical reciprocation, or not synchronized with vertical reciprocation, depending on factors such as whether the reciprocation is achieved actively or passively.

It will also be appreciated that vertical reciprocation may be carried out between the carrier and all regions of the build surface simultaneously (*e.g.,* where the build surface is rigid), or may be carried out between the carrier and different regions of the build surface at different times (*e.g.,* where the build surface is of a flexible material, such as a tensioned polymer film).

In some embodiments of the methods and compositions described above and below, the polymerizable liquid has a viscosity of 500 or 1,000 centipoise or more at room temperature and/or under the operating conditions of the method, up to a viscosity of 10,000, 20,000, or 50,000 centipoise or more, at room temperature and/or under the operating conditions of the method.

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.

## THAT WHICH IS CLAIMED IS:

1. A method of forming a three-dimensional object, comprising:

providing a carrier and an optically transparent member having a build surface, said carrier and said build surface defining a build region therebetween;

filling said build region with a polymerizable liquid, wherein said polymerizable liquid comprises magnetic particles dispersed therein, said magnetic particles comprising a polymerization initiator or a polymerization inhibitor; and

irradiating said build region through said optically transparent member to form a solid polymer from said polymerizable liquid while concurrently advancing said carrier away from said build surface to form said three-dimensional object from said solid polymer, while also concurrently:

(i) continuously maintaining a dead zone of polymerizable liquid in contact with said build surface by magnetically attracting or repulsing said magnetic particles comprising a polymerization initiator or polymerization inhibitor, and

(ii) continuously maintaining a gradient of polymerization zone (*e.g.,* an active surface) between said dead zone and said solid polymer and in contact with each thereof, said gradient of polymerization zone comprising said polymerizable liquid in partially cured form.

2. The method of claim 1, further comprising:

providing a magnet operatively associated with the build region and configured to attract or repulse the magnetic particles comprising a polymerization initiator or polymerization inhibitor.

3. The method of claim 1 or 2, wherein the magnetic particles are paramagnetic particles or ferromagnetic particles.

4. The method of claim 2 or 3, wherein said magnet is a permanent magnet.

5. The method of claim 2 or 3, wherein said magnet is an electromagnet.

6. The method of any preceding claim, wherein said optically transparent member is flexible or inflexible, porous or non-porous, and comprised of an inorganic material, an organic polymer, or a composite thereof.

7. The method of any one of claims 2-6, wherein said optically transparent member comprises the magnet.

8. The method of any one of claims 2-7, wherein said magnet is optically transparent.

9. The method of any preceding claim, wherein said irradiating step is carried out by maskless photolithography.

10. The method any preceding claim, wherein said gradient of polymerization zone and said dead zone together have a thickness of from 1 to 1000 microns.

11. The method of any preceding claim, wherein said gradient of polymerization zone is maintained for a time of at least 5, 10, or 20 seconds, or at least 1 or 2 minutes.

12. The method of any preceding claim, further comprising the step of disrupting said gradient of polymerization zone for a time sufficient to form a cleavage line in said three-dimensional object.

13. The method of any preceding claim, further comprising the step of heating said polymerizable liquid to reduce the viscosity thereof in said build region.

14. The method of any preceding claim, wherein said carrier has at least one channel formed therein, and said filling step is carried out by passing or forcing said polymerizable liquid into said build region through said at least one channel (*e.g.*, *(i)* directly through the growing three-dimensional object, such as in the case of a hollow object, *(ii)* through feed conduits fabricated concurrently but separately from the growing three-dimnensional object, or *(iii)* a combination thereof).

15. The method of any preceding claim, wherein said irradiating step is carried out with actinic radiation.

16. The method of any preceding claim, wherein said concurrently advancing is carried out at a cumulative rate of at least 10 microns per second.

17. The method of any preceding claim, wherein:

the total surface area of the build region occupies at least seventy percent of the total surface area of the build surface; and/or

wherein lateral movement of the carrier and object in any direction is not more than thirty percent of the width of said build region in the corresponding direction.

18. The method of any preceding claim, wherein said optically transparent member is stationary.

19. The method of any preceding claim, wherein

said advancing comprises unidirectionally advancing said carrier away from said optically transparent member; and/or

said advancing includes vertically reciprocating said carrier and said optically transparent member with respect to one another to speed or enhance the filling of said build region with said polymerizable liquid.

20. The method of any preceding claim, wherein said polymerizable liquid comprises an acid-catalyzed or cationically polymerizable liquid, and said inhibitor comprises a base.

