(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 480 287 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
08.05.2019 Bulletin 2019/19

(21) Application number: **17199802.4**

(22) Date of filing: **03.11.2017**

(51) Int Cl.:
C11D 3/10 *(2006.01)* ***C11D 3/04*** *(2006.01)*
C11D 3/20 *(2006.01)* ***C11D 7/12*** *(2006.01)*
C11D 7/06 *(2006.01)* ***C11D 7/26*** *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

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(54) **SOLID WATER-SOLUBLE CLEANING COMPOSITION**

(57) The present invention refers to solid water-soluble cleaning compositions usable for removing support material from three-dimensional objects formed by additive manufacturing, an aqueous solution prepared from such a composition and a method for removing support material from a three-dimensional object formed by additive manufacturing.

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Description

[0001] The present invention refers to solid water-soluble cleaning compositions usable for removing support material from three-dimensional objects formed by additive manufacturing, an aqueous solution prepared from such a composition and a method for removing support material from a three-dimensional object formed by additive manufacturing.

[0002] In particular, the present invention refers to a solid water-soluble cleaning composition for removing support material from a three-dimensional object formed by additive manufacturing, said composition comprising (a) at least 50 wt.% of at least one inorganic carbonate, (b) 0.1 to 15 wt.% of at least one alkali metal hydroxide, (c) 0.1 to 30 wt.% of at least one organic acid, and (d) 0.1 to 5 wt.% of at least one surfactant, wherein the weight percentages are based on the total weight of the composition. Additionally, the present invention relates to a package containing said solid water-soluble composition, to a kit comprising said package and instructions comprising information of dosing and/or use of the composition, to an aqueous solution obtainable by dissolution of the composition according to the invention, and to a method for removing support material from a three-dimensional object formed by additive manufacturing comprising (a) providing an aqueous solution obtained or obtainable by dissolution of a composition according to the invention, and (b) contacting the three-dimensional object formed by additive manufacturing with the aqueous solution to remove at least a part of the support material from the three-dimensional object, as well as to the use of a composition, package, kit or aqueous solution according to the invention for removing support material from a three-dimensional object formed by additive manufacturing.

[0003] Additive manufacturing is a technology enabling fabrication of arbitrarily shaped structures directly from computer data via additive formation steps (additive manufacturing). The basic operation of any additive manufacturing system consists of slicing a three-dimensional computer model into thin cross sections, translating the result into two-dimensional position data and feeding the data to control equipment, which fabricates a three-dimensional structure in a layer-wise manner.

[0004] Additive manufacturing comprises several building techniques, including three-dimensional printing such as three-dimensional (3D) inkjet printing, electron beam melting, stereolithography, selective laser sintering, laminated object manufacturing, and fused deposition modeling. By way of example, the 3D inkjet printing processes is performed by a layer-by-layer inkjet deposition of building materials. In this process the building material is dispensed from a dispensing head having a set of nozzles to deposit layers on a supporting structure. Depending on the building material, the layers may then be cured or solidified using a suitable device.

[0005] During the additive manufacturing process, the building material may include "object material", which is deposited to produce the desired model object, and frequently, another material is used to provide temporary support to the model object as it is being built. The other material is referred to herein and in the art as "support material", and is used to support specific areas of the object during building and for assuring adequate vertical placement of subsequent object layers. For example, in cases where model objects include overhanging features or shapes, e.g. curved geometries, negative angles, and/or voids, and the like, objects are typically constructed using adjacent support constructions, which are used during the printing and then subsequently removed in order to reveal the final shape of the fabricated model object.

[0006] The present invention concerns amongst others the provision of a solid water-soluble cleaning composition to address this removal process of support material from the object material after completion of the additive manufacturing process.

[0007] There are several support materials known in the art, e.g. water-soluble support materials for three-dimensional building have for example been described in U.S. Patent No. 6,228,923. Said document describes a water-soluble thermoplastic polymer - poly(2-ethyl-2-oxazoline) - for use as a support material in a 3D building process involving high pressure and high temperature extrusion of ribbons of selected materials onto a plate. Further water-soluble compositions suitable for support material in building a three-dimensional object are described, for example, in U.S. Patent Nos. 7,479,510, 7,183,335 and 6,569,373. Examples of further known and commonly used support materials in the art include SR-20, SR-30, SR-100 and SR-110 (FDM support materials of Stratasys, USA)

[0008] In general, the object material and the supporting material are initially liquid and subsequently hardened to form the required layer shape. The hardening process may be performed by a variety of methods, such as UV curing, phase change, crystallization, drying, etc. In all cases, the support material is deposited in proximity of the object material, enabling the formation of complex object geometries and filling of object voids. In such cases, the removal of the hardened support material is liable to be difficult and time consuming, and may damage the formed final object. The support material should harden rapidly in order to allow building of subsequent layers. Additionally, the hardened support material should have sufficient mechanical strength for holding the model material in place, and low distortion for avoiding geometrical defects.

