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(54) **Title:** METHODS OF SURFACE FINISHING OBJECTS PRODUCED BY ADDITIVE MANUFACTURING

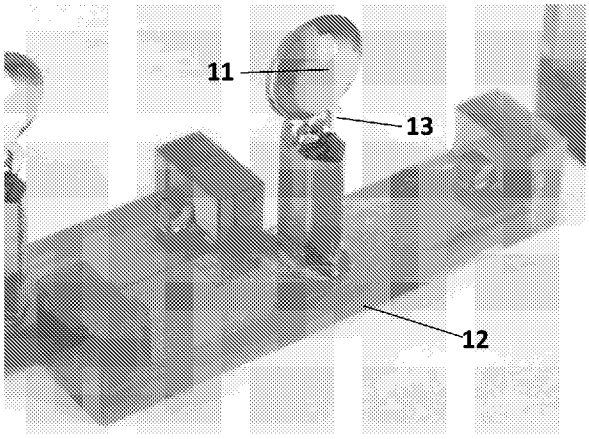

FIG. 1

(57) **Abstract:** Provided is a method of surface finishing an additively manufactured product, comprising: (a) providing an object comprised of a polymer, said object produced by the process of additive manufacturing from a light polymerizable resin, said object having residual resin from which it was produced remaining on a surface portion thereof in unpolymerized form; (b) partially removing said resin from said surface portion object under conditions in which a retained portion of said resin remains as a coating film on said surface portion; and then (c) light polymerizing said retained resin to form a surface coating on said surface portion therefrom and surface finish said additively manufactured product.

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METHODS OF SURFACE FINISHING OBJECTS PRODUCED BY ADDITIVE MANUFACTURING

Field of the Invention

The present invention concerns methods of surface finishing objects produced by additive manufacturing.

Background of the Invention

A group of additive manufacturing techniques sometimes referred to as "stereolithography" creates a three-dimensional object by the sequential polymerization of a light polymerizable resin. Such techniques may be "bottom-up" techniques, where light is projected into the resin on the bottom of the growing object through a light transmissive window, or "top-down" techniques, where light is projected onto the resin on top of the growing object, which is then immersed downward into the pool of resin.

The recent introduction of a more rapid stereolithography technique known as continuous liquid interface production (CLIP), coupled with the introduction of "dual cure" resins for additive manufacturing, has expanded the usefulness of stereolithography from prototyping to manufacturing (*see, e.g.*, US Patent Nos. 9,211,678; 9,205,601; and 9,216,546 to DeSimone et al.; and also in J. Tumbleston, D. Shirvanyants, N. Ermoshkin et al., Continuous liquid interface production of 3D Objects, *Science* 347, 1349-1352 (2015); *see also* Rolland et al., US Patent Nos. 9,676,963, 9,453,142 and 9,598,606).

N. Vaidya and O. Solgaard, *3D printed optics with nanometer scale surface roughness, Microsystems & Nanoengineering* **4**:18 (2018), describe a method for smoothing the surface of objects produced by stereolithography in which the object is washed, degassed in a vacuum, brush coated with a UV curable gel, again placed in a vacuum, spun or drained by gravity if needed, and then UV cured, to surface finish the objects. It would, however, be advantageous to develop techniques that may avoid additional brush, spray, or dip coating steps, potentially avoid a wash step, and simplify handling of the objects, as additional steps and handling like these provide additional opportunities for spoiling the surface when a highly decorative or precision surface is desired.

Summary of the Invention

Provided herein in accordance with some embodiments is a method of surface finishing an additively manufactured product, comprising: (a) providing an object comprised of a polymer, said object produced by the process of additive manufacturing from a light polymerizable resin, said object having residual resin from which it was produced remaining on a surface portion thereof in unpolymerized form; (b) partially removing said resin from said surface portion object under conditions in which a retained portion of said resin remains as a coating film on said surface portion; and then (c) light polymerizing said retained resin to form a surface coating on said surface portion therefrom and surface finish said additively manufactured product.

In some embodiments, the resin comprises a dual cure resin and the method further comprises, after step (c), the step of: (d) heating and/or microwave irradiating said object to further cure both said object and said surface coating.

In some embodiments, the partially removing step is carried out by spinning, blowing with a compressed gas, gravity draining, or a combination thereof.

