

Solvent recovery and waste isolation from additive manufactured object cleaning

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Clean 3D printed object (2) C) 22b Reuse neutralized waste solution (12) 20a 8) 106 22a Obtain waste solution (6) eparated activati of ink residuals 1) 3) 20h 23a 200 Collect waste solution (6) 2) 23t 100 Generate precipitate (14) 4) solution WO 2020/144156 A1 21b 10d 20d -use waste Separate precipitate (14) 210 5) Re-Collect decon solvent (16) 21d 6) 24b 21a Reuse decon solvent (16) 7) X) Discard neutralized waste solution (12) 20 20 Fig. 2

(54) Title: SOLVENT RECOVERY AND WASTE ISOLATION FROM ADDITIVE MANUFACTURED OBJECT CLEANING

(57) Abstract: Systems and methods for neutralizing, and preferably reusing, cleaning solvents (3) for cleaning 3D printed objects (2), wherein at least a part of a residual 3D printing ink comprised in the cleaning solvent (3) can be neutralized by a procedure of residual ink activation, preferably activated and neutralized by poly¬ merization and subsequent precipitation removal before solvent reuse or disposal. Further, the present invention relates to the safe disposal of residual activatable solidifiable inks for 3D printing, in particular in relation to the safe disposal of resid¬ ual activatable solidifiable inks for 3D printing photoactivatable mono- and/or oligomers.

TITLE OF INVENTION

Solvent recovery and waste isolation from additive manufactured object cleaning

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TECHNICAL FIELD

In the field of additive manufactured object cleaning there is proposed a method of solvent recovery and waste isolation for the reduction of the environmental impact of additive manufacturing of objects.

BACKGROUND

15 Additive manufacturing of objects or 3D printing has seen rapid growth over the last two decades and now is a matured technique for manufacturing of objects for prototyping and for serial production of objects of unusual geometry, which does not easily allow for classical top-down object 20 manufacturing, such as e.g. casting, molding or milling. In 3D printing, objects are manufactured in a bottom-up printing process by adding solidifiable material to the formed object sequentially produced layers, while concurrently in solidifying the object, until a solidified final shape of the object to be printed is formed. This is in contrast to 25 top-down printing processes such as e.g. micropatterning or photolithography, wherein objects to be printed are formed as single objects. Common advantages of the bottom-up approach are e.g. increases to complexity of object 30 morphology, rapid prototyping and/or individualization of printed objects.

During the process of 3D printing substantial amounts of waste solidifiable material is generated, both in the form

of unused material, but also in the form of unsolidified material ejected during the manufacturing process or retained on the surfaces of the solidified object or the printing equipment after the manufacturing process.

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Many of the solidifiable materials suitable for 3D printing, colloquially called inks, and comprising e.g. activatable mono- and oligomers, are environmentally problematic and must be disposed of as dangerous chemicals at designated disposal facilities and at significant costs.

The present invention relates to the safe disposal of such residual solidifiable materials for 3D printing, in the safe disposal of such particular for residual 15 solidifiable materials for 3D printing comprising activatable mono- and/or oligomers, in particular comprising photoactive mono- and/or oligomers. Throughout the present disclosure such solidifiable materials for 3D printing may colloquially be termed inks or 3D printing inks and residual solidifiable materials may colloquially be termed residual 20 ink or ink residuals.

In general, solidifiable materials for 3D printing comprise not only solidifiable components in the form of activatable 25 mono and/or oligomers, particularly photoactive mono and/or oligomers, but also comprise numerous further components such as e.g. colors, e.g. in the form of pigments, colored particulates, and/or colorants, co-polymers, solvents and surfactants, or initiators and/or catalysts may be present 30 in the 3D printing inks for enhanced polymerization of the printing ink.

The present invention is not concerned with 3D printing inks, which cannot be dissolved in a solvent, preferably a solvent

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comprising at least one organic solvent suitable for dissolving a mono and/or an oligomer suitable for use as a solidifiable reactant in a 3D printing and solidification process. Such inks not included in the present invention typically comprise meltable and/or hardenable polymer pastes and plastics, which are added to the object during printing in molten/fluid drops and subsequently allowed to harden in place. Rather, the present invention is concerned with solvent based 3D printing inks, preferably solvent based

To reduce the problem of rising cost and to minimize the problem of waste generation from solvent based 3D printing inks there has been increased interest in obtaining suitable 15 solutions to the disposal problem. In general, as many inks are susceptive to photo-initiation, it is possible to posttreat unreacted and concentrated solidifiable, solvent based 3D printing inks of the type contemplated in the present invention and thereby passivate these materials. WΟ 2017/009833 e.g. details a method and a system, wherein 20 unreacted and concentrated waste solidifiable, solvent based photoactive 3D printing material is collected and subjected to a subsequent, photo-initiated, passivation and polymerization process, whereby a disposable plastics material is formed. 25

A different problem of waste disposal related to the 3D printing process compared to the problem solved in WO 2017/009833, but potentially of much larger consequence, relates to unsolidified printing material retained on the surfaces of 3D printed objects after printing and/or on the surfaces of the printing equipment.

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To remove the retained 3D printing ink from the formed object after 3D printing, thorough washing of the object is necessary. If this is not done, the object is neither safe to handle after printing nor can post-curing treatments be applied without compromising the shape of the printed object. However, current washing methods generate significant amounts of washing solvent contaminated with 3D printing ink residuals. Additionally, clean-up of the printing equipment is a significant source of waste solvents comprising residual inks for 3D printing a 3D printed object.