21. The method of any preceding claim, wherein said irradiating step is carried out by:

*(i)* by either bottom-up three dimensional fabrication between a carrier and a build surface or top-down three dimensional fabrication between a carrier and a fill level, the fill level optionally defined by a build surface; and/or

*(ii)*, optionally with a stationary build surface; and/or

*(iii)* optionally while maintaining the resin in liquid contact with both the three-dimensional object and the build surface, and/or

*(iv)* optionally with said irradiating step carried out in a layerless manner,

each during the formation of at least a portion of the three-dimensional object.

22. An apparatus for forming a three-dimensional object from a polymerizable liquid, comprising:

(a) a support;

(b) a carrier operatively associated with said support on which carrier said three-dimensional object is formed;

(c) an optically transparent member having a build surface, with said build surface and said carrier defining a build region therebetween;

(d) a polymerizable liquid supply operatively associated with said build surface and configured to supply polymerizable liquid into said build region for solidification or polymerization, wherein said polymerizable liquid comprises magnetic particles dispersed therein, said magnetic particles comprising a polymerization initiator or a polymerization inhibitor;

(e) a radiation source configured to irradiate said build region through said optically transparent member to form a solid polymer from said polymerizable liquid;

(f) a controller operatively associated with said carrier and said radiation source for advancing said carrier away from said build surface to form said three-dimensional object from said solid polymer, 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 (*e.g.,* an active surface) between said dead zone and said solid polymer and in contact with each thereof, said gradient of polymerization zone comprising said polymerizable liquid in partially cured form; and

(g) a magnet operatively associated with the build region and configured to attract or repulse said magnetic particles comprising a polymerization initiator or a polymerization inhibitor in an amount sufficient to maintain the dead zone.

23. The apparatus of claim 22, wherein said magnetic particles are paramagnetic particles or ferromagnetic particles.

24. The apparatus of claim 22 or 23, wherein said magnet is a permanent magnet.

25. The apparatus of claim 22 or 23, wherein said magnet is an electromagnet.

26. The apparatus of any one of claims 22 to 25, wherein said optically transparent member comprises said magnet.

27. The apparatus of any one of claims 22-26, wherein said carrier has at least one channel formed therein, configured for supply of said polymerizable liquid into said build region through said at least one channel (*e.g., (i)* directly through the growing three-dimensional object, such as in the case of a hollow object, *(ii)* through feed conduits fabricated concurrently but separately from the growing three-dimensional object, or *(iii)* a combination thereof).

28. The apparatus of claim 27, wherein said carrier has a plurality of channels formed therein, configured for supply of different polymerizable liquids through different ones of said plurality of channels.

29. The apparatus of any one of claims 22-27, wherein said radiation source comprises a light source.

30. The apparatus of any one of claims 22-29, further comprising a spatial light modulation array operatively associated with said radiation source and said controller and configured to carry out irradiation of the polymerizable liquid by maskless photolithography.

31. The apparatus of any one of claims 22-30, wherein said carrier comprises a drive, said drive and said controller configured to advance said carrier unidirectionally away from said build surface and/or vertically reciprocate said carrier and said optically transparent member with respect to one another to speed or enhance the filling of said build region with said polymerizable liquid.