In some embodiments, the object is produced with a support connected thereto; and the partially removing step includes securing the object with said support. In some embodiments, the support is a sacrificial support, and the method further comprises separating the object from the sacrificial support after the partially removing step, optionally (but in some embodiments preferably) after the light polymerizing step, and optionally (but in some embodiments preferably), after the heating and/or microwave irradiating step, when present. In some embodiments, the sacrificial support comprises: a frame; and at least one, or a plurality, of struts interconnecting the object and the frame.

In some embodiments, the object of steps (a), (b) and (c) is unwashed.

In some embodiments, the retained portion of the resin is undiluted with solvent (e.g., not washed or otherwise diluted with solvent during step (b)) during said light polymerizing of step (c).

In some embodiments, the object comprises: *(i)* a lens, prism, mirror, light pipe, window, or combination thereof; *(ii)* a dental aligner; or *(iii)* a flexible or elastic lattice.

In some embodiments, the resin and object are light transmissive.

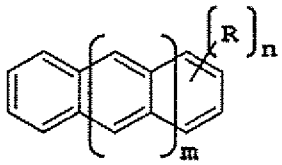
In some embodiments, the surface portion of the object is textured (*e.g.*, in a pattern or configuration that promotes the formation and/or retention of said coating film on said surface portion).

In some embodiments, the additively manufacturing is carried out by bottom-up or top-down stereolithography.

In some embodiments, the light polymerizing step (c) is carried out with UV light at a wavelength of from 350 nm to 400 nm (e.g., 350 nm, 370 nm, 380 nm, 385 nm, 390 nm, etc.).

In some embodiments, the resin comprises: *(i)* light-polymerizable monomers, prepolymers, or a combination thereof (*e.g.*, in an amount of from 5 or 10 percent by weight to 80 or 90 percent by weight); *(ii)* a photoinitiator (*e.g.*, in an amount of from 0.1 percent by weight to 4 percent by weight); and *(iii)* a polysubstituted linear polyacene (*e.g.*, anthracene) ultraviolet light absorbing compound that is polysubstituted with substituents independently selected from the group consisting of: bromo, chloro, -Se-R', and -S-R', where each R' is independently selected from alkyl, aryl, and arylalkyl (*e.g.*, in an amount of 0.01, 0.05 or 0.1 percent by weight to 1 or 5 percent by weight).

In some embodiments, the polyacene is selected from the group consisting of naphthalene, anthracene, tetracene, pentacene, and hexacene. In some embodiments, the polysubstituted linear polyacene ultraviolet light absorbing compound has a structure of **Formula I:**



(I)

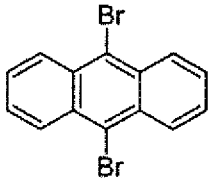
wherein:

m is 0, 1, 2, 3, 4 or 5;

n is from 2 to 4, 6 or 8; and

each R is independently selected from the group consisting of: bromo, chloro, -Se-R', and -S-R', where each R' is independently selected from alkyl, aryl, and arylalkyl. In some embodiments, each R' is bromo.

In some embodiments, the compound of Formula I is selected from the group consisting of 9,10-dibromoanthracene, 2,3,9,10-tetrabromoanthracene, and 5,11-dibromotetracene. In some embodiments, the compound of Formula I is:



In some embodiments, the light-polymerizable monomers, prepolymers, or combination thereof are free-radical polymerizable.

In some embodiments, the resin further comprises a reactive diluent (*e.g.*, in an amount of 1 or 2 percent by weight to 30 or 40 percent by weight).

In some embodiments, the resin comprises a dual cure resin.

In some embodiments, the resin has a light absorption coefficient, alpha, of from 0.0005 or 0.001, to 0.01 or 0.05.

In some embodiments, the object is rigid, flexible, or elastic.

Also provided herein is an object produced by a method as taught herein.

By forming the surface coating directly, from the same resin from which the object is produced, the present invention can obviate the need for the wash step and the brush coating step described in Vaidya and Solgaard referenced above.

Brief Description of the Drawings

FIG. 1 is a photograph of a first non-limiting example of a lens produced in accordance with methods of the present invention.

FIG. 2 is a photograph of a second non-limiting example of a lens produced in accordance with methods of the present invention.

The foregoing and other objects and aspects of the present invention are explained in greater detail in the drawings herein and the specification set forth below. The disclosures of all United States patent references cited herein are to be incorporated herein by reference.

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.