In Fig. 1 is schematically detailed the current standard procedure (10) for cleaning a 3D printed object (2) comprising in a cleaning step C) immersing the object (2) in 15 a cleaning solvent (3) comprised in a container (4) and submitting the object (2) and the solvent (3) to mechanical agitation thereby obtaining 1) a waste solution (6) comprising dissolved and/or dispersed residuals of any such inks for 3D printing the 3D printed object (2) as were used during the 3D printing process. Typically, the cleaning 20 solvent (3) is kept in a solvent reservoir (7) for a cleaning solvent prior to use. In the figure solid arrows (10a-10c) indicate the process flow direction for necessary process steps of the cleaning procedure (10), with dotted arrows 25 (10d-e) indicating the process flow direction оf an alternative of the procedure (10), which can be optionally implemented, as detailed below. An initial waste solution (6) is obtained as soon as the cleaning step C) is initiated, but in the prior art the obtained waste solution (6) is generally an equilibrium solution obtained after a batch 30 step C). The method (20) of the present cleaning in invention, as will be detailed, is however functional as soon as at least some waste solution (6) has been generated, whereby the method (20) of the invention can be implemented

both for batch cleaning in step C) as well as for in-flow cleaning, more suitable for mass production.

- Typically, mechanical agitation comprises such methods as shaking, solvent flushing, pulsed vacuum, sonication, or most 5 preferred ultrasonication, typically using an agitation station (1) comprising a container (4) for the cleaning solvent (3) and mechanical agitation means (5). The mechanical agitation means (5) usually are selected from amongst a number of common mechanical agitation means, but 10 most commonly used are shaking means for shaking the container comprising the cleaning solvent (3) and the 3D printed object (2); flushing means for flushing cleaning solvent (3) past, preferred rapidly past, the 3D printed object (2), e.g. by using a circulation pump or stirring the 15 solvent comprised in the container; pulsed vacuum means, sonication means and/or most preferred ultrasonication means .
- 20 After mechanical agitation, the solvent (3) now comprises part or all of the residual ink, which remained on the surface of the 3D printed object (2) from the 3D printing process, thus forming a waste solution (6), upon which 2) the waste solution (6) is collected and X) discarded, preferably by 25 disposal as a dangerous chemical substance.

Sometimes, however, the waste solution (6) can be reused if it is not too contaminated, seldom more than 3 to 4 times, or a sequence of decreasingly contaminated waste solutions 30 can be used for cleaning the 3D printed object (2). A system currently in use for exposing a 3D printed object (2) to a series of decreasingly contaminated cleaning solvents is detailed in CH7060157B1, wherein the object (2) to be cleaned is contained in an ultrasonication chamber, and sequentially

exposed to ultrasonication in decreasingly contaminated cleaning solvents (3). Eventually, after a number of uses, the most contaminated cleaning solvent (3) is 2) collected as a waste solution (6), typically in a waste reservoir (8) for a waste solution, and X) disposed of as a dangerous chemical substance.

In WO 2009/140449 there is detailed a method of cleaning a 3D printed object using solvent flushing in a dish-washer type apparatus. The apparatus comprises an actinic radiation source for post-cleaning curing of the cleaned 3D-printed object. At least one pump allows the cleaning solvent to circulate the dish-water type apparatus on a closed-loop circulation flow path comprising a filter for filtering out any particulate material removed from the 3D printed object during cleaning. After cleaning, the 3D printed object may be subjected to post-curing by irradiation.

It is disclosed in WO 2009/140449 that while post-curing takes place, a secondary circulation pump for cleaning fluid 20 may be active, for placing the cleaning liquid on the bottom of apparatus, whereby it may absorb some radiation during post-curing partly allowing particles of build material to become activated and to react, which reacted particles can subsequently be filtered from the cleaning fluid by the 25 comprised filter. A draw-back to the setup disclosed in WO 2009/140449 is the use of irradiation activation in an atmosphere comprising flammable organic solvents аt saturation and oxygen. Further, the desired post-activation of residual particles of build material is only partial as 30 the cleaning liquid will at least partially be in the shadow of the 3D-printed object to be cured during irradiation.

In particular, WO 2009/140449 discloses use of an agitation means and an irradiation means built into the same cleaning station. The cleaning station of WO 2009/140449 defines a large cleaning space, which comprises not just the agitation means and also comprises means for holding and rotating the 5 3D printed object to be cleaned, while the irradiation means are arranged to irradiate the entire cleaning space. Waste solvent comprising residual ink particles to be activated in WO 2009/140449 covers only the bottom of cleaning space and therefore, as the cleaning station in WO 2009/140449 is for 10 simple organic solvents that evaporates easily, waste solvent is lost to the atmosphere inside the cleaning space of the cleaning station of WO 2009/140449 and is mixed with any present oxygen (atmospheric levels) . Apart from solvent loss 15 due to evaporation and increased pollution therefrom, the mixed atmosphere comprising oxygen and organic vapors in the presence of an irradiation source constitutes a safety risk.

As the manner in which cleaning of 3D printed objects is 20 currently effectuated generates significant amounts of waste solutions, which must be disposed of in expensive procedures at designated disposal plants, there is currently a need for methods and systems for neutralizing waste solutions obtained by the cleaning of 3D printed objects but also, and in 25 particular, for decontaminating the waste solutions and for increasing the reusability of the cleaning solvents for use in cleaning of 3D printed objects and/or printing equipment, whereby solvent use can be reduced and cost efficiency obtained.

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The present inventors accordingly suggest systems and methods for reusing cleaning solvents, wherein at least a part of the comprised residual 3D printing ink is activated and neutralized, preferably polymerized and subsequently removed

before solvent reuse by subjecting the waste solution to a procedure of residual ink activation for obtaining a neutralized waste solution spatially separated from the 3Dprinted object. However, as will be detailed herein, the

5 methods and systems of the current invention are also suitable for use with other 3D printing systems, e.g. with cell-printers for biological 3D printing in aqueous solutions .

