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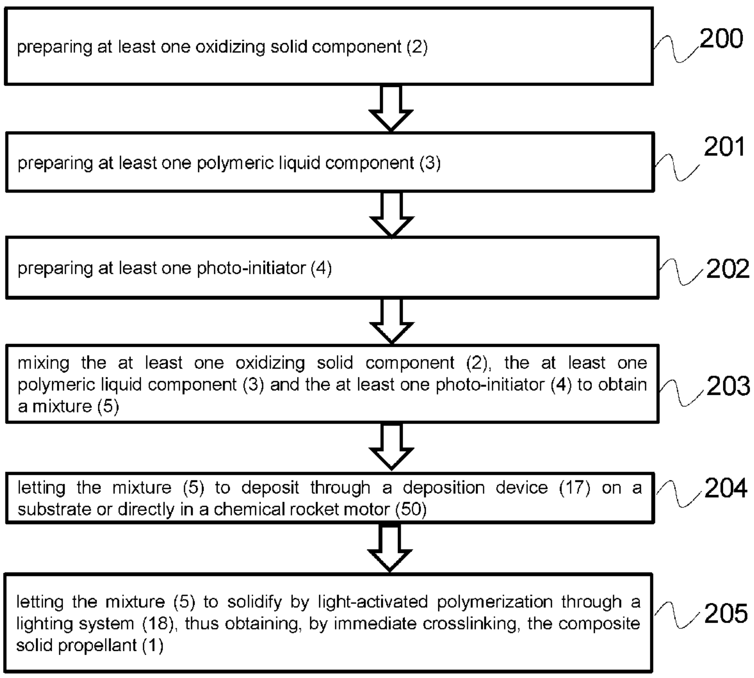


Fig. 2

(57) Abstract: The invention relates to a manufacturing process, and to the relevant manufacturing plant, of composite solid propellant (1) for a chemical rocket motor (50) wherein at least one oxidising solid component (2), at least one polymeric liquid component (3) and at least one photo-initiator (4) are used, this photo-initiator (4) being necessary for the polymerization and the layered local crosslinking of the composite solid propellant (1). The invention also relates to the composite solid repellent (1) for a chemical rocket motor (50), obtained by the aforesaid manufacturing process or produced in the aforesaid manufacturing plant, having reduced toxicity and a lower chemical risk. The invention finds advantageous applications in the fields of civil and military aerospace propulsion, security and gas generation systems for emergency and non- emergency devices, as well as in the civil and military explosive field.

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# "Composite propellant manufacturing process based on deposition and light-activated polymerization for solid rocket motors"

## DESCRIPTION

### TECHNICAL FIELD

The present invention relates to heterogeneous energy materials and, in particular, to composite solid propellants for chemical rocket motors.

Specifically, the present invention relates to a manufacturing process, and to the relevant manufacturing plant, of composite solid propellants for chemical rocket motors.

The present invention finds advantageous applications in the fields of civil and military aerospace propulsion (missiles, space launchers, naval guns), security (airbag) and emergency power generation systems (gas-generators, swelling systems, portable chemical extinguishing systems, warning signs) as well as in the civil and military explosive field.

### STATE OF THE ART

It is known, from the patent document CN107283826, a hybrid manufacturing process simultaneously involving classical methods, such as crosslinking by means of thermostatic cycles in temperature-controlled ovens and adoption of photo-initiators.

Specifically, according to the aforesaid document and with reference to FIG. 1, a polymer (step 100) is added with a photosensitive polymer (step 101), into which powdered oxidising elements (step 102), suitable crosslinking agents of the family of isocyanates (step 103) and a photo-initiator (step 104) are incorporated.

Then all the ingredients are mixed (step 105) in preparation to the shaping step (step 106).

During manufacturing, the desired shape is imposed to the propellant thanks to a partial polymeric crosslinking borne by the photosensitive fraction (step 107), in order to obtain a structure capable of self-sustaining while maintaining the shape.

The following step provides the real and actual solidification ("curing") (step 108), which is carried out in a conventional way, by means of thermal cycles in appropriate ovens; this step is necessary for the definitive curing process by means of isocyanates, allowing the crosslinking of the remaining polymeric component.

The process according to the patent document CN107283826, therefore, is very complex and capable of reducing only the limits relevant to the producible geometries.

Moreover, the process according to the aforesaid document presents a high environmental impact, a considerable chemical risk for operators, high costs of the manufacturing due to the need of the curing step and considerable risks associated to the curing step.

Moreover, the process according to the aforesaid document does not make it possible to produce grains characterized by desired chemical non-uniformities, in order to better control the final performances of the grains themselves; in fact, it is not possible to vary the composition of the mixture and to obtain local modifications of the chemical composition used.