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

"Alkyl" as used herein alone or as part of another group, refers to a straight or branched chain hydrocarbon containing from 1 to 10 carbon atoms. Representative examples of alkyl include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, 3-methylhexyl, 2,2-dimethylpentyl, 2,3-dimethylpentyl, n-heptyl, n-octyl, n-nonyl, n-decyl, and the like. "Loweralkyl" as used herein, is a subset of alkyl, in some embodiments preferred, and refers to a straight or branched chain hydrocarbon group containing from 1 to 4 carbon atoms. Representative examples of lower alkyl include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, and the like. Such groups can be unsubstituted or substituted with one or more (e.g., one, two, three, four, etc.) independently selected electron-donating or electron-withdrawing groups.

"Aryl" as used herein alone or as part of another group, refers to a monocyclic carbocyclic ring system or a bicyclic carbocyclic fused ring system having one or more aromatic rings. Representative examples of aryl include, azulenyl, indanyl, indenyl, naphthyl, phenyl, tetrahydronaphthyl, and the like. The term "aryl" is intended to include both substituted and unsubstituted aryl unless otherwise indicated and these groups may be substituted with the same groups as set forth in connection with alkyl and loweralkyl above. Such groups can be unsubstituted or substituted with one or more (e.g., one, two, three, four, etc.) independently selected electron-donating or electron-withdrawing groups.

"Arylalkyl" as used herein refers to an aryl group as described above, covalently coupled to an alkyl group as described above, which alkyl group is in turn coupled to the core molecule.

"Electron-withdrawing" and "electron-donating" refer to the ability of a substituent to withdraw or donate electrons relative to that of hydrogen if the hydrogen atom occupied the same position in the molecule. These terms are well understood by one skilled in the art and are discussed in Advanced Organic Chemistry, by J. March, John Wiley and Sons, New York, N.Y., pp. 16-18 (1985), incorporated herein by reference. Examples of such electron withdrawing and electron donating groups or substituents include, but are not limited to halo, nitro, cyano, carboxy, alkylcarboxy, loweralkenyl, loweralkynyl, loweralkanoyl (e.g.,

formyl), carboxyamido, aryl, quaternary ammonium, aryl (loweralkanoyl), carbalkoxy and the like; acyl, carboxy, alkanoyloxy, aryloxy, alkoxysulfonyl, aryloxysulfonyl, and the like; hydroxy, alkoxy or loweralkoxy (including methoxy, ethoxy and the like); loweralkyl; amino, alkylamino, lower alkylamino, di(loweralkyl)amino, aryloxy (such as phenoxy), mercapto, loweralkylthio, lower alkylmercapto, disulfide (loweralkyldithio) and the like; 1-piperidino, 1-piperazino, 1-pyrrolidino, acylamino, hydroxyl, thiolo, alkylthio, arylthio, aryloxy, alkyl, ester groups (e.g., alkylcarboxy, arylcarboxy, heterocyclocarboxy), azido, isothiocyanato, isocyanato, thiocyanato, cyanato, and the like. One skilled in the art will appreciate that the aforesaid substituents may have electron donating or electron withdrawing properties under different chemical conditions. *See, e.g.,* US Patent No. 8,933,065 to Kohn.

"Caping" as used herein refers to unintended polymerization of a photopolymerizable resin during additive manufacturing, particularly stereolithography, in regions for which no polymerization is intended, frequently leading to distortion of the object and rejection of that object.

1. RESINS.

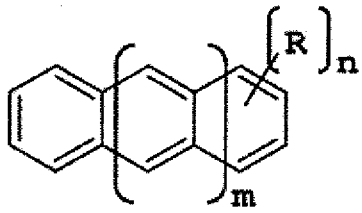
Any suitable light polymerizable stereolithography resin can be used in the present invention. Numerous examples are known, including but not limited to those set forth in US Patent Nos. 9,211,678; 9,205,601; and 9,216,546 to DeSimone et al.

In some embodiments, dual cure resins are preferred. Such dual cure resins are known and described in, for example, US Patent Nos. 9,676,963, 9,453,142 and 9,598,606 to Rolland et al.

In some embodiments, pigements and dyes, or other particles, can be included in the resins, such as where a light-transmissive but tinted object is desired, or where a reflective coating is to be applied to the object.