10 SUMMARY OF THE INVENTION

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In a first aspect and embodiment of the invention there is disclosed a method (20) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), the method comprising:

- obtaining a waste solution (6) comprising residuals of at least one ink for 3D printing a 3D printed object
 (2) dissolved and/or dispersed in at least one cleaning solvent (3) from a procedure (10) of cleaning said 3D printed object (2) in said cleaning solvent (3);
- 3) subjecting said waste solution (6) to a procedure of residual ink activation in an activation space (132) arranged for preventing, during residual ink activation, evaporation of the waste solution (6) and access of oxygen, for obtaining a neutralized waste solution (12).

In one embodiment of the present invention there is disclosed herein a method (30) of neutralizing and decontaminating a 30 waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), the method comprising:

> obtaining a waste solution (6) comprising residuals of at least one ink for 3D printing a 3D printed object
> (2) dissolved and/or dispersed in at least one cleaning

solvent (3) from a process of cleaning said 3D printed object (2) in said cleaning solvent (3);

2) optionally, collecting said waste solution (6);

- 3) subjecting said waste solution (6) to a procedure of residual ink activation in an activation space (132) arranged for preventing, during residual ink activation, evaporation of the waste solution (6) and access of oxygen, thereby generating activated ink residuals for forming a waste precipitate (14) comprising inactivated residual ink;
 - 4) generating said waste precipitate (14) comprising inactivated residual ink;
 - 5) separating said waste precipitate (14) from said waste solution (6) thereby obtaining a decontaminated solvent (16) as a product of said separation;

 - 7) reusing said decontaminated solvent (16) as a cleaning solvent (3) for cleaning a 3D printed object (2).

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In a second aspect and embodiment of the invention there is herein disclosed a system (40) for implementing a method (20,30) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), the system comprising an agitation station (1), defining an 25 (40) agitation space (102) for comprising a 3D printed object (2) to be cleaned in a cleaning solvent (3), an activation station (13) for executing a procedure of residual ink activation for obtaining a neutralized waste solution (12), 30 the activation station (13) defining an activation space (132) for comprising the waste solution (6) during residual ink activation within the activation space (132), thereby preventing evaporation of said waste solution (6) and access of oxygen, and a waste reservoir (8) for a neutralized waste

solution (12), sequentially arranged on a waste solution flowpath (43a-c); pumping means (17); and a controller for executing a method (20,30) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3) according to any of the embodiments of the first aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

- 10 Fig. 1: Prior Art disposal of waste solutions from cleaning
 3D printed object in a solvent.
 - Fig. 2: Flowchart of the method according to the invention.
 - Fig. 3: Experimental confirmation of working principle.
 - **Fig. 4:** System for implementing a first aspect of the invention .
 - Fig. 5: Simple setup comprising recycling for experimental confirmation of working principle.

DETAILED DESCRIPTION

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In accordance with the aspects and embodiments of the present invention as detailed herein, the present invention relates to systems and methods for neutralizing, and preferably reusing, cleaning solvents (3) for cleaning 3D printed objects (2), wherein at least a part of a residual 3D printing 25 ink comprised in the cleaning solvent (3) can be neutralized by a procedure of residual ink activation, preferably activated and neutralized by polymerization and subsequent precipitation removal before solvent reuse or disposal. Further, the present invention relates to the safe disposal 30 of residual activatable solidifiable inks for 3D printing, in particular in relation to the safe disposal of residual activatable solidifiable inks for 3D printing comprising

activatable mono- and/or oligomers, in particular comprising photoactivatable mono- and/or oligomers.

The herein presented method of neutralizing (20) a waste solution (6) comprising at least one cleaning solvent (3) 5 for cleaning a 3D printed object (2) of the invention is for a waste solution (6) obtained from a procedure (10) for cleaning a 3D printed object (2) in at least one cleaning solvent (3), the method (20) obtaining as its end result either neutralized waste solution (12), which can 10 be discarded at lowered costs and risks, or cleaned or decontaminated solvent (16), which can be reused in procedures for cleaning a 3D printed object (2) in at least one cleaning solvent (3), the reusable decontaminated solvent 15 (16) hereby substituting for unused cleaning solvent (3).

Throughout the present disclosure there is mentioned, and made use of, the terms neutralization, neutralizing, methods of neutralizing, and/or neutralized waste solution for describing elements of the invention. Collectively these 20 terms are used to describe the outcome of, and the products of the outcome of, the methods of the invention, wherein neutralization is intended to be understood in common meaning in science as being rendered neutral, e.g. by inactivation, with respect to an unwanted outcome, such as e.g. further 25 reactions of remaining active species in the waste solutions produced in 3D printing. The resulting waste solutions of the invention are not, per se, purified as an end result of applying the methods of the invention. Rather the degree of 30 contamination of the waste solution is decreased by neutralization of the waste comprised in the waste solution, e.g. by inactivation of reactive species, and in some embodiments also by removal of neutralized waste from the waste solutions. For purification of the cleaned waste

solutions of the invention, further process steps of solvent purification are necessary. Such further process steps of solvent purification are generally known in the art of purifying solvent and can be applied by the skilled person if purification is subsequently intended after waste solution neutralization .

Per se, the present method (20) is suitable for application with other contaminated solvents obtained through other 10 processes and comprising activatable materials, which can be neutralized or, preferably, neutralized and precipitated. However, these applications fall outside the scope of the present invention, as end-results for the decontaminated solvent (16) will differ and the main advantage of the 15 present methods, i.e. reusability of the decontaminated solvent (16) as a cleaning solvent (3) for cleaning a 3D printed object (2), of the invention will not be obtained if contaminated solvents are used, which are not suitable for use in cleaning a 3D printed object (2).