[0009] Support structures for use in building 3D models in digital manufacturing systems are typically classified in two categories: Break-away support materials and soluble support materials. Break-away support materials may be manually broken away from the resulting 3D models by hand or using tools. In comparison, soluble support materials may be

dissolved in aqueous solutions, typically requiring heat and agitation for optimal dissolution. The mechanical methods are labor intensive and are often unsuited for small intricate parts, and therefore chemical dissolution methods are preferably used.

[0010] For dissolving the support material, the fabricated/printed object is commonly immersed in water or in a solvent that is capable of dissolving the support material, while not affecting the object material. The solutions utilized for dissolving the support material are also referred to herein and in the art as "cleaning solution" or "cleaning composition". In many cases, however, the support removal process may involve hazardous materials, manual labor and/or special equipment requiring trained personnel, protective clothing and expensive waste disposal. In addition, the dissolution process is usually limited by diffusion kinetics and may require very long periods of time, especially when the support constructions are large and bulky. Furthermore, post-processing may be necessary to remove traces of a 'mix layer' on model object surfaces. The term "mix layer" refers to a residual layer of mixed hardened object and support materials formed at the interface between the two materials on the surfaces of the object being fabricated, by object and support materials mixing into each other at the interface between them.

[0011] There are two main approaches for dissolving support structures/support material from a completely fabricated 3D model after the additive manufacturing process:

The first of said approaches is described in e.g. WO 2017/029658 A1, in which the inventors describe novel aqueous alkaline cleaning solutions containing a combination of two alkaline substances, which are an alkali metal hydroxide and an alkali metal silicate, each at a concentration of no more than 3 weight percent of the total weight of the solution. A drawback of said cleaning solution is that it is already in a liquid state, which impedes the transport and the storage of said cleaning solution. Furthermore, the concentration of the alkali metal hydroxide in the cleaning solution is high, representing in a very alkalic solution.

[0012] The second approach is described in e.g. US 2011/0186081 A1, which teaches amongst others a variety of different solid support removal compositions, which include one or more oxidizing agents, one or more chelating agents, and one or more pH modifiers, wherein the concentration of the oxidizing agent(s) in the composition is high enough to assist in the removal of soluble support structures from 3D models. As suitable hydrate-based oxidizing agents for use in the support removal composition US 2011/0186081 A1 describes sodium perborates, such as sodium perborate monohydrate, sodium perborate trihydrate, sodium perborate tetrahydrate, hence, according to US 2011/0186081 A1 the dissolution capacity of the solid cleaning composition upon dilution in water is based on perhydrate-based oxidizing agents. Such compositions appear to have several drawbacks, although they allow a facilitated transport in comparison to the solutions described in WO 2017/029658 A1. For example, the solid compositions described in US 2011/0186081 A1 are hazardous to the environment and the user, who requires to wear protective clothing like gloves and protection goggles. Furthermore, the packaging of said compositions has to be intricate and therefore costly as the oxidizing per-compound has to be separated from the remaining ingredients of the cleaning composition to avoid the negative impact of the oxidizing agent on said ingredients before the actual cleaning process has started.

[0013] Therefore, it was an object of the present invention to provide a solid water-soluble cleaning composition that overcomes the above-mentioned drawbacks, hence, a solid water-soluble cleaning composition for removing support material from a three-dimensional object formed by additive manufacturing that upon dissolution in water allows a high cleaning performance, while being less harmful to the user and the environment and being cost-efficient.

[0014] This object is met by the cleaning composition of the present invention, hence, by a solid water-soluble cleaning composition for removing support material from a three-dimensional object formed by additive manufacturing, the composition comprising (a) at least 50 wt.% of at least one inorganic carbonate, (b) 0.1 to 15 wt.% of at least one alkali metal hydroxide, (c) 0.1 to 30 wt.% of at least one organic acid, and (d) up to 5 wt.% of at least one surfactant, wherein the weight percentages are based on the total weight of the composition.

[0015] The composition of the present invention provides when dissolved in an aqueous solution, preferably in water, high alkalic reserves, allowing a prolonged use of the solution for dissolving the support material. Concurrently said solution is less harmful for the user and the environment as compositions of the prior art.