Light transmissive resins used in the present invention optionally, but in some embodiments preferably, include an ultraviolight light absorbing compound. While such compounds are known, currently preferred (for their ability to reduce "caping" during additive manufacturing) are polysubstituted linear polyacenes (*e.g.,* naphthalene, anthracene, tetracene, pentacene, hexacene). These compounds are polysubstituted with two or more of bromo, chloro, -Se-R', -S-R', or combinations thereof, where each R' is independently selected from alkyl, aryl, and arylalkyl.

More particularly, the light absorbing compounds can have a structure of **Formula I:**



(I)

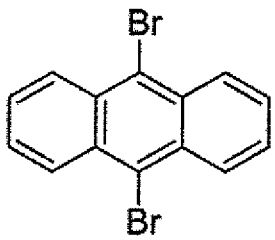
wherein:

m is 0, 1, 2, 3, 4 or 5;

n is from 2 to 4, 6 or 8; and

each R is independently selected from the group consisting of: bromo, chloro, -Se-R', and -S-R', where each R' is independently selected from alkyl, aryl, and arylalkyl. In some embodiments, bromo is preferred.

Examples of suitable compounds include, but are not limited to, 9,10-dibromoanthracene, 2,3,9,10-tetrabromoanthracene, and 5,11-dibromotetracene. A particular example has the structure:



2. METHODS.

Techniques for additive manufacturing are known. Suitable techniques include bottom-up and top-down additive manufacturing, generally known as stereolithography. 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 No. 2013/0292862 to Joyce, and US Patent Application Publication No. 2013/0295212 to Chen et al. The disclosures of these patents and applications are incorporated by reference herein in their entirety.

In some embodiments, stereolithography is carried out by Continuous Liquid Interface Production (CLIP). CLIP is known and described in, for example, US Patent Nos.

9,211,678; 9,205,601; and 9,216,546 to DeSimone et al.; and also in J. Tumbleston, D. Shirvanyants, N. Ermoshkin et al., Continuous liquid interface production of 3D Objects, *Science* 347, 1349-1352 (2015). *See also* R. Janusziewcz et al., Layerless fabrication with continuous liquid interface production, *Proc. Natl. Acad. Sci. USA* 113, 11703-11708 (2016). Other examples of methods and apparatus for carrying out particular embodiments of CLIP include, but are not limited to: Batchelder et al., US Patent Application Pub. No. US 2017/0129169; Sun and Lichkus, US Patent Application Pub. No. US 2016/0288376; Willis et al., US Patent Application Pub. No. US 2015/0360419; Lin et al., US Patent Application Pub. No. US 2015/0331402; D. Castanon, S Patent Application Pub. No. US 2017/0129167; B. Feller, US Pat App. Pub. No. US 2018/0243976 (published Aug 30, 2018); M. Panzer and J. Tumbleston, US Pat App Pub. No. US 2018/0126630 (published May 10, 2018); and K. Willis and B. Adzima, US Pat App Pub. No. US 2018/0290374 (Oct. 11, 2018).

Other approaches for carrying out CLIP that can be used in the present invention and potentially obviate the need for a semipermeable "window" or window structure include utilizing a liquid interface comprising an immiscible liquid (*see* L. Robeson et al., WO 2015/164234), generating oxygen as an inhibitor by electrolysis (*see* I. Craven et al., WO 2016/133759), and incorporating magnetically positionable particles to which the photoactivator is coupled into the polymerizable liquid (*see* J. Rolland, WO 2016/145182).

In one non-limiting embodiment, the object may be produced on a Carbon Inc. M1 or M2 additive manufacturing apparatus, available from Carbon, Inc., 1089 Mills Way, Redwood City, California 94063 USA.

After the object is formed by additive manufacturing, resin retained on the surface thereof is partially removed. This removal may be by any suitable technique, but spinning of the part sufficient to centrifugally separate some of the resin is preferred, and blowing the resin off with a compressed gas (*e.g.*, air, nitrogen, etc.), either manually or by passing the object under an air knife, is also preferred.

After partial separation of the resin, the remaining resin is further polymerized on the surface by exposure to light (*e.g.*, ultra-violet light) at an appropriate intensity and duration. Such exposure may be carried out by any suitable technique, such as by placing a batch of objects in a light box, passing the objects in a continuous fashion through a light tunnel, etc. In some embodiments, the light is at a longer UV wavelength with low absorbance of from 350 nm to 400 nm, such as 350 nm, 370 nm, 380 nm, 385 nm, 390 nm, etc.