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primarily concerned The present invention is with neutralization of organic solvents comprising residual ink for reuse in a cleaning procedure for a 3D printed object (2) . This reflects the current standards of 3D printing inks, which use carbon based substances and components, which can 25 be removed from 3D printed objects (2) by cleaning using cleaning solvents (3) such as, preferably, isopropanol; or isopropanol comprising other organic solvents for enhanced cleaning of ink components not directly dissolvable or 30 dispersible in isopropanol. Herein isopropanol or 2-propanol is preferably used over the systematic IUPAC name propan-2ol.

Typically, ethanol can be a component, sometimes even substituting isopropanol, whereas other organic solvents are usually not used due to the associated higher toxic risks. Nevertheless, such other organic solvents having higher toxic risks than isopropanol and/or ethanol may be present in small amounts for enhancing cleaning efficacy for one or more components comprised in the printing inks. Also, some cleaning solutions may comprise small amounts of surface active components, however, where surface active components have been used, it is common to cleanse the 3D printed object in two steps, the first step using the composition (2) comprising the surfactant, and the second step using a composition without surfactants for also removing residuals of surfactant.

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The present methods (20) are not per se concerned with the composition of the cleaning solvents (3) prior to cleaning a 3D printed object (2) as long as the resulting waste solution (6) obtained from the cleaning procedure (10) involving the 20 cleaning solvent (3) results in a waste solution (6) which can be activated and, preferred, upon activation generate a waste precipitate (14) which can be separated from the waste solution (6) in sufficient amounts, such that a neutralized cleaning solvent (12) or, preferred, a neutralized and 25 decontaminated, and most preferably reusable, decontaminated solvent (16) can be generated after applying the methods (20) of the present invention on the obtained waste solution (6) .

A separate issue is the use of aqueous solutions for 3D 30 printing of biological material. It is a surprising advantage of the present methods (20) that they are suitable for use with biological materials as will be detailed below, and that hence the cleaning solvent (3) may be water, and that the resulting waste solution (6) may be an aqueous solution.

However, due to biological purity requirements, e.g. for sterilization, it is generally not recommended to reuse the decontaminated aqueous solvent (16). Nevertheless, due to the neutralization and/or decontamination process employed according to the invention, disposal costs for the aqueous solutions will be reduced.

Accordingly, in the aspects and embodiments of the present method (20), the cleaning solvent (3) can be any cleaning 10 solvent (3) suitable for use in a cleaning procedure for cleaning a 3D printed object (2). In a preferred embodiment thereof, the cleaning solvent (3) can be any cleaning solvent (3) suitable for use in a cleaning procedure (10) for cleaning a 3D printed object (2), which cleaning procedure 15 comprises submerging the 3D printed object (2) in the cleaning solvent (3) and applying mechanical agitation, preferably using mechanical agitation means as defined herein.

- 20 In a further, and even more preferred embodiment of the above embodiments of the cleaning solvent (3), the cleaning solvent (3) is either water or an organic solvent comprising 2 or 3 carbon atoms or mixtures thereof.
- 25 When the cleaning solvent (3) is an organic solvent comprising 2 or 3 carbon atoms, most suitable options for low toxicity comprise ethanol, acetone, 1-propanol, isopropanol (2-propanol), or mixtures thereof, with ethanol or isopropanol being more preferred, and most preferred being 30 isopropanol (2-propanol).

As mentioned, the cleaning solvent (3) may comprise at least one solvent (3) as main component selected as detailed above in mixture with at least one further solvent, selected as

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detailed above, in smaller amounts. In some embodiments, the at least one further solvent is present in an amount below 50% w/w of total solvent, preferably present in an amount below 40% w/w of total solvent, below 30% w/w of total solvent, below 20% w/w of total solvent, below 10% w/w of total solvent, or even more preferably below 5% w/w of total solvent. If two or more further solvents are present, the sum of their total mass is present to below 50% w/w of total solvent, preferably present in an amount below 40% w/w of total solvent, below 30% w/w of total solvent, below 20% w/w of total solvent, below 10% w/w of total solvent, or even more preferably to below 5% w/w of total solvent.

Contrary to the prior art in WO 2017/009833, which concerns direct polymerization of surplus ink, the present invention 15 relates to processes occurring in a solvent downstream of the finished 3D printed object (2), usually in dilution. The present invention builds on the surprising realization by the present inventors that the by-weight concentration of residual activatable solidifiable inks in the cleaning 20 solvents (3) commonly used for cleaning after 3D printing, in some circumstances can be sufficiently high, despite the dilution due to the cleaning process, for subsequent in activation and neutralization, solvent preferably neutralization by precipitation of at least a part of the 25 residual ink components dissolved and/or dispersed in cleaning solvents (3) used for cleaning a 3D printed object (2).

30 Accordingly, and in the broadest aspect of the present invention, there is disclosed: A method (20) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), the method comprising:

WO 2020/144156

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- obtaining a waste solution (6) comprising residuals of at least one ink for 3D printing a 3D printed object
 (2) dissolved and/or dispersed in at least one cleaning solvent (3) from a procedure (10) for cleaning a 3D printed object (2) in a cleaning solvent (3);
- 3) subjecting the waste solution (6) to a procedure of residual ink activation in an activation space (132) arranged for preventing, during residual ink activation, evaporation of the waste solution (6) and access of oxygen, for obtaining a neutralized waste solution (12).

The method (20) according to the broadest aspect of the present invention is schematically represented in the 15 flowchart of Fig. 2, showing the relation between all the embodiments of the present invention, c.f. Fig. 2, arrow 20b. Fig. 3, as will be further detailed in the Experimental Section, shows a simple experimental confirmation of the working principle of the present invention, wherein 20 activation in step 3) is performed using UV-light. The broadest aspect of the present invention according to the method (20), is visualized in Fig. 3A.

