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(54) Title: ADAPTIVE LIGHT SHEET FOR REDUCING OFF-TARGET PHOTOEXCITATION IN VOLUMETRIC PRINTING INCLUDING TWO WAVELENGTHS

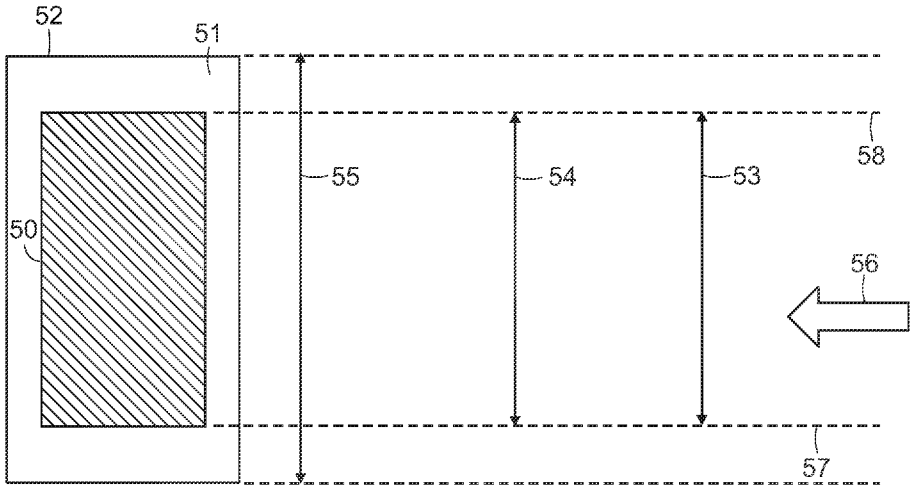

FIG. 5

(57) Abstract: The present invention includes methods for reducing photoexcitation of a photoswitchable photoinitiator in volumetric printing including a volume of a photohardenable composition at locations in the volume at which intersection of two wavelengths does not occur; methods of three-dimensional (3D) printing including dual-wavelength photoexcitation of a photohardenable composition included in a volume, the method including photoexcitation by a modified or controllably-sized light sheet including a first wavelength and an optical projection including a second wavelength; and methods for extending the reuse-printing lifetime of a photohardenable composition including a photoswitchable photoinitiator. Preferably the photohardenable composition includes the dual- wavelength photoinitiator and a photohardenable resin component. The present invention also includes a photohardenable composition including a photoswitchable photoinitiator with an improved reuse-printing lifetime.

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[Continued on next page]

MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

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Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US23/83218

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. B29C 64/171; B33Y 10/00; B33Y 70/00; B33Y 99/00; G03F 7/031; G03F 7/20 (2023.01)
ADD. C08F 2/50 (2023.01)

CPC - INV. B29C 64/171; B33Y 10/00; B33Y 70/00; B33Y 99/00; G03F 7/031; G03F 7/2051
ADD. C08F 2/50

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)
See Search History document

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

Electronic database consulted during the international search (name of database and, where practicable, search terms used)
See Search History document

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 2021/0162670 A1 (FORD GLOBAL TECHNOLOGIES, LLC) 03 June 2021; Fig. 2; Paragraphs: [0021-0073]	1-13, 29-42, 88-94, 99-101, 134-135 --- 14-28, 43-59, 95-98, 102-107, 136-140
Y	WO 2020/064779 A1 (STICHTING NEDERLANDSE WETENSCHAPPELIJK ONDERZOEK INSTITUTEN) 02 April 2020; Columns 11-18	14-26, 43-57, 95-98, 102-103, 106-107, 137, 138, 139/98, 139/137, 140/98, 140/137
Y	US 5,071,337 A (HELLER, T. ET AL.) 10 December 1991; Column 6	27-28, 58-59, 104-105
Y	CN 114031713 A (UNIV HUAZHONG SCIENCE TECH) 11 February 2022; Paragraphs: [0005-0009]	136, 139/136, 140/136
A	US 2022/0305723 A1 (XOLO GMBH) 29 September 2022; see entire document	1-59, 88-107, 134-140
A	US 2020/0361152 A1 (LAWRENCE LIVERMORE NATIONAL SECURITY, LLC ET AL.) 19 November 2020; see entire document	1-59, 88-107, 134-140

☐ 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
"D" document cited by the applicant in the international application
"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
01 May 2024 (01.05.2024)	MAY 31 2024
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US23/83218

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.: 141
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:
-***-Please See Supplemental Page-***-

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 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.:
1-59, 88-107, 134-140

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.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US23/83218

-***-Continued From Box No. III: Observations where unity of invention is lacking-***-

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fee must be paid.

Group I: Claims 1-59, 88-107, and 134-140 are directed toward a method of three-dimensional (3D) printing.
Group II: Claims 60-87, 108-136, and 139-140 are directed toward a method of volumetric printing with reduced photoexcitation of a photoswitchable photoinitiator included in the printing volume.

The special technical features of Group I include at least wherein the light sheet is modified in one or more regions to reduce regions of the volume exposed only to first excitation light thereby reducing photoexcitation of the photoswitchable photoinitiator in the photohardenable composition.

The special technical features of Group II include at least projecting an optical image generated with the second excitation light along a projection axis to a selected location in the volume, wherein the optical image is oriented perpendicular to the projection axis, wherein the optical image is oriented perpendicular to the projection axis.

The common technical features shared by Groups I & II are exposing a volume of a photohardenable composition including a photoswitchable photoinitiator and a photohardenable resin component to a projected optical image created by second excitation light and a light sheet generated with first excitation light such that the optical image and light sheet intersect, preferably in a common plane, at a selected location in the volume to induce polymerization or cross-linking of the composition at the selected location; wherein the height dimension of the light sheet that is directed into the volume along the light sheet illumination axis is controlled such that height dimension of the light sheet is less than the height dimension of the volume of the photohardenable composition through which it is directed and greater than or equal to the height dimension of the projected optical image in the volume in the selected plane, and wherein the light sheet at least fully overlaps the projected optical image in the volume in the selected plane. However, these common features are previously disclosed by US 2020/0361152 A1 to Lawrence Livermore National Security, LLC et al. (hereinafter "LLNS"). LLNS discloses exposing a volume of a photohardenable composition including a photoswitchable photoinitiator and a photohardenable resin component to a projected optical image created by second excitation light and a light sheet generated with first excitation light such that the optical image and light sheet intersect, preferably in a common plane (photocuring photosensitive resins; [0021]), at a selected location in the volume to induce polymerization or cross-linking of the composition at the selected location (forming a solid polymeric material; [0021]); wherein the height dimension of the light sheet that is directed into the volume along the light sheet illumination axis is controlled such that height dimension of the light sheet is less than the height dimension of the volume of the photohardenable composition through which it is directed and greater than or equal to the height dimension of the projected optical image in the volume in the selected plane, and wherein the light sheet at least fully overlaps the projected optical image in the volume in the selected plane (cross-linking by imaging from light curing radiation at a desired depth (height) to form an object in a containment vessel which would have a greater height than the object; Fig. 2; [0063-0064] & [0073-007]).

Since the common technical features are previously disclosed by the LLNS reference, these common features are not special and so Groups I-II lack unity.