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(54) Title: FORMULATION FOR 3D PRINTING AND A 3D PRINTED ARTICLE

(57) Abstract: A flowable liquid formulation for 3D printing is described. The formulation comprises from 0.1 to 25wt.% radiopaque particles, wherein at least 50% by weight of the particles have a diameter of at most 100 nm. The formulation further comprises monomeric, oligomeric and/or polymeric precursors adapted for polymerization to form a solidified article. Also described is an article (100) formed by 3D printing, the article (100) comprising a first 3D printed region (110) having a first radiopacity and a second 3D printed region (120) having a second radiopacity, wherein the first radiopacity is greater than the second radiopacity. Also described is a method of forming the article (100).

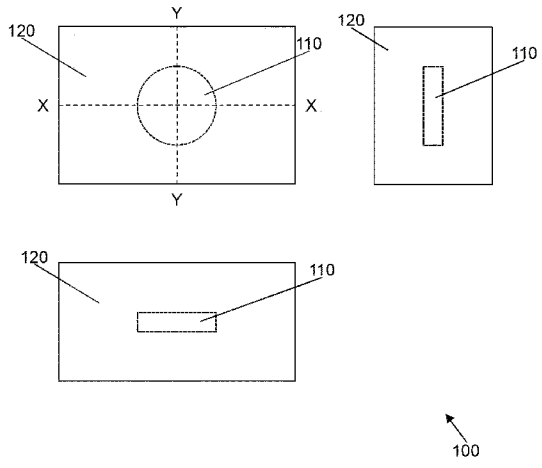

Fig. 1

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[Continued on next page]

Declarations under Rule 4.17:

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

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/EP2018/073748

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/22 G03F7/00 B33Y70/00 B29C64/106 B33Y10/00
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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)
C08K G03F B33Y B29C

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 508 834 A2 (3D SYSTEMS INC [US]) 23 February 2005 (2005-02-23)	1-7
A	paragraphs [0001], [0035], [0036], [0082] example 2 claims	12-16

X	US 2010/041789 A1 (NEFFGEN STEPHAN [DE] ET AL) 18 February 2010 (2010-02-18)	1-7
A	paragraphs [0011] - [0017], [0045], [0050] - [0054], [0131], [0142], [0143] table 1	12-16

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

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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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	Behm, Sonja

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2018/073748

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.:

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.

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/064573 A2 (3M INNOVATIVE PROPERTIES CO [US]; SHUKLA BRIAN A [US]; CRAIG BRADLEY D) 18 May 2012 (2012-05-18)	1-7
A	table 2 examples page 6, lines 9-15	12-16

X	US 2016/113846 A1 (WILLNER ALEXANDER [DE] ET AL) 28 April 2016 (2016-04-28)	1-7
A	paragraphs [0259], [0260], [0352] - [0371] table 1	12-16

X	WO 2015/165363 A1 (CHINESE ACAD INST CHEMISTRY [CN]) 5 November 2015 (2015-11-05)	1-7
A	examples	12-16

X	HSIN-TA WANG ET AL: "In Vitro Biocompatibility, Radiopacity, and Physical Property Tests of Nano-Fe3O4 Incorporated Poly-l-lactide Bone Screws", POLYMERS, vol. 9, no. 12, 26 May 2017 (2017-05-26), page 191, XP055531928, DOI: 10.3390/polym9060191	14-16
A	abstract page 2, paragraph 2 page 3, paragraph 2.3	1-7,12, 13

X	EP 3 162 469 A1 (GEN ELECTRIC [US]) 3 May 2017 (2017-05-03)	8-11
A	paragraphs [0023] - [0024] claims 8, 19	1-7, 12-16

X	WO 2014/039825 A2 (MAKERBOT IND LLC [US]) 13 March 2014 (2014-03-13)	8-11
A	paragraphs [0117] - [0125] figure 14	1-7, 12-16

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

1. claims: 1-7, 12-16

- A flowable liquid formulation for 3D printing comprising: from 0.1 to 25 wt.% radiopaque particles, wherein at least 50% of the particles have a diameter of at most 100 nm; and monomeric, oligomeric and/or polymeric precursors adapted for polymerization to form a solidified article,
- A method of forming an article by 3D printing comprising: printing a first 3D printed region having a first radiopacity from a first polymerizable formulation; printing a second 3D printed region having a second radiopacity from a second polymerizable formulation, wherein the first radiopacity is greater than the second radiopacity; polymerizing the first polymerizable formulation and the second polymerizable formulation; wherein the first formulation is as defined above and
- Use of a flowable liquid formulation comprising from 0.1 to 25 wt.% radiopaque particles, wherein at least 50% of the particles have a diameter of at most 100 nm, to provide a first 3D printed region of a 3D printed article having a radiopacity of at least 400 HU.

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2. claims: 8-11

- An article formed by 3D printing, the article comprising a first 3D printed region having a first radiopacity and a second 3D printed region having a second radiopacity, wherein the first radiopacity is greater than the second radiopacity, preferably by at least 5 Hounsfield Units (HU).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/073748

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1508834 A2	23-02-2005	EP 1508834 A2	23-02-2005
		JP 3971412 B2	05-09-2007
		JP 2005060673 A	10-03-2005
		JP 2007290391 A	08-11-2007
		US 2005040562 A1	24-02-2005
		US 2006267252 A1	30-11-2006
US 2010041789 A1	18-02-2010	EP 2153812 A1	17-02-2010
		EP 2548546 A1	23-01-2013
		US 2010041789 A1	18-02-2010
WO 2012064573 A2	18-05-2012	EP 2637629 A2	18-09-2013
		JP 5956453 B2	27-07-2016
		JP 2014502294 A	30-01-2014
		US 2013224692 A1	29-08-2013
		WO 2012064573 A2	18-05-2012
US 2016113846 A1	28-04-2016	CA 2910018 A1	23-04-2016
		DE 102015220373 A1	28-04-2016
		EP 3011949 A1	27-04-2016
		US 2016113846 A1	28-04-2016
WO 2015165363 A1	05-11-2015	US 2017253681 A1	07-09-2017
		WO 2015165363 A1	05-11-2015
EP 3162469 A1	03-05-2017	CA 2945096 A1	20-04-2017
		CN 107030849 A	11-08-2017
		EP 3162469 A1	03-05-2017
		JP 6371356 B2	08-08-2018
		JP 2017078511 A	27-04-2017
		US 2017106587 A1	20-04-2017
WO 2014039825 A2	13-03-2014	EP 2892703 A2	15-07-2015
		US 2014070461 A1	13-03-2014
		US 2014074274 A1	13-03-2014
		US 2016039151 A1	11-02-2016
		WO 2014039825 A2	13-03-2014