A manufacturing process, and the relevant manufacturing plant, of composite solid propellants for chemical rocket motors able to realize geometries of the grain currently precluded with chemical gradients thereinside, would satisfy the needs of several applications such as, for example, the civil and military aerospace propulsion, security and emergency power generation systems.

The present invention, which relates to such a manufacturing process and to the relevant manufacturing plant, aims at responding to the aforesaid needs.

In particular, the present invention aims at solving the technical problem concerning the internal geometries of the grain, necessary for the correct control and sizing of the thrust of the produced gas, currently severely limited by the manufacturing process based on mould casting and shaping with chuck.

Moreover, the present invention aims at achieving control of the chemical composition of the grain, allowing variations in the composition to better control the performance profile of the finished product; currently this has been achieved only with two different compositions with simple stratification (first part of grain composition A and second part of grain composition B, as per known technique developed for some military applications), therefore without a targeted local control.

Moreover, the present invention aims at decreasing the manufacturing risk associated with the curing step in oven with controlled temperature cycles; the elimination of this step not only aims at reducing costs, but also aims at reducing the risks associated with keeping at controlled temperature the almost shaped propellant grain.

Moreover, the present invention aims at reducing the chemical risk associated with the use of normally adopted crosslinking agents (isocyanates), which are known carcinogens; the replacement of these with suitable photo-initiators having characteristics of almost total non-toxicity reduces the risks associated with exposure during manufacturing, as well as the environmental impact during use, as well as the manufacturing cost.

It is also known the scientific publication by M.S. McClain, I.E. Gunduz e S.F. Son entitled "Additive manufacturing of ammonium perchlorate composite propellant with high solids loadings" and published by ELSEVIER, in which the results obtained after testing about three-dimensional printing of propellants obtained by mixing HTPB and powdered ammonium perchlorate (in addition to some additives and crosslinking agents) for a first family of samples and Illumabond 60–7105 and powdered ammonium perchlorate for a second family of samples are presented.

The aforesaid publication reports how it is possible to print small specimens by exploiting the characteristic of high viscosity of the propellant using HTPB as a binder and then curing in oven, and how it is possible to obtain crosslinking with ultraviolet radiation for 30 minutes through the use of Illumabond 60-7105.

In brief therefore, up to the present moment, as far as the Inventors know, there are no known solutions that simultaneously allow to expand the geometries achievable in manufacturing while guaranteeing control of the local chemical composition, simplifying the manufacturing process (with the aim of reducing costs and decreasing the risk associated thereto) as well as to reduce the chemical risk given the replacement of the classically used crosslinking agent (known carcinogen) with an adequate acting one, capable of crosslinking monomers commonly used or easily available and at low cost in few moments, immediately reaching the desired final result.

Therefore, the manufacturing process and the relevant manufacturing plant of composite solid propellants for chemical rocket motors according to the present invention intend to remedy this lack.

**OBJECTS AND SUMMARY OF THE INVENTION**

It is an object of the present invention to overcome the drawbacks of the prior art linked to the need of using a hybrid process, thus completely freeing from the use of classic crosslinkers (isocyanates), as well as from the thermal cycles step necessary for curing.

Furthermore, it is an object of the present invention to overcome the drawbacks of the prior art linked to the use of isocyanates as crosslinking agents, substantially reducing the chemical risk during manufacturing given the exposure of the operators, as well as during use given the generated gases.

These objects are achieved with the manufacturing process, and the relevant manufacturing plant, of composite solid propellant for chemical rocket motors according to the present invention that, advantageously and thanks to the presence of a photo-initiator, allow the polymerization and the layered local crosslinking of the composite solid propellant in one step.

The manufacturing process, and the relevant manufacturing plant, of composite solid propellant for chemical rocket motors according to the present invention for the first time, as far as the Inventors know, allows geometries nor realizable so far and local control of the chemical composition, substantially simplifying the associated manufacturing method, as well as reducing the risks related thereto (both in terms of safety, as well as from the point of view of chemical exposure to reagents).

Compared to the existing solutions, the present invention has, as advantages, the simplification of the process capable of reducing manufacturing and chemical exposure risks, as well as the total replacement of the curing step with temperature cycles, by means of ultraviolet radiation sufficient to obtain the finished product with exposure of only few seconds; the use of non-highly functionalized polymers also involves, together with the elimination of the isocyanates and the curing step under temperature control, the lowering of the manufacturing costs.

Specifically, the aforesaid and other objects and advantages of the invention, which will become apparent from the following description, are achieved with a manufacturing process according to claim 1.