Contrary to WO 2009/140449, wherein agitation and activation of residual ink particles is done in a shared space, the present invention improves on the prior art by providing a separate activation space (132) arranged for preventing, during residual ink activation, evaporation of the waste solution (6) and access of oxygen. Thereby loss of waste 30 solution (6) to evaporation is prevented and safety risks due to oxygen mixed with flammable organic solvents in the presence of an irradiation source are eliminated. In the systems (40) implementing the methods (20) of the invention,

this is done by spatially separating the agitation station

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(1) from the activation station (13) and arranging these sequentially on a waste solution flowpath (43a-c). Thereby the activation space (132) comprising the waste solution (6) during residual ink activation can be arranged to prevent solvent evaporation and access of oxygen thereby overcoming the drawbacks of the prior art. Surprisingly, as detailed in the Experimental Section, the spatial separation of agitation and activation allows for increased neutralization of the waste solvent (6), allowing neutralization to comprise not just residual ink particles but also dissolved mono- and oligomers comprised in the waste solution (6). Another welcome benefit lies in a significant reduction in volume for the cleaning systems (40) of the invention compared to the cleaning system disclosed in WO 2009/140449, as will be

15 further detailed below.

As with the flowchart of Fig. 1, also for the flowchart detailed in Fig. 2 solid arrows (20a-20f) indicate the process flow direction for the preferred embodiments of the methods of the invention with dotted arrows (21a-24b) showing

- 20 the process flow direction of optional or less preferred embodiments, as will be detailed herein below. Thin, dotted arrows (loc-e) indicate elements of the prior art cleaning procedure (10) which can be independently implemented in the cleaning step c).
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As such, and in accordance with a preferred embodiment of the present invention, the step c) of cleaning a 3D printed object (2) in a cleaning solvent (3) is in accordance with the procedure (10) of the prior art as detailed in the present disclosure .

As can be seen, process steps C), 1), 2) and X) with the option of reusing the waste solution (6) for cleaning the 3D printed object (2) result in executing the prior art cleaning

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procedure (10) as detailed above. The present invention deviates from the prior art cleaning procedure (10) either after step 1), solid arrow (20b), in that it is, as mentioned, possible to initiate the method (20) of the invention, in its broadest aspect, as soon as the cleaning procedure (10) in step C) has been initiated. Normally, however, the method (20) of the invention will not be initiated until after termination of the cleaning procedure (10), implementing step 2) of optionally collecting the waste solution (6), dotted arrows (23a-b), and prior to activating the waste solution (6) in step 3).

In the context of the present invention suitable procedures of residual ink activation will vary dependent on the mode 15 of ink activation that was originally used for activating the inks during the additive manufacturing process. In general, a suitable procedure for activating a specific ink for additive manufacturing will also be a suitable procedure for activating residuals of the same ink. In the art in particular UV-activation is used, but also other types of 20 activation by photon irradiation, such as e.g. visible or IR-activation are known in the art and are suitable for use with the present invention, when a specific ink so demands. In the preferred embodiments of the present invention activation by photon irradiation is activation by UV-25 irradiation. In some situations also chemical ink activation can be advantageous, e.g. with biological systems and strongly absorbing inks, but chemical ink activation is generally less preferred to photon irradiation activation as 30 the addition of activation chemicals leads to buildup of further impurities in the cleaning solvent, thereby reducing the number of times that the neutralized solvents (12) can be recycled for cleaning a 3D printed object.

Accordingly, in an embodiment of the method (20) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), there is disclosed the method (20) further comprising: 2) collecting the waste solution (6) after obtaining the waste solution (6) and prior to subjecting the waste solution (6) to a procedure of residual ink activation for obtaining a neutralized waste

- solution (12).
- In a further embodiment of the method (20) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), there is disclosed the method (20) further comprising: 8) reusing the neutralized waste solution (12) in a procedure (10) for cleaning a 3D printed object 15 (2).

Eventually, after a number of reuses, the neutralized waste solution (12) becomes unusable as a cleaning solvent (3) and may be discarded, step X) after having first undergone a final procedure of 3) subjecting the waste solution (6) to a procedure of residual ink activation for obtaining a neutralized waste solution (12), c.f. Fig. 2 following the arrows 20c and 21a. Alternatively, but less preferred, it is in all embodiments of the present invention possible to exit the method (20) of the invention after collecting the waste solution (6) in step 2), c.f. Fig. 2, thin dotted arrow 10c. Exiting after step 2), however, leaves a part of the waste solution (6) not neutralized, which is undesirable.

30 In Fig. 4 there is detailed a system (40) for implementing the method (20) according to the above embodiments of the present invention in its broadest aspect. The system (40) comprises an agitation station (1), defining an agitation space (102) for comprising a 3D printed object (2) to be

cleaned in a cleaning solvent (3), an activation station (13) for executing a procedure of residual ink activation for obtaining a neutralized waste solution (12), the activation station (13) defining an activation space (132) for comprising the waste solution (6) during residual ink activation within the activation space (132), thereby preventing evaporation of the waste solution (6) and access of oxygen, and a waste reservoir (8) for a neutralized waste solution (12), sequentially arranged on a waste solution flowpath (43a-c); pumping means (17); and a controller for executing a method (20) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3) according to any of the aspects and embodiments of the present invention.

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In accordance with the present invention, the agitation station (1) and the activation station (13) are spatially separated as a consequence of their sequential arrangement on the same waste solution flowpath (43a-c), and hence do 20 not provide a common space for comprising a waste solution (6) as in WO 2009/140449, but two separate spaces (102,132) for comprising a waste solution (6).