[0016] As used in the present disclosure the definition "at least one" means that at least one type of a particular defined compound is comprised in the composition, but also more than one type of a compound falling under the according definition can be present. Thus, "at least one" includes one, two, three, four, five or more compounds differing from each other, but falling under the mentioned definition. If the term "at least one" is used in combination with a range of an amount, the range refers to the whole amount of the compound(s) present in the composition, which means that the combined amounts of the several types of compounds falling under the compound definition represent the claimed range.

[0017] In a preferred embodiment of the present invention the composition comprises less than 10 wt.% of any oxidizing per-compound(s), preferably less than 5 wt.%, more preferred less than 2 wt.%. Most preferably the cleaning composition is substantially free of any oxidizing per-compound(s). Furthermore, the composition preferably comprises less than 1 wt.% of an alkali metal silicate, preferably less than 0.5 wt.%, more preferred less than 0.3 wt.%. Most preferably the

cleaning composition is substantially free of any alkali metal silicate. Furthermore, preferably the composition is substantially free of any enzyme(s), zeolites, polymers and/or phosphates, since such components are not necessary for the present approach.

[0018] In terms of the present invention "substantially free of" means that the respective compound is not volitionally added to the composition, thus, the composition doesn't comprise more than 0.1 wt.%, preferably not more than 0.05 wt.%, even more preferred less than 0.02 wt.% of the respective compound.

[0019] In terms of the present invention the definition "oxidizing per-compound(s)" refers to any compound comprising a -O-O- group, including inorganic or organic peroxy compounds, in particular such per-compounds usually included in detergent compositions for bleaching, e.g. H_2O_2 or H_2O_2 generating compositions like peroxy acids, percarbonates, perborates, natrium persulfate, peroxide disulfate, etc.

[0020] The solid water-soluble cleaning composition of the present invention comprises as component (a) at least 50 wt.% based on the total weight of the composition of at least one inorganic carbonate. Said component (a) may preferably represent 50 wt.% to 95 wt.%, more preferred 55 to 90 wt.%, even more preferred 60 to 80 wt.% of the total cleaning composition. The composition preferably comprises as the at least one inorganic carbonate component (a) at least one alkali metal carbonate, wherein the amount of alkali metal carbonate preferably is in an amount in the range from 50 to 100 wt.%, more preferred in the range of 60 to 98 wt.%, even more preferred in the range of 70 to 95 wt.% based on the total weight of the carbonate component (a). The inorganic carbonate component (a) may also comprise at least two different alkali metal carbonates in a combined amount in the range from 50 to 100 wt.%, more preferred in the range of 60 to 98 wt.%, even more preferred in the range of 70 to 95 wt.%, based on the total weight of the carbonate component (a).

[0021] Examples for suitable alkali metal carbonates are all salts of the formula M_2CO_3, wherein M is selected from alkali earth metals, preferably M is Na or K. In a preferred embodiment the composition of the present invention comprises at least two alkali metal carbonates, wherein said two compounds are present in a weight ratio from 3:1 to 1:3, such as from 2:1 to 1:2 or from 1.2:1 to 1:1.2. Preferably said compounds are Na_2CO_3 and K_2CO_3.

[0022] Further, the inorganic carbonate component (a) of the solid water-soluble cleaning composition of the present invention may comprise at least one alkali metal bicarbonate wherein the amount of alkali metal bicarbonate preferably is in the range from 5 to 20 wt.%, based on the total weight of the carbonate component (a). The inorganic carbonate component (a) may also comprise at least two different alkali metal bicarbonates in a combined amount in the range from 5 to 20 wt.%, preferably in the range of 8 to 15 wt.%, based on the total weight of the carbonate component (a).

[0023] Examples of suitable bicarbonate compounds are compounds of the formula $MHCO_3$, wherein M is selected from alkali earth metals, preferably M is Na or K. Particularly preferred M is Na.

[0024] Furthermore, the inorganic carbonate component (a) may comprise (i) at least one alkali metal carbonate and (ii) at least one alkali metal bicarbonate wherein the total amount of the alkali metal carbonate(s) and the alkali metal bicarbonate(s) is in an amount in the range from 50 to 100 wt.%, based on the total weight of the carbonate component (a). If the composition comprises as the carbonate compound (a) at least one alkali metal carbonate and at least one alkali metal bicarbonate, the weight ratio of the (combined) carbonate(s) to the (combined) bicarbonate(s) is preferably in the range from 20:1 to 2:1, preferably in the range of from 15:1 to 5:1, more preferred of from 12:1 to 8:1.