Preferred embodiments and variants of the manufacturing process according to the present invention form the subject matter of the dependent claims 2 to 13.

Another independent aspect of the present invention relates to a manufacturing plant and forms the subject matter of claim 14.

Preferred embodiments and variants of the manufacturing plant according to the present invention form the subject matter of the dependent claims 15 to 19.

Another independent aspect of the present invention relates to a composite solid propellant for a chemical rocket motor and forms the subject matter of claim 20.

Preferred embodiments and variants of the composite solid propellant for a chemical rocket motor according to the present invention form the subject matter of the dependent claims 21 to 28.

It is understood that all the appended claims form an integral part of the present description and that each of the technical features claimed therein is possibly independent and autonomously usable with respect to the other aspects of the invention.

It will be immediately evident that countless changes (for example relevant to shape, sizes, arrangements and parts with equivalent functionalities) can be brought to what described without departing from the scope of the invention as claimed in the appended claims.

Advantageously, the technical solution according to the present invention allows:

- creating geometries precluded by the classic casting method;
- allowing detailed control on the chemical composition of the grain;
- reducing the manufacturing risk associated with the curing step in ovens with temperature control;
- reducing the chemical risk associated with the use of isocyanates as crosslinking agents, both during manufacturing and during use;
- reducing the manufacturing cost given the replacement of the curing step (with the related necessary instrumentation) with an ultraviolet radiation step; and
- reducing the manufacturing costs given the possibility of using non-highly

functionalized polymers, therefore of greater cost.

Further advantageous features will appear more evident from the following description of preferred but not exclusive embodiments, provided by way of pure and non-limiting example.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The present invention will be described hereinbelow by means of some preferred embodiments, given by way of non-limiting example, with reference to the attached drawings. These drawings illustrate different aspects and examples of the present invention and, where appropriate, similar structures, components, materials and/or elements in different figures are denoted by similar reference numbers.

FIG. 1 is a flowchart of a manufacturing process according to the prior art;

FIG. 2 is a flowchart of the manufacturing process according to the present invention;

FIG. 3 is a cut-away perspective view of a solid propellant rocket motor with the main components highlighted; and

FIG. 4 is a schematic representation of the manufacturing plant according to the present invention.

**DETAILED DESCRIPTION OF THE INVENTION**

While the invention is susceptible of various modifications and alternative constructions, some preferred embodiments are shown in the drawings and will be described in detail hereinbelow.

It should be understood, however, that there is no intention to limit the invention to the specific illustrated embodiments, but, on the contrary, the invention aims at covering all modifications, alternative constructions, and equivalents that fall in the scope of the invention as defined in the claims.

In the following description, therefore, the use of “for example”, “etc.”, “or” indicates non-exclusive alternatives without any limitation, unless otherwise indicated; the use of “also” means “including, but not limited to” unless otherwise indicated; the use of “includes / comprises” means “includes / comprises, but not limited to” unless otherwise indicated.

The present invention is based on the innovative concept of using the photo-crosslinking of a photosensitive polymer or of a resin made photosensitive by the addition of a suitable additive.

The polymer mainly used in the propulsive field is hydroxyl terminated polybutadiene (HTPB), which has a characteristic polymeric chain containing hydroxyl groups at the ends and a series of C=C or C-C double and single bonds inside the molecule.

A normal polyaddition crosslinking requires the addition of isocyanates (NCO functional group) in order to connect the molecules to each other by the action between the NCO functional groups and the hydroxyl terminations.

The Inventors have, instead, discovered that photo-crosslinking allows to exploit the C=C double bond, which is activated by the addition of a suitable additive that allows the opening of the double bond, which then becomes a radical, ready to be bound to another peer thereof under the action of the photo-initiator; in this way, the three-dimensional molecular chain necessary to give elastic properties is constructed, making the material solid.

In the present description, the term "photo-initiator" means Darocur 1173 or similar for function and ability to actively interact with the selected polymeric components.

In the present description, the term "crosslinking agent / curing agent" means a compound belonging to the family of isocyanates.

In the present description, the term "additives" means all those components, solid or liquid, added to the mixture with the intention of modifying its rheological characteristics during processing, as well as the mechanical and/or ballistic performances of the finished product and/or of stability and/or of aging; in order to consider the compound as an additive and not as a main reagent, the concentration preferably stands at maximum values of 5% by weight and certainly not higher than 10% by weight.