In some embodiments (employing "dual cure" resins), the object is then further cured, such as by heating. Heating may be active heating (*e.g.*, baking in an oven, such as an

electric, gas, solar oven or microwave oven, or combination thereof), or passive heating (*e.g.*, at ambient (room) temperature). Active heating will generally be more rapid than passive heating and in some embodiments is preferred, but passive heating—such as simply maintaining the intermediate at ambient temperature for a sufficient time to effect further cure—may in some embodiments also be employed.

The present invention is further described in the following non-limiting examples.

EXAMPLES

Example objects made in accordance with methods of the present invention are shown in **FIG. 1 and FIG. 2**. These objects were produced from a light transmissive, amber-tinted, cyanate ester dual cure resin, available from Carbon Inc., 1089 Mills Way, Redwood City, California 94063 USA, in accordance with known procedures for such resins. *See, e.g.,* US 2019/0010343 to Menyo et al., which is incorporated by reference herein.

FIG. 1 shows a lens **11** mounted on a supporting frame **12** by an interconnecting frangible struts **13.** The frame **12** can be used to handle and secure the object during manufacturing steps such as separating and heating as described above, and then the lens separated from the frame by breaking struts **13.**

The embodiment of **FIG. 2** similarly shows a lens **21** produced in a frame **22**, and secured to the frame by struts **23,** but here the struts are not frangible, and the frame is intended as a fixture for both handling the lens during manufacture, and for securing the lens into the device in which it will reside. For this purpose the struts **23** are optional (for example, the lens can be connected directly to a full or partial circumferential frame), or can take any of a variety of forms, such as a peripheral "skirt" surrounding the lens and connecting the lens to the frame.

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.

What is claimed is:

1. A method of surface finishing an additively manufactured product, comprising:

(a) providing an object comprised of a polymer, said object produced by a process of additive manufacturing from a light polymerizable resin, said object having residual resin from which it was produced remaining on a surface portion thereof in unpolymerized form;

(b) partially removing said resin from said surface portion of the object under conditions in which a retained portion of said resin remains as a coating film on said surface portion; and then

(c) light polymerizing said retained resin to form a surface coating on said surface portion therefrom and surface finish said additively manufactured product.

2. The method of claim 1, wherein said resin comprises a dual cure resin and said method further comprises, after step (c), the step of:

(d) heating and/or microwave irradiating said object to further cure both said object and said coating.

3. The method of any preceding claim, wherein said partially removing step is carried out by spinning, blowing with a compressed gas, gravity draining, or a combination thereof.

4. The method of any preceding claim, wherein:

said object is produced with a support connected thereto; and

said partially removing step includes securing said object with said support.

5. The method of claim 4, wherein said support is a sacrificial support, and said method further comprises separating said object from said sacrificial support after said partially removing step, optionally (but in some embodiments preferably) after said light polymerizing step, and optionally (but in some embodiments preferably), after said heating and/or microwave irradiating step, when present.

6. The method of claim 5, wherein said sacrificial support comprises:

a frame; and

at least one, or a plurality, of struts interconnecting said object and said frame.

7. The method of any preceding claim, wherein said object of steps (a), (b) and (c) is unwashed.

8. The method of any preceding claim, wherein said retained portion of said resin is undiluted with solvent (e.g., not diluted with solvent during step (b)) during said light polymerizing of step (c).

9. The method of any preceding claim, wherein said object comprises:

(i) a lens, prism, mirror, light pipe, window, or combination thereof;

(ii) a dental aligner; or

(iii) a flexible or elastic lattice.

10. The method of any preceding claim, wherein said resin and said object are light transmissive.

11. The method of any preceding claim, wherein said surface portion is textured (*e.g.,* in a pattern or configuration that promotes the formation and/or retention of said coating film on said surface portion).

12. The method of any preceding claim, wherein said additively manufacturing is carried out by bottom-up or top-down stereolithography.

13. The method of any preceding claims, wherein said light polymerizing step (c) is carried out with UV light at a wavelength of from 350 nm to 400 nm (e.g., 350 nm, 370 nm, 380 nm, 385 nm, 390 nm, etc.).