[0025] As component (b) the composition of the present invention comprises an alkali metal hydroxide in an amount of 0.1 to 15 wt.%, preferably in an amount of 0.5 to 10 wt.%, more preferred in an amount of 0.8 to 5 wt.% and most preferred in an amount of 1 to 3 wt.% based on the total cleaning composition. Said alkali hydroxide preferably is selected from sodium hydroxide (NaOH) and potassium hydroxide (KOH) and is most preferred sodium hydroxide.

[0026] The cleaning composition of the present invention further comprises as component (c), an organic acid component in an amount of 0.1 to 30 wt.% based on the total amount of the cleaning composition. Preferably the organic acid component (c) comprises a polybasic carboxylic acid (polycarboxylic acid), which means a carboxylic acid having more than one acid group, preferably at least two, more preferred at least three carboxylic acid groups. Examples of such polybasic carboxylic acids are succinic acid, maleic acid, malonic acid, fumaric acid, adipinic acid, glutaric acid, tartaric acid and citric acid. The polybasic carboxylic acid preferably comprises citric acid, wherein the citric acid preferably is present in the composition in the form of coated particles or core-shell particles having a core comprising citric acid, and a coating comprising a water-soluble compound.

[0027] A preferred coating comprises sugar polymers like cellulose, starch, starch derivatives, maltodextrin, pectines like glycogene, preferably maltodextrin, or salts of low molecular weight acids, preferably acids comprising one, two or three acid groups. A particular preferred coating is a coating comprising or consisting of a salt of a low molecular weight acid. With low molecular weight acid an acid (as free acid) is meant having a molecular weight of below 400g/mol, preferably below 350 g/mol, more preferred below 300 g/mol. Said low molecular weight acid comprises at least one carboxyl group, preferably at least two, more preferred three carboxyl groups. The preferred salt of a low molecular acid is an alkali metal citrate, preferably Na-citrate. A coating with Tri-Na citrate is particularly preferred.

[0028] Another suitable water soluble low molecular weight compound is any type of a low molecular weight sugar or an amino acid or a salt thereof having a molecular weight of below 400g/mol, preferably below 350 g/mol, more preferred

below 300 g/mol. Examples of "low molecular weight compounds" are C_3-C_6 sugars in aldose or ketose form like allose, altrose, glucose, mannose, gulose, idose, galactose, talose, psicose, fructose, sorbose, tagatose, xylulose, ribulose, ribose, arabinose, xylose, lyxose, threose, erythrose, erythrulose, dihydroxy acetone or glycerol aldehyde or disaccharides like for example saccharose, lactose, maltose or Isomalt or oligosaccharides comprising 3 to 10 sugar units or amino acids, preferably natural amino acids (commonly contained in natural proteins) without being restricted to the mentioned examples. One preferred low molecular weight compound is the sugar Isomalt ST, comprising 6-O-α-D-glucopyranosyl-D-sorbite and 1-O-α-D-glucopyranosyl-D-mannite dihydrate units.

[0029] One particular advantage of these materials is on one side the water solubility / dispersibility on the other hand the non-toxicity of the compounds.

[0030] In a particularly preferred embodiment the coating consists essentially of the mentioned water dissolvable material(s)l, this means that the coating comprises less than 10 wt.%, preferably less than 5 wt.%, more preferred less than 2 wt.%, even more preferred less than 1 wt.% and most preferred less than 0.5 wt.% of other materials.

[0031] When referring to the water dissolvable material, a material herein is defined as being "water-soluble/dissolvable/dispersible" when more than 99% of a coating (layer) with a thickness of up to 0.5 mm of such material dissolves within 10 minutes, preferably within 5 min in a common 2L beaker containing 1 L of deionised water at 40° C which is stirred with a stirrer revolving at 200 r. p.m. It is pointed out that materials can be used as ingredients for the coating which itself may not be soluble, but e.g. dispersible, as long as the coating comprising said material is dissolved by water.

[0032] Particular preferred embodiments of component (c) comprising a core of citric acid and a water dissolvable coating are the commercially available products "Citrocoat® N" or "citric acid DC" provided by Jungbunzlauer, Germany. Citrocoat® N represents particles having a core of citric acid coated with sodium citrate, prepared by applying NaOH-solution to the surface of granulated citric acid, whereas "citric acid DC" comprises a core of citric acid, coated with maltodextrin. The most preferred embodiment is Citrocoat® N.