With reference to FIG. 1, it is observed that a manufacturing process according to the prior art comprises the following steps:

- preparing the prepolymer (step 100),
- preparing the photosensitive polymer (step 101),
- preparing the oxidiser (step 102),

- preparing the curing agent (step 103),
- preparing the photo-initiator agent (step 104),
- mixing the components (step 105),
- continuously depositing the material (step 106),
- partially curing the product by ultraviolet radiation (step 107), and
- curing the finished product with controlled temperature cycles (step 108).

With reference to FIG. 2, a manufacturing process of a composite solid propellant 1 for a chemical rocket motor 50 forms an aspect independent and usable autonomously with respect to the other aspects of the invention, which process comprises the following steps:

- preparing at least one oxidising solid component 2 (step 200);
- preparing at least one polymeric liquid component 3 (step 201);
- preparing at least one photo-initiator 4 (step 202);
- mixing the at least one oxidising solid component 2, the at least one polymeric liquid component 3 and the at least one photo-initiator 4 to obtain a mixture 5 (step 203);
- letting the mixture 5 to deposit through a deposition device 17 on a substrate or directly in the chemical rocket motor 50 (step 204);
- letting the mixture 5 to cure by light-activated polymerization through a lighting system 18, thus obtaining, by immediate crosslinking, the composite solid propellant 1 (step 205).

Optionally the manufacturing process of a composite solid propellant 1 for a chemical rocket motor 50 further comprises, between steps 202 and 203, the following steps:

- preparing at least one powdered fuel 6; and/or
- preparing at least one additive 7.

The composite solid propellant 1 according to the present invention is a grain that, preferably, has a diameter ranging between 1 cm and 500 cm, preferably between 10 cm and 350 cm, with a length/diameter ratio ranging between 0.1 and 50, preferably between 1 and 15.

Preferably the oxidising solid component 2 is chosen from ammonium perchlorate, ammonium nitrate, ammonium dinitramide, 1,3,5-Trinitroperhydro-1,3,5-triazine, 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane, 2,2-Dinitroethene-1,1-diammine, guanylurea dinitramide, Hexanitrohexaazaisowurtzitane, potassium nitrate, potassium perchlorate, sodium and nitroguanidine perchlorate, more preferably it is a crystalline oxidiser.

Preferably the polymeric liquid component 3 is chosen from diacrylate polybutadiene, hydroxyl polybutadiene, carboxylic polybutadiene, polypropylene glycol, polyethylene glycol, polybutadiene acrylonitrile and similar acrylates, polyalkylene oxide, polycaprolactone, adipate polyglycol, glycidyl azide polymer, polyglycidyl nitrate, biazidomethyloxethane in copolymer with other polymeric or monomeric substances or with catalysts, more preferably it is a monomer or a prepolymer.

Preferably the photo-initiator 4 is chosen from the compounds of the ketone family capable of activating radical polymerization reactions and, more preferably, from the compounds capable of activating the Norrish reactions; even more preferably the photo-initiator 4 is Darocure 1173.

Preferably the powdered fuel 6, having micrometric or nanometric size, is chosen from metal or metal alloys powders of beryllium, aluminium, boron, zirconium or magnesium, even mixed together; more preferably it is an aluminium metal powder; it is also possible the inclusion of nano-materials in the mixture with percentages higher than 5%.

The specific advantage given by the addition of the powdered fuel 6 resides in the ballistic characteristics of the propellant, given the density increase of the propellant and the combustion temperature increase.

Preferably the additive 7 is chosen from metal oxides (preferably of iron, lead, zirconium, copper, silicon or magnesium), their combinations at a level both atomic and in mechanical mixture, and fluorides (preferably of lithium).

The specific advantage given by the addition of the additive 7 is the possibility of exercising a detailed control (“fine tuning”) of the ballistic performances of the finished product.

Preferably the mixing of step 203 takes place under conditions below the ambient pressure, preferably between 300 mbar and 1 bar, for a mixing time ranging between half an hour and one day depending on the materials used and of the quantities employed, and at a temperature ranging between 35 °C and 100 °C, preferably ranging between 50 °C and 70 °C.

Preferably the mixture 5 has viscosity property ranging between 400 Pa.s and 10,000 Pa.s.

Preferably the deposition of step 204 takes place under conditions of ambient pressure and temperature, in a controlled composition atmosphere or standard air, with a speed ranging between 10 and 500 mm/s depending on the adopted deposition device 17, for a time ranging between 1 hour and 5 days, in relation to the size of the extruder nozzle (ranging from 0.5 mm to 5 cm in diameter), to the deposition thickness as well as to the volume to be extruded in order to realise the composite solid propellant 1. By way of example, a cylindrical grain is considered characterized by a diameter of 50 cm and a height of 1.5 m with a central hole of 10 cm in diameter; this will be characterized by a volume of about 28.2743 $cm^3$. By extruding with a nozzle of 1 $cm^2$ at a speed of 100 mm/s with a thickness of 5 mm, the process will require a manufacturing time of approximately 16 hours. By means of a lamination system, depositing the material in 1 mm thick successive layers, two hundred concentric passages are necessary in order to obtain the whole desired volume; with a deposition speed of 10 cm/min an estimated time of about 3 h is estimated.