14. A method of any preceding claim, said resin comprising:

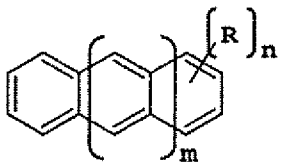
(i) light-polymerizable monomers, prepolymers, or a combination thereof (*e.g.,* in an amount of from 5 or 10 percent by weight to 80 or 90 percent by weight);

(ii) a photoinitiator (*e.g.,* in an amount of from 0.1 percent by weight to 4 percent by weight); and

(iii) a polysubstituted linear polyacene (e.g., anthracene) ultraviolet light absorbing compound that is polysubstituted with substituents independently selected from the group consisting of: bromo, chloro, -Se-R', and -S-R', where each R' is independently selected from alkyl, aryl, and arylalkyl (*e.g.,* in an amount of 0.01, 0.05 or 0.1 percent by weight to 1 or 5 percent by weight).

15. The method of claim 14, wherein said polyacene is selected from the group consisting of naphthalene, anthracene, tetracene, pentacene, and hexacene.

16. The method of claim 14, wherein said polysubstituted linear polyacene ultraviolet light absorbing compound has a structure of **Formula I:**



(I)

wherein:

m is 0, 1, 2, 3, 4 or 5;

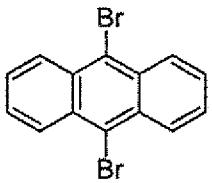
n is from 2 to 4, 6 or 8; and

each R is independently selected from the group consisting of: bromo, chloro, -Se-R', and -S-R', where each R' is independently selected from alkyl, aryl, and arylalkyl.

17. The method of claim 16, wherein each R is bromo.

18. The method of claim 16, wherein said compound of Formula I is selected from the group consisting of 9,10-dibromoanthracene, 2,3,9,10-tetrabromoanthracene, and 5,11-dibromotetracene.

19. The method of claim 16, wherein said compound of Formula I is:



20. The method of any one of claims 14 to 19, wherein said light-polymerizable monomers, prepolymers, or combination thereof are free-radical polymerizable.

21. The method of any preceding claim, wherein said resin further comprises a reactive diluent (*e.g.*, in an amount of 1 or 2 percent by weight to 30 or 40 percent by weight).

22. The method of any preceding claim, wherein said resin comprises a dual cure resin.

23. The method of any preceding claim, wherein said resin has a light absorption coefficient, alpha, of from 0.0005 or 0.001, to 0.01 or 0.05.