[0033] An optional, but preferred ingredient of the cleaning composition of the present invention is component (d), which is at least one surfactant. The surfactant(s) representing component (d) comprise at least one surfactant selected from the group consisting of non-ionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants and mixtures or combinations thereof. If present, the surfactant(s) of component (d) are present in the cleaning composition in a total amount of 0.1 to 5 wt.%, preferably in an amount of 0.2 to 3 wt.%, more preferred in an amount of 0.3 to 1 wt.% based of the total amount of the cleaning composition. Preferably the surfactant(s) comprise(s) at least one anionic surfactant e.g. selected from an alkyl sulfate, alkyl sulfonate, sulfosuccinate or alkoxylated derivatives of any of the foregoing or a mixture or combination thereof.

[0034] Besides the ingredients (a) to (d) mentioned above the composition according to further may preferably comprise as a further compound (e) at least one chelating agent, e.g. in an amount of up to 1 wt.%, preferably in an amount of 0.01 to 0.5 wt.% of the total composition. The at least one chelating agent preferably comprises a nitrogen-containing compound having a plurality of acetate groups such as salts, particularly sodium salts, of nitrilotriacetic acid, methylglycinediacetic acid, ethylenediaminetetraacetic acid, iminodisuccinic acid, ethylenediamine iminodisuccinic acid or diethylenetriaminepentaacetic acid, preferably tetrasodium-*N,N*-bis(carboxylatomethyl)-L-glutamate, an oxalate such as disodium oxalate salt or a combination of any of the foregoing.

[0035] The composition of the present invention may comprise minor amounts of up to 1 wt.% of further ingredients, e.g. fillers, perfumes, dyes, or similar, however, according to the present invention this is not necessary. Thus, said cleaning composition may consist of the ingredients (a), (b), (c), (d), (e) and (f), or even of the ingredients (a), (b), (c), (d) and (e).

[0036] In a preferred embodiment of the composition of the present invention said cleaning composition is in a powder or granulate form comprising of:

(a1) 60 to 85 wt.% of at least one alkali metal carbonate,
(a2) 5 to 20 wt.% of at least one alkali metal bicarbonate,
(b) 0.5 to 5 wt.% of at least one alkali metal hydroxide,
(c) 5 to 15 wt.% of at least one organic acid,
(d) 0.1 to 1 wt.% of at least one surfactant, and
(e) 0.01 to 0.5 wt.% of at least one chelating agent,
(f) 0 to 1 wt.% of further ingredients selected from filler, perfume or dyes,

wherein the weight percentages are based on the total weight of the cleaning composition. In a preferred embodiment said cleaning composition is consisting of said components.

[0037] The composition according to the invention preferably is provided in the form of a powder, granulate or compacted body, wherein said powder or granulate optionally is provided in form of a packaged unit dose or the compacted body preferably is a compressed tablet, particularly preferred prepared from the powder or granulate of the composition.

[0038] The composition may be provided in powder or granulate form either in a container containing the composition

for self-dosing by the user, thus, the container comprises the composition as a free-flowing powder or granulate, or the composition is provided in form of a pre-dosed composition as a unit dose, e.g. a compressed tablet, a bag or a small package or a pouch comprising the composition including a portion of the composition for a single use. Such a unit dose may comprise the composition in an amount in the range of from 10 to 400 g, e.g. from 15 to 200 g, from 20 to 100 g or from 25 to 50 g, dependent from the desired amount for a single use. Commonly the unit doses are in a weight range of from 10 to 60 g, in particular if it is provided as a pouch or tablet.

[0039] If a pouch is provided, or if the tablet is packaged, preferably a water-soluble material is used to wrap the cleaning composition. Providing the composition in a water-soluble material, e.g. a water-soluble film or water-soluble container, has the advantage that the user doesn't come in direct contact with the cleaning composition. Suitable water-soluble materials for packaging cleaning compositions are known in the art and include e.g. polyvinyl alcohol, polylactic acid, gelatine, however, any other suitable material, which can be provided in form of a water-soluble film can be used.

[0040] Again, when referring to the water-soluble material, a material herein is defined as being "water-soluble/dissolvable/dispersible" when more than 99% of a film (layer) with a thickness of up to 0.5 mm of such a material dissolves within 10 minutes, preferably within 5 min in a 2 L beaker containing 1 L of deionised water at 40° C which is stirred with a stirrer revolving at 200 r. p.m, wherein in case of the film it should be considered as sufficiently dissolved, when the content of the package is completely delivered into the water.