Preferably the curing of step 205 takes place simultaneously with the deposition step 204, by means of an ultraviolet radiation system suitable for obtaining the composite solid propellant 1 and by radiating with the equivalent (in terms of exposure/power ratio) of 100 $mW/cm^2$ for 30-60 seconds.

Preferably the light-activated polymerization of step 205 takes place under conditions of ambient pressure and temperature, in a controlled composition atmosphere or standard air, by means of light-activated polymerization/curing reaction of radical type, following radiation with an ultraviolet system suitable for obtaining the composite solid propellant 1.

With reference to FIG. 3, it can be observed that a chemical rocket motor 50 comprises a casing 55, often internally lined with an insulating layer 54, that insulates the casing 55 from the real and actual grain 1 and from the high temperatures during operation.

Other fundamental elements of the chemical rocket motor 50 are the ignition system 51, the nozzle structure 57 characterized by a well-defined throat geometry 56; the geometry 53 internal to the grain 1 is also fundamental for the performance characteristics of the motor.

Through the careful definition in the design phase, it is possible to control the final performances of the chemical rocket motor 50.

With reference to FIG. 4, a manufacturing plant 10 of a composite solid propellant 1 for a chemical rocket motor 50 also forms an aspect independent and usable autonomously with respect to the other aspects of the invention, which plant comprises:

- a first storage tank 11 of at least one oxidising solid component 2,
- a second storage tank 12 of at least one polymeric liquid component 3,
- a third storage tank 13 of at least one photo-initiator 4,
- a mixer 16,
- a deposition device 17, and
- a lighting system 18.

Optionally, the manufacturing plant 10 further comprises:

- a fourth storage tank 14 of at least one powdered fuel 6.

Optionally, the manufacturing plant 10 further comprises:

- a fifth storage tank 15 of at least one additive 7.

Preferably the mixer 16 is a device equipped with mechanical agitators capable of making the product homogeneous and with sealing systems to prevent contamination of the mixture 5 mixture, and it is made available to the deposition and/or extrusion system.

Preferably the deposition device 17 is a system equipped with a dispenser having known shape and dimensions with suitable apparatus for continuous supply of mixed product, which supply may occur by piston system, by worm screw or by other similar system; more preferably it is an extruder or a lamination system.

The deposition device 17 is, in general, a supply system of the mixture then capable of extruding it through an opening or a nozzle of known dimensions, or by lamination of successive states with controlled thickness.

Preferably the lighting system 18 is an ultraviolet or visible radiation lighting system and it is positioned together with the deposition device 17 for obtaining the immediate crosslinking of the mixture 5 and, consequently, the composite solid propellant 1.

Moreover, a composite solid propellant 1 for a chemical rocket motor 50 forms an aspect independent and usable autonomously with respect to the other aspects of the invention, which composite solid propellant 1 comprises:

- at least one oxidising solid component 2,
- at least one polymeric liquid component 3,
- at least one photo-initiator 4.

Preferably, the composite solid propellant 1 is obtained by the manufacturing process or is produced in the manufacturing plant as previously described.

Preferably the composite solid propellant 1 is a grain having a diameter ranging between 1 cm and 500 cm, preferably between 10 cm and 350 cm, with a length/diameter ratio ranging between 0.1 and 50, preferably between 1 and 15.

The composite solid propellant 1 of the invention contains oxidiser between 40 and 95% by weight, preferably between 60 and 90% by weight, metal powders between 0 and 30% by weight, preferably between 0 and 22% by weight, polymer or prepolymer between 5% and 40% by weight, preferably between 10 and 20% by weight, and has visual properties of an opaque solid, having a white colouring if formed without the use of metal powders and additives, or a light grey colouring if enriched with metal powders, or a different colouring depending on the possible additive used and on its natural colouring; to the touch it is a compact and homogeneous solid with a gummy-tending consistency; the desired mechanical characteristics requires a tensile failure strength ranging between 0.3 and 0.9 MPa and a compression failure strength ranging between 7 and 17 MPa.