Preferably, the system (40) is produced as a cleaning station 25 in a single unit. The cleaning station may be comprised in, and fluidly connected to, the 3D printer system producing the 3D printed object (2) or may be stand-alone to the 3D printer system. If the system (40) is comprised in, and fluidly connected to, the 3D printer system, it is possible 30 to treat the waste printing solution from the 3D printing process for producing the 3D printed object (2) using the systems and methods of the present invention additional to the waste solution (6) from cleaning the 3D printed object (2), as well as any waste solution generated by cleaning the

3D printing system, and in particular reusing the cleaning solvent for these purposes.

The pumping means (17) can be located on the waste solution 5 flowpath (43a-c) as indicated in Fig. 4, but this placement is not mandatory in all embodiments, and the skilled person may use any suitable placement of the pumping means (17) in accordance with custom in the art of moving fluids. In general, the pumping means (17) will be at least one pump 10 for moving liquids, but other pumping means (17) are suitable as well in accordance with the custom in the art.

In embodiments of the system (40) implementing step 8) of the method (20) of the invention, it is possible to move the 15 neutralized waste solution (12) back along the waste solution flowpath (43a-c) to the agitation station (1) using e.g. a two-way pump (17), it is however preferable to bypass the activation station (13) by means of a return flowpath (44).

In one embodiment, the waste reservoir (8) for a neutralized 20 waste solution (12) permits the discard of the neutralized waste solution (12) via a discard flowpath (45) downstream from the waste reservoir (8). In some embodiments of the present invention, the system (40) comprises at least two waste reservoirs (8,8a) for a neutralized waste solution (12) 25 arranged in parallel on the waste solution flowpath (43a-c). Thereby the at least two waste reservoirs (8,8a) can be arranged to contain increasingly contaminated neutralized waste solutions (12), whereby a method of reusing a decreasingly contaminated waste solution (12) for cleaning a 30 3D printed object (2) in accordance with the prior art can be implemented into the method (20) of the invention. When present, the discard flowpath (45) then connects to the reservoir of the at least two waste reservoirs (8,8a)

comprising the most contaminated neutralized waste solution (12) .

In a preferred embodiment of the system (40) of the 5 invention, the system (40) further comprises a solvent reservoir (7) for a cleaning solvent (3) connected to the agitation station (1) by a cleaning solvent flowpath (42) upstream to the agitation station (1). Thereby a compact, stand-alone cleaning station (40) can be obtained having only 10 few potential contact zones for a user operating the cleaning station (40).

In some embodiments, control of the flow of solvent (3) and solutions (6,12) can be regulated by operating valves (41a-15 h). The operation of valves for the proper flow of fluids is in general considered within the skills of the person in the art.

In accordance with the method (20) of the present invention, suitable mechanical agitation may comprise shaking, solvent flushing, pulsed vacuum, sonication, or most preferred ultrasonication . In accordance with the embodiments of the system (40) of the present invention, mechanical agitation is preferably implemented using an agitation station (1), cf. Fig. 4, comprising a container (4) for the cleaning solvent (3) and mechanical agitation means (5).

The mechanical agitation means (5) of the invention can be selected from amongst a number of mechanical agitation means 30 commonly known to the skilled person. Preferably used in the embodiments of the systems (40) of the present invention are shaking means for shaking the container comprising the cleaning solvent (3) and the 3D printed object (2); flushing means for flushing cleaning solvent (3) past, preferred

rapidly past, the 3D printed object (2), e.g. by using a circulation pump or stirring the solvent comprised in the container; pulsed vacuum means, sonication means or, most preferred, ultrasonication means.

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The system (40) implementing the method (20) of the invention detailed in Fig. 4 is illustrated in its broadest aspect. The activation station (13) will be described in more detail below, however in Fig. 4, the activation station (13) is exemplified by comprising irradiation means (31), preferably ultraviolet (UV) irradiation means (131), which throughout the present disclosure is the preferred means for executing a procedure of residual ink activation for obtaining a neutralized waste solution (12).

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As mentioned it is an important element of the present invention that the activation station (13) is defining a activation space (132) for comprising the waste solution (6) during residual ink activation within the aforementioned activation space (132), for preventing evaporation of the waste solution (6) and access of oxygen to the aforementioned

The experiments show a simple realization of the activation 25 station (13), wherein the defined activation space (132) is defined by the interior of a simple graduated cylinder, which is open to the atmosphere in one direction. However, due to the different time scale of residual ink activation (minutes) and post-curing of a 3D-printed object (tens of minutes),

activation space (132) during residual ink activation.

30 the activation station (13) of the experiments sufficiently provides an activation space (132) for preventing evaporation and oxygen access during irradiation.

It is however preferred in the embodiments of the invention that the activation space (132) for comprising the waste solution (6) during residual ink activation shall be an essentially closed activation space (132). This can e.g. be

5 provided by filling a container and sealing it during residual ink activation, suitable e.g. for chemical activation of the waste solution.

However and preferably, the essentially closed activation space (132) is provided by a flow container, such as e.g. a flow tube or pipe, comprising at least a window transparent to activation irradiation from irradiation means (131) comprised in the activation station (13), and arranged for permitting a flow of waste solution (6) through the flow 15 container when the activation station (13) is in use. Such a flow container provides a minimized activation space (132) which, since only liquid is flowing through the flow container, provides an optimized combination of activation and speed of operation, while preventing evaporation and 20 oxygen access.

The procedure of residual ink activation will be discussed in more detail below, however it is worth mentioning, that an additional advantage of using UV-radiation can be observed 25 when the 3D printed object (2) has been printed using a biological material, e.g. cells, in water. Passing such waste water (6) comprising a biological material past the activation station (13) comprising UV-irradiation means (131) allows for neutralization/killing of the biological 30 material comprised in the waste water (6) according to wellknown mechanisms of UV-activation and neutralization/killing

by radicals formation in the biological material, thereby reducing the biological hazard class of the waste water (6)

and concurrently reducing the cost of discarding it, even if reuse will seldom be an option.