[0041] The invention further refers to an aqueous solution obtainable by adding the composition of any of claims 1 to 12 to water or an aqueous buffer. Said aqueous solution can be obtained by adding an amount of 5 to 60 g, preferably an amount of 10 to 40 g/l, more preferably an amount of 15 to 35 g/l, even more preferably an amount of 20 to 30 g/l and most preferred an amount of 23 to 25 g/l of a composition as described above in 1 l of water or an aqueous buffer, preferably in water. Further said aqueous solution can be obtained by adding at least ingredients corresponding to ingredients (a) to (d) and optionally (e) and/or (f) in amounts as defined above to water or an aqueous solution, resulting in a solution corresponding to the present invention.

[0042] The solution obtained or obtainable by adding the composition to water as defined above commonly has a pH in the range of from pH 9 to 12, preferably in the range of from pH 10 to 11.

[0043] The powder, granulate, compressed tablet or pouch comprising the cleaning composition can be provided together with any instructions for dosing and/or preparing the aqueous solution in form of a kit comprising said composition in any of the mentioned forms and said instructions. Said kit furthermore might comprise any device or further instructions suitable for carrying out a method for removing any support material from a three-dimensional object formed by additive manufacturing, particularly a method as described below.

[0044] One of the particular advantages of the cleaning composition of the present invention is that the solution obtainable by adding the cleaning composition according to the present invention to water (or an aqueous buffer) can be used longer for the removing of support material from an object prepared by additive manufacturing compared to known compositions provided on the market, due to the high alkali reserves of the composition. Thus, the usage of the present cleaning composition reduces the need of changing the cleaning solution, thus, a higher amount (in gram) of the support material can be dissolved per liter of the cleaning solution compared to formerly known solutions offered on the market. This reduces the costs and the necessary handling steps. Additionally, due to the content of the components any change of the cleaning solution is less harmful for the user, since the cleaning solution comprises less, or even doesn't comprise any oxidizing per-compounds and less or even no highly alkalic silicates.

[0045] According to the present invention furthermore a method for removing support material from a three-dimensional object formed by additive manufacturing is provided, said method comprising:

(a) providing an aqueous solution obtainable by dissolution of a cleaning composition according to the invention as defined above, and

(b) contacting the three-dimensional object formed by additive manufacturing with the aqueous solution to remove at least a part of the support material from the three-dimensional object.

[0046] The solution in step (a) can be provided as described above, either by dissolving the mentioned amount of the cleaning composition of the present invention in water (or an aqueous buffer), or by adding the ingredients (a) to (d) and optionally (e) and/or (f) separately to water in according amounts.

[0047] In step (b) a three-dimensional object formed by additive manufacturing and comprising support material which preferably should not be comprised in the final product is contacted with the aqueous solution provided in step (a). This can be carried out e.g. either by immersing said three-dimensional object in the aqueous solution, e.g. in a bath, preferably under agitation of the solution, or by spraying said aqueous solution onto the three-dimensional object, e.g. like in a dishwashing machine or a car wash site.

[0048] In a preferred embodiment of the method the aqueous solution is heated and preferably maintained to a temperature in the range of from 60 to 90 °C, preferably 65 to 75°C, for and/or during the contact with the three-dimensional object. It is preferred that the three-dimensional object is subjected to the heated aqueous solution in step (b) for a time

period of from 20 min to 12 hours to remove the support material successfully.

[0049] Advantageously, for the successful total dissolution of the support material the aqueous solution is used in such an amount that an amount corresponding to 0.1 to 2 g of the solid cleaning composition of the present invention is contacted with 1 g of the support material to be dissolved. The support material to be dissolved is material any commonly used for these purposes, which itself is not dissolvable in distilled water, however, is dissolvable in the aqueous solution of the present invention.

[0050] After dissolving the support material, the three-dimensional object optionally, but preferably might be rinsed with water or an aqueous, preferably non-alkalic solution after step (b).

[0051] The invention refers also to the use of a composition according to any of the embodiments described herein or to a package, tablet or pouch as described herein, a kit or an aqueous solution for removing a support material from a three-dimensional object formed by additive manufacturing, wherein said removing preferably is carried out by a method as described herein. The support material preferably is a polymeric material which is soluble in the aqueous solution as described herein, in particular an acid functional polymer or copolymer material, without being limited. Examples of the state of the art are e.g. the materials as described in WO2017/02968 being curable support materials (page 20 to 27 of WO2017/02968) or the materials described in US 6,228,923; US 7,479,510; US 7,183,335 or US 6,569,373 as being suitable support materials. Support materials for the purpose of forming three-dimensional objects by additive manufacturing are well known in the art and readily available on the market, e.g. the support materials sold by Stratasys, USA under the tradenames SR-10, SR-20, SR-30, SR-35, SR-100 and SR110.