Preferably the at least one oxidising solid component 2 is chosen from ammonium perchlorate, ammonium nitrate, ammonium dinitramide, 1,3,5-Trinitroperhydro-

1,3,5-triazine, 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane, 2,2-Dinitroethene-1,1-diammine, guanylurea dinitramide, Hexanitrohexaazaisowurtzitane, potassium nitrate, potassium perchlorate, sodium and nitroguanidine perchlorate, more preferably it is a crystalline oxidiser.

Preferably the at least one polymeric liquid component 3 is chosen from diacrylate polybutadiene, hydroxyl polybutadiene, carboxylic polybutadiene, polypropylene glycol, polyethylene glycol, polybutadiene acrylonitrile and similar acrylates, polyalkylene oxide, polycaprolactone, adipate polyglycol, glycidyl azide polymer, polyglycidyl nitrate, biazidomethyloxethane in copolymer with other polymeric or monomeric substances or with catalysts, more preferably it is a monomer or a prepolymer.

Preferably the at least one photo-initiator 4 is chosen from the compounds of the ketone family capable of activating radical polymerization reactions and, more preferably, from the compounds capable of activating the Norrish reactions; even more preferably, the at least one photo initiator 4 is Darocure 1173.

Optionally, the composite solid propellant 1 further comprises:

- at least one powdered fuel 6; and/or
- at least one additive 7.

Preferably the at least one powdered fuel 6, having micrometric or nanometric size, is chosen from metal or metal alloys powders of beryllium, aluminium, boron, zirconium or magnesium, even mixed together; more preferably it is an aluminium metal powder; it is also possible the inclusion of nano-materials in the mixture with percentages higher than 5%.

Preferably the additive 7 is chosen from metal oxides (preferably of iron, lead, zirconium, copper, silicon or magnesium), their combinations at a level both atomic and in mechanical mixture, and fluorides (preferably of lithium).

The manufacturing process, the manufacturing plant and the composite solid propellant for chemical rocket motors according to the present invention are described in greater detail hereinbelow with reference to the following Examples, which have been developed on the basis of experimental data and which must be intended as illustrative but not limitative of the present invention.

**Example 1**

Formulation containing single-mode ammonium perchlorate 200 $\mu m$ as oxidiser 2 in a percentage of 80% by weight, HTPB as prepolymer 3 in a percentage ranging from 15 to 20% by weight, Darocure 1173 as photo-initiator 4 in a percentage of 4% on the prepolymer amount, aluminum powder 30 $\mu m$ as solid fuel 6 in a percentage ranging from 0 to 5% and Pentaerythritol tetrakis(3-mercaptopropionate) as additive 7 in a percentage of 14% of the prepolymer.

The whole is mixed and deposited in layers of variable thickness (tested 0.5 – 0.8 – 1.0 - 1.3 – 1.5 – 1.8 – 2.0 – 2.2 mm) and crosslinked both in inert environment and in standard atmosphere with ultraviolet radiation (spectrum concentration around 390 $nm$) with intensity equal to about 100 mW/cm$^2$ for 30-60 seconds.

The samples obtained show integrity and compactness, they are characterized by a white colouring if in the absence of metal powders, a silver colouring in the presence of metal powders; the surface is corrugated and dry to the touch.

**Example 2**

Formulation containing single-mode ammonium perchlorate 200-100 $\mu m$ as oxidiser 2 in a percentage of 80% by weight, HTPB as prepolymer 3 in a percentage ranging from 15 to 20% by weight, Darocure 1173 as photo-initiator 4 in a percentage of 4% on the prepolymer amount, aluminum powder 70 $\mu m$ as solid fuel 6 in a percentage ranging from 0 to 5% and Pentaerythritol tetrakis(3-mercaptopropionate) as additive 7 in a percentage of 14% of the prepolymer.

The whole is mixed and deposited in layers of variable thickness (tested 0.5 – 0.8 – 1.0 - 1.3 – 1.5 – 1.8 – 2.0 – 2.2 mm) and crosslinked both in inert environment and in standard atmosphere with ultraviolet radiation (spectrum concentration around 390 $nm$) with intensity equal to about 100 mW/cm$^2$ for 30-60 seconds.

The samples obtained show integrity and compactness, they are characterized by a white colouring if in the absence of metal powders, a light grey colouring in the presence of metal powders; the surface is corrugated and dry to the touch.

**Example 3**

Formulation containing single-mode ammonium perchlorate 200 $\mu m$ as oxidiser 2 in a percentage of 80% by weight, PBDDA as prepolymer 3 in a percentage ranging from 15 to 20% by weight, Darocure 1173 as photo-initiator 4 in a percentage of 4% on the prepolymer amount, aluminum powder 70 $\mu m$ as solid fuel 6 in a percentage ranging from 0 to 5%.