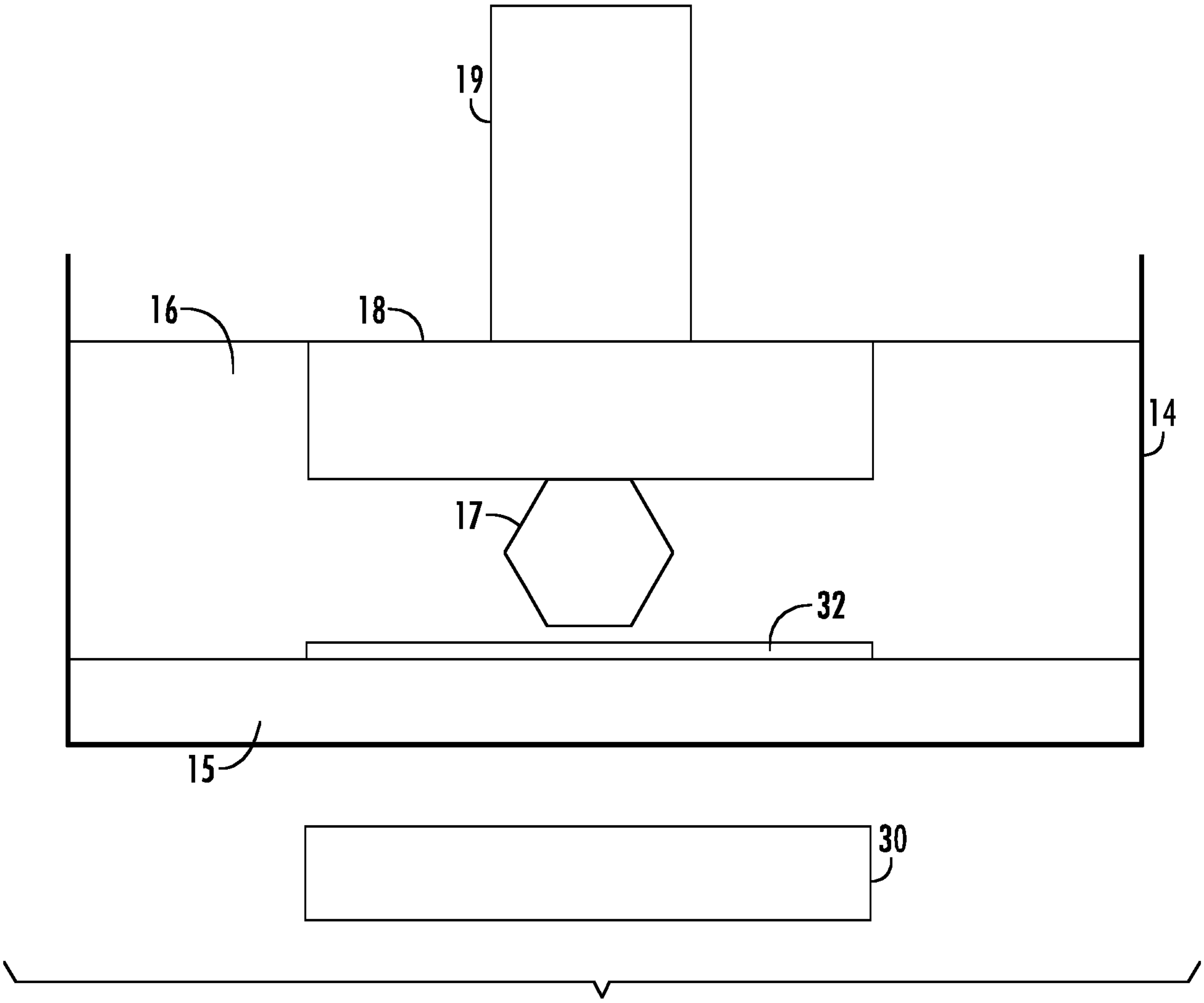


FIG. 1

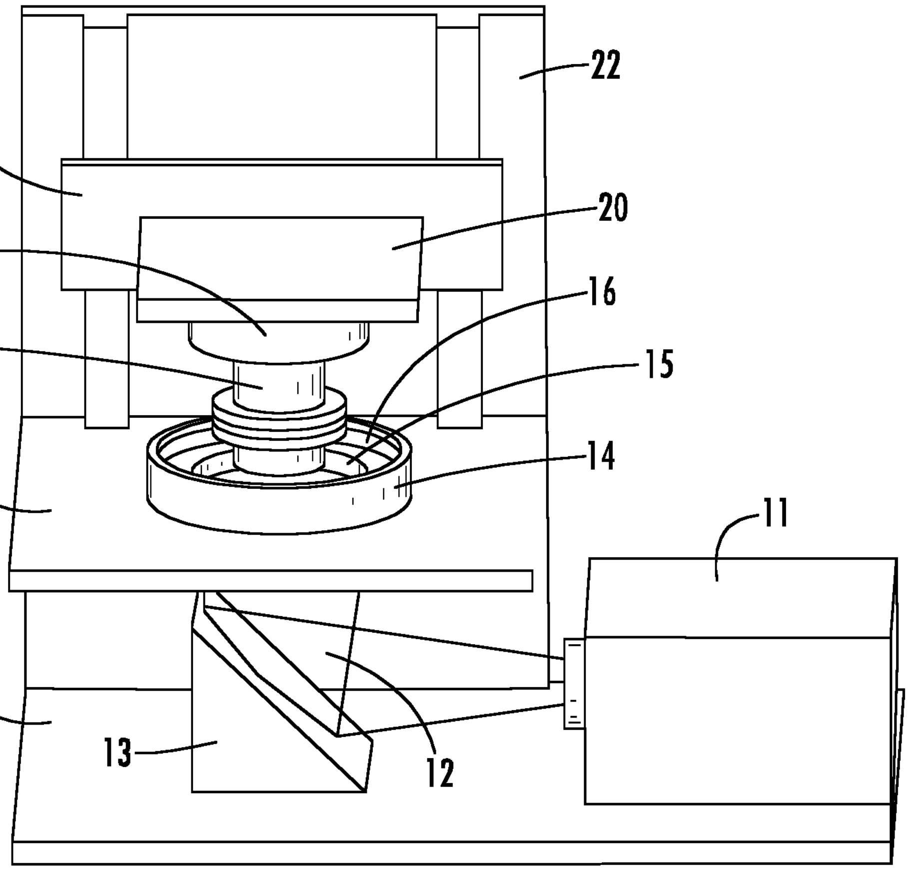
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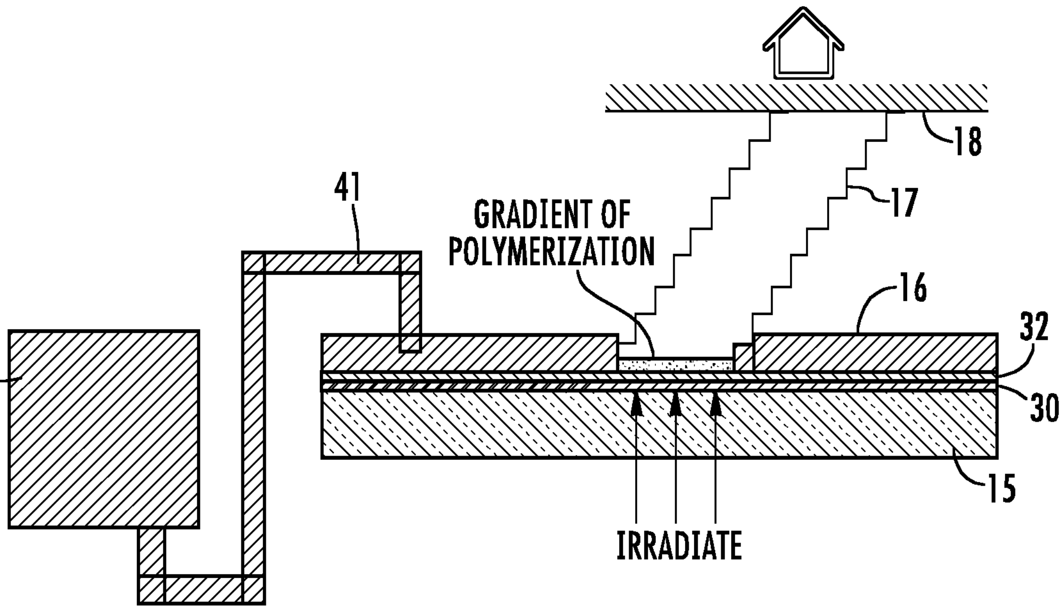
FIG. 2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GRADIENT OF POLYMERIZATION
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32
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15
IRRADIATE

FIG. 3

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/021750

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. B29C67/00 B33Y10/00 B33Y30/00 B33Y40/00
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)
B29C B33Y

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. |
|---|---|---|
| A | WO 2014/126834 A2 (EIPI SYSTEMS INC [US]) 21 August 2014 (2014-08-21) figure 1 pages 4, 16 | 1-31 |
| A | WO 2013/026087 A1 (ZYDEX PTY LTD [AU]; ELSEY JUSTIN [AU]) 28 February 2013 (2013-02-28) page 24, lines 1-5 | 1-31 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 8 June 2016 | 17/06/2016 |

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

# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

International application No
PCT/US2016/021750

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 2014126834 A2 | 21-08-2014 | CA 2898103 A1 | 21-08-2014 |
| | | CA 2898106 A1 | 21-08-2014 |
| | | CN 105122135 A | 02-12-2015 |
| | | CN 105452958 A | 30-03-2016 |
| | | EP 2956822 A2 | 23-12-2015 |
| | | EP 2956823 A2 | 23-12-2015 |
| | | JP 2016509963 A | 04-04-2016 |
| | | JP 2016509964 A | 04-04-2016 |
| | | KR 20150117273 A | 19-10-2015 |
| | | KR 20150117275 A | 19-10-2015 |
| | | TW 201447478 A | 16-12-2014 |
| | | US 2015097315 A1 | 09-04-2015 |
| | | US 2015097316 A1 | 09-04-2015 |
| | | US 2015102532 A1 | 16-04-2015 |
| | | US 2016059484 A1 | 03-03-2016 |
| | | US 2016059486 A1 | 03-03-2016 |
| | | US 2016059487 A1 | 03-03-2016 |
| | | WO 2014126834 A2 | 21-08-2014 |
| | | WO 2014126837 A2 | 21-08-2014 |
| WO 2013026087 A1 | 28-02-2013 | AU 2012300179 A1 | 13-03-2014 |
| | | EP 2744640 A1 | 25-06-2014 |
| | | US 2014191442 A1 | 10-07-2014 |
| | | WO 2013026087 A1 | 28-02-2013 |