Examples

Example 1: Dissolving performance for support material

[0052] The dissolving performance of different aqueous solutions were considered by measuring the time needed for dissolving a predetermined amount of support material from a three-dimensional object formed by additive manufacturing. The dissolution time was measured in (A1) an aqueous solution comprising 12 g/l of a composition according to the invention, (A2) an aqueous solution comprising 24 g/l of a composition according to the invention, (B) an aqueous solution obtained by dissolution of 36.5 g/l of a composition known in the art (Ecoworks® support removal composition of Stratasys; as disclosed in US 2011/0186081 A1, prepared according to the instructions of the manufacturer).

[0053] Similar three-dimensional printed objects formed by additive manufacturing comprising the same amount of object material and support material were incubated in either an aqueous solution according to (A1), (A2) or (B) as mentioned above. Said printed objects had the same weight, size, three-dimensional scale and surface area with regards to the object and support material in order to provide comparable results:

Table 1:

Solution comprising solid composition dissolved in water	Time for complete removal of 3.88g support material [min]
Inventive solution A1	86
Inventive solution A2	69
Comparison solution B	102

[0054] Composition A comprised

(a1) two alkali metal carbonates,
(a2) Na bicarbonate,
(b) sodium hydroxide,
(c) citric acid, coated
(d) an anionic surfactant, and
(e) a chelating agent.

[0055] The experiments were repeated 3-times. The above shown time periods in minutes represent the average of the measured times per experiment for each composition. It can be seen, that the inventive composition provides an aqueous solution removing the support material noticeably faster than the comparative Example, even though only one third of the amount of the inventive composition is added to water to prepare the aqueous solution, compared to the composition of the art.

[0056] Furthermore, it has to be mentioned that in all experiments, regardless which composition at different dosages

has been used, the object material was not affected and removed by the respective used aqueous solutions.

Example 2: Dissolution capacity

[0057] In a second experiment the dissolution capacity of (A2) an aqueous solution obtained by dissolving 24 g/l of a composition according to the invention and (A3) an aqueous solution obtained by dissolving 36 g/l of a composition according to the invention was analyzed in comparison to the dissolution capacity of (B) an aqueous solution obtained by dissolving 109,5 g/l of a composition known in the art (Ecoworks® support removal composition of Stratasys; support removal composition as disclosed in US 2011/0186081 A1) on a frequently used soluble support material in additive manufacturing in the art (SR-30®, Stratasys, USA). To determine the dissolution capacity in each experiment 72 g of a soluble support material was provided as the material to be dissolved, which was submitted to the standard HP removal system of 3D printed models, "short cycle" (corresponding to about 3 hours removal time, including rinsing of the model; see Hewlett Packard user handbook), the removal process used 5 l of the aqueous solutions per run.

	Comp. A2	Comp. A3	Comp. B
Soluble support material	SR-30	SR-30	SR-30
Amount of SR-30 before incubation	72 g	72 g	72 g
Total amount of composition (in 5l)	120 g	180 g	548 g
Incubation time	90 min	90 min	90 min
Amount of SR-30 after incubation	17.7 g	7.87 g	24.43 g
Dissolution capacity (dissolved amount)	54.3 g	64.13 g	47.57 g

[0058] As can be clearly seen, the aqueous solutions comprising the compositions of the present invention dissolve considerably more of the support material during the same program of the HP removal system as the solution comprising the composition of the art, even though noticeably less amount of the composition was used. This shows that the dissolution performance obtainable with the composition according to the invention allows saving of costs, time and handling steps.

Claims

1. A solid water-soluble cleaning composition for removing support material from a three-dimensional object formed by additive manufacturing, the composition comprising:

   (a) at least 50 wt.% of at least one inorganic carbonate,
   (b) 0.1 to 15 wt.% of at least one alkali metal hydroxide,
   (c) 0.1 to 30 wt.% at least one organic acid, and
   (d) 0 to 5 wt.% at least one surfactant,

   wherein the weight percentages are based on the total weight of the composition.

2. The composition according to claim 1, wherein the composition comprises less than 10 wt.% of any oxidizing per-compound(s) and/or less than 1 wt.% of an alkali metal silicate.