The whole is mixed and deposited in layers of variable thickness (tested 0.5 – 0.8 – 1.0 - 1.3 – 1.5 – 1.8 – 2.0 – 2.2 mm) and crosslinked both in inert environment and in standard atmosphere with ultraviolet radiation (spectrum concentration around 390 $nm$) with intensity equal to about 100 mW/cm$^2$ for 30-60 seconds.

The samples obtained show integrity and compactness, they are characterized by a slightly amber colouring if in the absence of metal powders, a light grey colouring in the presence of metal powders; the surface is corrugated and dry to the touch.

**Example 4**

Formulation containing single-mode ammonium perchlorate 200-100 $\mu m$ as oxidiser 2 in a percentage of 80% by weight, PBDDA as prepolymer 3 in a percentage ranging from 15 to 20% by weight, Darocure 1173 as photo-initiator 4 in a percentage of 4% on the prepolymer amount, aluminum powder 70 $\mu m$ as solid fuel 6 in a percentage ranging from 0 to 5%.

The whole is mixed and deposited in layers of variable thickness (tested 0.5 – 0.8 – 1.0 - 1.3 – 1.5 – 1.8 – 2.0 – 2.2 mm) and crosslinked both in inert environment and in standard atmosphere with ultraviolet radiation (spectrum concentration around 390 $nm$) with intensity equal to about 100 mW/cm$^2$ for 30-60 seconds.

The samples obtained show integrity and compactness, they are characterized by a slightly amber colouring if in the absence of metal powders, light grey colouring in the presence of metal powders; the surface is corrugated and dry to the touch.

The manufacturing process, the manufacturing plant and the composite solid propellant for chemical rocket motors according to the present invention are compared with known solutions, as described hereinbelow.

The values reported for the known art refer to specimens characterized by compositions similar to those tested in laboratory; it should be remembered that these values refer to propellants produced with the classical method, whereby through the use of HTPB as polymeric element, isocyanates as crosslinking elements and ammonium perchlorate as oxidiser.

The ranges and values reported for propellants according to the prior art are indicative, since they are influenced by variations in composition and by the application speed of the load during the test.

The tested ranges and values for the propellants according to the invention are calculated as the maximum and minimum obtained values from tests performed on the family of specimens made for each composition.

No distinction is made between material enriched with metal powders and material free from metal powders, since the variation in mechanical amounts is not significant.

The results of the comparison between the present invention and the known solutions are summarized in the below Table.

TABLE

| | Propellant according to a classical process | Propellant according to the invention - HTPB | Propellant according to the invention - PBDDA |
|---|---|---|---|
| Tensile failure strength [MPa] | 0.30 – 0.90 | 0.49 – 0.87 | 0.59 – 1.59 |
| Compression failure strength [MPa] | 7 - 17 | 6.10 – 9.15 | 3.30 – 4.23 |

The above Table shows how the propellants according to the invention are comparable to what is commonly used, actually making them a viable alternative. This feature is essential in order to show the possibility of use of the proposed propellant in the hypothesized application fields, since it must fulfil defined mechanical characteristics in order to be suitable for the chosen use.

However, it should be underlined how these features are determined by a degree of controllability; by modifying the specific ratios between the various constituent elements, it is possible to bring the produced propellant towards the desired failure strength value, moving in any case within the limits imposed by the mission loads.

As it can be deduced from the above, the innovative technical solution herein described has the following advantageous features:

- production of geometries precluded before;
- elimination of the curing step in thermostatic oven;
- elimination of toxic and known carcinogenic chemical reagents (isocyanates);
- simplification of the manufacturing process with achievement of the finished product by means of a single manufacturing step;
- possibility of fine tuning with variation of the percentages of reagents during the deposition step, in order to obtain a chemical gradient (and therefore a performance gradient) in the grain .

From the above description it is evident, therefore, how the manufacturing process, the manufacturing plant and the composite solid propellant for chemical rocket motors according to the present invention allow to achieve the proposed objects.

It is equally evident, to a person skilled in the art, that it is possible to make modifications and further variations to the solution described with reference to the attached figures, without thereby departing from the teaching of the present invention and from the scope as defined by the appended claims.