However, and in general, 3D printing is normally concerned 5 with the addition of hardenable polymeric materials to an object (2) under construction, in particular with the addition of hardenable polymerizable materials to an object (2) under construction, and the present invention will be further discussed in that context.

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As known is from the prior art, ink residuals from the 3D printing process remain attached to the surfaces of 3D printed objects (2) and/or printing equipment after 3D printing. The interactions between the ink residuals and the 3D printed object (2) are usually non-specific and the 3D

printed objects can therefore suitably be cleaned in a combination treatment of cleaning solvent (3) and mechanical agitation as known from the prior art procedure (10). Thereby ink residuals are dissolved and/or dispersed in the selected 20 cleaning solvent (3) forming the aforementioned waste solution (6).

The experimental results of Fig. 3A documents a typical situation, wherein there is both dissolved and dispersed ink 25 residuals in the cleaning solvent (3) in larger amounts after cleaning, making the resulting waste solution (6) turbid. Such turbid waste solutions (6) are typically observed after performing first cleanings in cleaning solvents (3) using mechanical agitation according to the prior art procedure 30 (10). Typically, clear waste solutions (6) are observed only after submitting the 3D printed object to at least two prior art cleaning procedures (10) using fresh cleaning solvent (3), often only after at least three prior art cleaning procedures (10) using fresh cleaning solvent (3).

The composition of the waste solution (6) resulting from performing a cleaning procedure (10) of the prior art will differ depending on the initial composition of the 3D printing ink. Also partially solidified residuals from the formation process of the 3D printed object (2) will often be present in the waste solution (6) typically dispersed therein. The present invention builds on the surprising realization by the present inventors that the by weight concentration of residual activatable solidifiable inks in the cleaning solvents (3) commonly used for cleaning after 3D printing in some circumstances can be sufficiently high for subsequent in solvent activation and precipitation of ink components.

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As is well-known to the skilled person in polymer chemistry, polymer formation from a solution of dissolved and/or dispersed mono- and/or oligomers in a solvent depend on exceeding a critical concentration of formation below which, 20 the concentration of the reactants, i.e. mono- and/or oligomers, is too low for reaction with an activated species in the solvent before solvent inactivation or reorganization of the activated species occurs. As a result, when the concentration of reactants is too low, the activatable 25 species become inactivated and polymerization is terminated.

In relation to the broadest aspect of the present invention, this is advantageous, and used herein as detailed above, as the toxicity of the waste solutions (6) can be reduced merely

30 by activating the ink residuals in step 3) in the waste solution (6) c.f. Fig. 2, even where the waste solutions (6) comprise diluted ink residuals below the above mentioned critical concentration of formation.

In such diluted waste solutions the activated ink residuals will, although activated, not necessarily react by polymerization as a consequence of the activation, but may fail to find a reaction partner before inactivation and thus 5 will not form a precipitate, but rather form dissolved and/or dispersed inactivated ink residuals in the waste solution (6). However, these inactivated ink residuals are no longer available for reaction and therefore, the resulting neutralized waste solution (12) comprising the inactivated 10 ink residuals will be less dangerous and less costly to discard, which in itself represents a beneficial advantage over the present state of the art.

The inventors have however observed, that the most common 15 situation, however, will be that the waste solutions (6) are sufficiently concentrated for exceeding the critical concentration of polymer formation from activated ink residuals, residual ink polymerization will take place, and a waste precipitate (14) will be formed in addition to any partially solidified residuals from the formation process of 20 the 3D printed object (2), c.f. Fig. 3. This waste precipitate (14) is simple to remove using separation means (15), such as filters, centrifuges or other separation means as are generally known to the skilled person. Fig. 5 shows the system and experimental setup used to generate the 25 results presented in Fig. 3, wherein a suction filter (15) located on the waste solution flowpath (43) after the activation station (13) using UV-irradiation (131) and before the pumping means (17), here a suction pump (17), the 30 placement corresponding to a location on section (43b) of the waste solution flow path (43a-c) of Fig. 4.

Accordingly, there is disclosed herein in one embodiment of the present invention: A method (30) of neutralizing and

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decontaminating a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), the method comprising :

- obtaining a waste solution (6) comprising residuals of at least one ink for 3D printing a 3D printed object
 (2) dissolved and/or dispersed in at least one cleaning solvent (3) from a process of cleaning said 3D printed object (2) in said cleaning solvent (3);
 - 2) optionally, collecting said waste solution (6);
- 10 3) subjecting said waste solution (6) to a procedure оf residual ink activation in an activation space (132) arranged for preventing, during residual ink activation, evaporation of the waste solution (6) and access of oxygen, thereby generating activated ink 15 residuals for forming a waste precipitate (14)comprising inactivated residual ink;
 - 4) generating said waste precipitate (14) comprising inactivated residual ink;
 - 5) separating said waste precipitate (14) from said waste solution (6) thereby obtaining a decontaminated solvent (16) as a product of said separation;
 - 6) optionally, collecting said decontaminated solvent (16); and/or
 - 7) reusing said decontaminated solvent (16) as a cleaning solvent (3) for cleaning a 3D printed object (2).

In the methods (20,30) detailed above and in Figs. 2 and 4, the waste solution (6) is collected in intermediate steps between cleaning of the 3D printed object (2) and activating 30 the subsequent polymerization of the ink residuals. These collection steps are, however, merely optional and can be dispensed with, when the volumes of waste solution (6) generated by cleaning the 3D printed object (2) are sufficient for carrying out the activation step 3). Often,

however, in small scale laboratories and with at-home 3D printing equipment, it is advantageous to collect a sufficient volume of waste solution (6) prior to activating the waste solution (6) for precipitation generation and separation in steps 3) and 4).