3. The composition according to any one of the preceding claims, wherein the inorganic carbonate component (a) comprises at least one alkali metal carbonate, wherein the at least one alkali metal carbonate preferably is in an amount in the range from 50 to 100 wt.%, based on the total weight of the carbonate component (a).

4. The composition according to claim 3 comprising a mixture of two different alkali metal carbonates, preferably in a weight ratio from 5:1 to 1:5, even more preferred in a weight ratio from 4:1 to 1:4, even more preferred in a weight ratio from 3:1 to 1:3, even more preferred in a weight ratio from 2:1 to 1:2, and most preferred in a weight ratio from 1.2:1 to 1:1.2.

5. The composition according to any one of the preceding claims, wherein the carbonate component (a) comprises at

least one alkali metal bicarbonate, preferably in an amount in the range from 5 to 20 wt.%, based on the total weight of the carbonate component (a), wherein preferably at least one alkali metal bicarbonate is sodium bicarbonate.

6. The composition according to any one of the preceding claims, wherein the carbonate component (a) comprises (i) at least one alkali metal carbonate and (ii) at least one alkali metal bicarbonate, wherein the weight ratio of (i) and (ii) is preferably in the range from 20:1 to 2:1.

7. The composition according to any one of the preceding claims, wherein the alkali metal hydroxide component (b) comprises potassium hydroxide and/or sodium hydroxide, preferably sodium hydroxide.

8. The composition according to any one of the preceding claims, wherein the organic acid component (c) comprises a polybasic carboxylic acid, wherein the polybasic carboxylic acid preferably comprises citric acid, wherein the citric acid preferably is present in the composition in the form of coated particles or core-shell particles having a core comprising citric acid, which is at least partially coated by a layer comprising citrate.

9. The composition according to any one of the preceding claims, wherein the surfactant component (d) comprises at least one surfactant selected from the group consisting of non-ionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants and mixtures or combinations thereof, preferably comprising an anionic surfactant such as an alkyl sulfate, alkyl sulfonate, sulfosuccinate or alkoxylated derivatives of any of the foregoing or a mixture or combination thereof.

10. The composition according to anyone of the preceding claims further comprising at least one chelating agent, wherein the at least one chelating agent preferably comprises a nitrogen-containing compound having a plurality of acetate groups such as salts, particularly sodium salts, of nitrilotriacetic acid, methylglycinediacetic acid, ethylenediaminetetraacetic acid, iminodisuccinic acid, ethylenediamine iminodisuccinic acid or diethylenetriaminepentaacetic acid, preferably tetrasodium-*N,N*-bis(carboxylatomethyl)-L-glutamate, an oxalate such as disodium oxalate salt or a combination of any of the foregoing.

11. The composition according to any one of the preceding claims, being a powder or granulated composition comprising:

(a1) 60 to 85 wt.% of at least one alkali metal carbonate,
(a2) 5 to 20 wt.% of at least one alkali metal bicarbonate,
(b) 1 to 5 wt.% of at least one alkali metal hydroxide,
(c) 5 to 15 wt.% of at least one organic acid,
(d) 0.1 to 1 wt.% of at least one surfactant, and
(e) 0.01 to 0.5 wt.% of at least one chelating agent,
(f) 0 to 1 wt.% of further ingredients selected from filler, perfume or dyes

wherein the weight percentages are based on the total weight of the composition.

12. The composition according to any one of the preceding claims, wherein the composition is in the form of a powder, granulate or compacted body, wherein said powder or granulate optionally is provided in form of a packaged unit dose or the compacted body preferably is a compressed tablet.

13. An aqueous solution obtainable by adding and dissolving the composition of any of claims 1 to 12 to water or an aqueous solution, preferably by adding an amount of 5 to 60 g, preferably 10 to 40 g/l, more preferably 15 to 35 g/l, even more preferably 20 to 30 g/l and most preferred an amount of 23 to 25 g/l of a composition of any of claims 1 to 12 into 1 l of water or an aqueous buffer.

14. A method for removing support material from a three-dimensional object formed by additive manufacturing comprising:

(a) providing an aqueous solution according to claim 13, and
(b) contacting the three-dimensional object formed by additive manufacturing with the aqueous solution to remove at least a part of the support material from the three-dimensional object.

15. The method according to claim 14, wherein the contacting in step (b) comprises immersing the three-dimensional object in a bath of the aqueous solution, or wherein the contacting in step (b) comprises spraying the aqueous

solution to the three-dimensional object, for example in a dishwashing machine.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 19 9802

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	24 April 2018	Richards, Michael

CATEGORY OF CITED DOCUMENTS

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