24. The method of any preceding claim, wherein said object is rigid, flexible, or elastic.

25. An object produced by a method of any preceding claim.

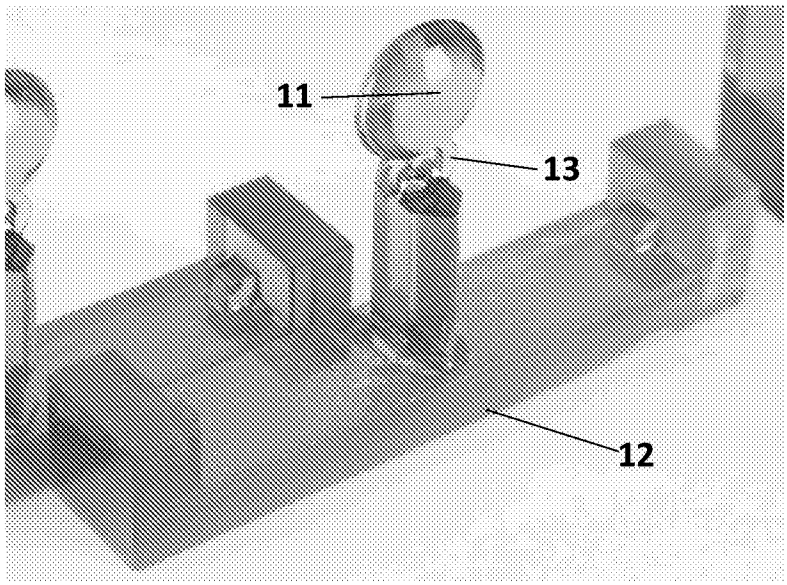


FIG. 1

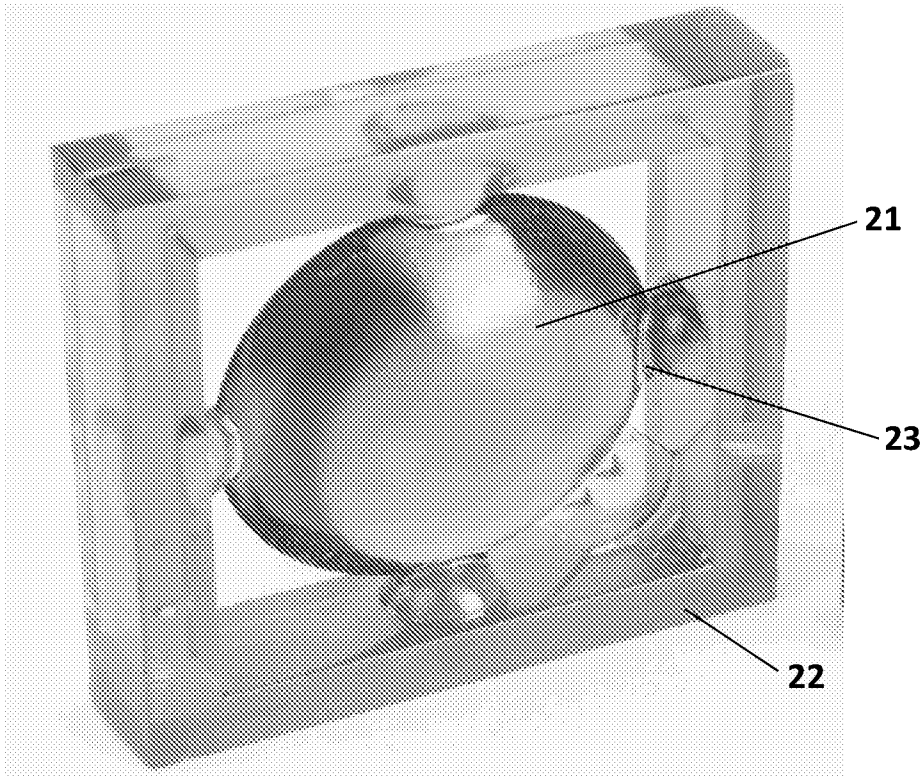


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/058709

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29C64/124 B29C64/30 B29C71/04 B33Y10/00 B33Y40/20
B33Y80/00 B29C64/40
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.
X Y	US 2003/068584 A1 (FARNWORTH WARREN M [US] ET AL) 10 April 2003 (2003-04-10) paragraphs [0003], [0013], [0017], [0064], [0065]; figures 1, 7	1,3,7,8, 11-13,25 2,9,10, 22,24
Y	US 2017/174827 A1 (GU XINYU [US] ET AL) 22 June 2017 (2017-06-22) paragraphs [0007] - [0011]	2,22
Y	US 2015/102532 A1 (DESIMONE JOSEPH M [US] ET AL) 16 April 2015 (2015-04-16) paragraph [0069]; figure 21	9,10,24

☐ 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	Date of mailing of the international search report
28 January 2020	25/03/2020

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

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/058709

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.:

1-3, 7-13, 22, 24, 25

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: 1-3, 7-13, 22, 24, 25

methods and products comprising:
- resin comprises a dual cure resin and said method further comprises, after step (c), the step of heating and/or microwave irradiating said object to further cure both said object and said coating;
- partially removing step is carried out by spinning, blowing with a compressed gas, gravity draining, or a combination thereof;
- the object is unwashed before the surface finish step;
- the resin is undiluted with solvent;
- a lens, prism, mirror, light pipe, window, or combination thereof, or a dental aligner, or a flexible or elastic lattice;
- the resin and the object are light transmissive;
- the surface portion is textured;
- additively manufacturing is carried out by bottom-up or top-down stereolithograph;
- light polymerizing step is carried out with UV light at a wavelength of from 350 nm to 400 nm;
- the object is rigid, flexible, or elastic.

The problem solved by these features is how to perform the surface finish of an object manufactured by stereolithography;

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2. claims: 4-6

methods comprising:
- an object produced with a support connected thereto; and the partially removing step includes securing said object with said support;
- a support which is a sacrificial support, and separating said object from said sacrificial support after the partially removing step;
- a sacrificial support comprising: a frame; and at least one, or a plurality, of struts interconnecting the object and said frame.

The problem solved by these features is how to maintain the shape of the object during its manufacture and surface finish process;

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3. claims: 14-21, 23

methods comprising:
the chemical composition of the resin

The problem solved by these features is how to select the components of the resin to manufacture the object by stereolithography and achieve the desired surface finish;

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/058709

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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