EXAMPLES

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In Fig. 3 there is detailed a simple experimental 10 confirmation of the working principle underlying the general method (20) of the invention and achieved using the experimental setup (11) detailed in Fig 5.

A 3D printed object (2) was cleaned in a first cleaning step 15 C) using mechanical agitation (ultrasound) in isopropanol (3) in an ultrasonic bath (1). After ultrasonication, the obtained 1) waste solution (6) was collected 2) in a graduated cylinder (132) from the ultrasonic bath (1), c.f. Fig. 3A. The resulting waste solution (6) after cleaning was too turbid for looking through. Polymerization was activated 20 3) using ultraviolet light (13), which within a short time generated 4) an insoluble waste precipitate (14) in the The resulting waste precipitate (14) isopropanol. was separated 5) from the solvent by filtration (c.f. Fig. 3C) a suction 25 filter (15) and a pump (17), thereby using generating a decontaminated or cleaned solvent (16), which was subsequently collected 6) c.f. Fig. 3B, and reused 7) in the cleaning of further 3D printed objects at step C). The process was repeatable.

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CLOSING COMMENTS

The term "comprising" as used in the claims does not exclude other elements or steps. The term "a" or "an" as used in the claims does not exclude a plurality. A single processor or

- 5 claims does not exclude a plurality. A single processor or other unit may fulfill the functions of several means recited in the claims.
- Although the present invention has been described in detail 10 for purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art without departing from the scope of the invention.

CLAIMS

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- 1. A method (20) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), the method comprising:
 - obtaining a waste solution (6) comprising residuals of at least one ink for 3D printing a 3D printed object
 (2) dissolved and/or dispersed in at least one cleaning solvent (3) from a procedure (10) of cleaning said 3D printed object (2) in said cleaning solvent (3);
 - 3) subjecting said waste solution (6) to a procedure of residual ink activation in an activation space (132) arranged for preventing, during residual ink activation, evaporation of said waste solution (6) and access of oxygen, for obtaining a neutralized waste solution (12).
- 2. A method (20) for neutralizing a waste solution (6) according to claim 1, the method further comprising: 2) collecting said waste solution (6) after obtaining said waste solution (6) and prior to subjecting said waste solution (6) to said procedure of residual ink activation.
- 3. A method (20) for neutralizing a waste solution (6) according to either claim 1 or claim 2, the method further comprising: 8) reusing said neutralized waste solution (12) in a procedure (10) for cleaning a 3D printed object (2).
- 30 4. A method (20) for neutralizing a waste solution (6) according to any of the preceding claims, wherein said procedure of residual ink activation is a 4) procedure of generating activated ink residuals for forming a waste precipitate (14) comprising inactivated residual ink.

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5. A method (30) of neutralizing and decontaminating a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3) according to any of the preceding claims, the method comprising:

- obtaining a waste solution (6) comprising residuals of at least one ink for 3D printing a 3D printed object
 (2) dissolved and/or dispersed in at least one cleaning solvent (3) from a process of cleaning said 3D printed object (2) in said cleaning solvent (3);
 - 2) optionally, collecting said waste solution (6);
- 3) subjecting said waste solution (6) to a procedure of residual ink activation in an activation space (132) arranged for preventing, during residual ink activation, evaporation of said waste solution (6) and access of oxygen, thereby generating activated ink residuals for forming a waste precipitate (14) comprising inactivated residual ink;
- 20 4) generating said waste precipitate (14) comprising inactivated residual ink;
 - 5) separating said waste precipitate (14) from said waste solution (6) thereby obtaining a decontaminated solvent (16) as a product of said separation;
- 25 6) optionally, collecting said decontaminated solvent (16); and/or
 - 7) reusing said decontaminated solvent (16) as a cleaning solvent (3) for cleaning a 3D printed object (2).
- 30 6. A method according to any of the claims 1 to 5, wherein said activation space (132) is an essentially closed activation space (132).

7. A system (40) for implementing a method (20,30) for neutralizing a waste solution (6) from cleaning a 3D printed object (2) in a cleaning solvent (3), the system (40) comprising an agitation station (1), defining an agitation space (102) for comprising a 3D printed object (2) to be cleaned in a cleaning solvent (3), an activation station (13) for executing a procedure of residual ink activation for obtaining a neutralized waste solution (12), said activation station (13) defining an activation space (132) for comprising said waste solution (6) during residual ink activation within said activation space (132), thereby preventing evaporation of said waste solution (6) and access of oxygen, and a waste reservoir for a neutralized waste solution (12), sequentially (8) arranged on a waste solution flowpath (43a-c); pumping means (17); and a controller for executing a method for neutralizing a waste solution (6) from (20, 30)cleaning a 3D printed object (2) in a cleaning solvent (3) according to any of preceding claims 1 to 5.

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8. A system (40) according to claim 7 further comprising a solvent reservoir (7) for a cleaning solvent (3) connected to said agitation space (102) by a cleaning solvent flowpath (42) upstream to said agitation station (1).

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- 9. A system (40) according to either claim 7 or 8 further comprising separation means (15) located on said waste solution flowpath (43b) after said activation station (13).
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- 10. A system according to any of the claims 7 to 9, wherein said activation space (132) is an essentially closed activation space (132).

11. A system according to any of the claims 7 to 10, wherein said activation space (132) is a flow container comprising at least a window transparent to activation irradiation from irradiation means (131) comprised in the activation station (13), and arranged for permitting a flow of waste solution (6) through the flow container when the activation station (13) is in use.

12. A system according to claim 11, wherein said irradiation 10 means (131) are UV-irradiation means.



Prior Art Fig. 1 WO 2020/144156



Fig. 2



Fig. 4





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International application No PCT/EP2020/050170

A. CLASSIFICATION OF SUBJECT MATTER INV. B08B3/14 B29C64/35 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) B08B 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

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