CLAIMS

1. A manufacturing process of a composite solid propellant (1) for a chemical rocket motor (50) comprising the following steps:
   - preparing at least one oxidising solid component (2) (step 200);
   - preparing at least one polymeric liquid component (3) (step 201);
   - preparing at least one photo-initiator (4) (step 202);
   - mixing said at least one oxidising solid component (2), at least one polymeric liquid component (3) and at least one photo-initiator (4) to obtain a mixture (5) (step 203);
   - letting said mixture (5) to deposit through a deposition device (17) on a substrate or directly in the chemical rocket motor (50) (step 204);
   - letting said mixture (5) to cure by light-activated polymerization through a lighting system (18), thus obtaining, by immediate crosslinking, the composite solid propellant (1) (step 205).
2. The manufacturing process according to claim 1 further comprising, between steps 202 and 203, the following steps:
   - preparing at least one powdered fuel (6); and/or
   - preparing at least one additive (7).
3. The manufacturing process according to claim 1 or 2, wherein said composite solid propellant (1) is a grain, said grain having a diameter ranging between 1 cm and 500 cm, preferably between 10 cm and 350 cm, with a length/diameter ratio ranging between 0.1 and 50, preferably between 1 and 15.
4. The manufacturing process according to any of the preceding claims, wherein said at least one oxidising solid component (2) is chosen from ammonium perchlorate, ammonium nitrate, ammonium dinitramide, 1,3,5-Trinitroperhydro-1,3,5-triazine, 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane, 2,2-Dinitroethene-1,1-diammine, guanylurea dinitramide, Hexanitrohexaazaisowurtzitane, potassium nitrate, potassium perchlorate, sodium and nitroguanidine perchlorate, preferably it is a crystalline oxidiser.
5. The manufacturing process according to any of the preceding claims, wherein said at least one polymeric liquid component (3) is chosen from diacrylate

polybutadiene, hydroxyl polybutadiene, carboxylic polybutadiene, polypropylene glycol, polyethylene glycol, polybutadiene acrylonitrile and similar acrylates, polyalkylene oxide, polycaprolactone, adipate polyglycol, glycidyl azide polymer, polyglycidyl nitrate, biazidomethyloxethane in copolymer with other polymeric or monomeric substances or with catalysts, preferably it is a monomer or a prepolymer.

6. The manufacturing process according to any of the preceding claims, wherein said at least one photo-initiator (4) is chosen from the compounds of the ketone family capable of activating radical polymerization reactions and, preferably, from the compounds capable of activating the Norrish reactions.

7. The manufacturing process according to any of the preceding claims, wherein said at least powdered fuel (6), having micrometric or nanometric size, is chosen from metal or metal alloys powders of beryllium, aluminium, boron, zirconium or magnesium, even mixed together, it is preferably an aluminium metal powder.

8. The manufacturing process according to any of the preceding claims, wherein said at least one additive (7) is chosen from metal oxides (preferably of iron, lead, zirconium, copper, silicon or magnesium), their combinations at a level both atomic and in mechanical mixture, and fluorides (preferably of lithium).

9. The manufacturing process according to any of the preceding claims, wherein the mixing of step 203 takes place under conditions below the ambient pressure, preferably between 300 mbar and 1 bar, for a mixing time ranging between half an hour and one day depending on the materials used and of the quantities employed, and at a temperature ranging between 35 °C and 100 °C, preferably ranging between 50 °C and 70 °C.

10. The manufacturing process according to claim 9, wherein said mixture (5) has the viscosity property ranging between 400 Pa.s and 10,000 Pa.s.

11. The manufacturing process according to any of the preceding claims, wherein the deposition of step 204 takes place under conditions of ambient pressure and temperature, in a controlled composition atmosphere or standard air, with a speed ranging between 10 and 500 mm/s depending on the adopted deposition device (17), for a time ranging between 1 hour and 5 days, in relation to the size of

the extruder nozzle (ranging from 0.5 mm to 5 cm in diameter) and to the deposition thickness both in the case of nozzle and lamination system, as well as to the volume to be extruded in order to realise the composite solid propellant (1).

12. The manufacturing process according to any of the preceding claims, wherein the curing of step 205 takes place simultaneously with the deposition step 204, by means of an ultraviolet radiation system suitable for obtaining the composite solid propellant (1) and by radiating with the equivalent (in terms of exposure/power ratio) of 100 $mW/cm^2$ for 30-60 seconds.

13. The manufacturing process according to claim 12, wherein the light-activated polymerization of step 205 takes place under conditions of ambient pressure and temperature, in a controlled composition atmosphere or standard air, by means of light-activated polymerization/curing reaction of radical type, following radiation with an ultraviolet system suitable for obtaining the composite solid propellant (1).

14. A manufacturing plant (10) of a composite solid propellant (1) for a chemical rocket motor (50) comprising:
    - a first storage tank (11) of at least one oxidising solid component (2),
    - a second storage tank (12) of at least one polymeric liquid component (3),
    - a third storage tank (13) of at least one photo-initiator (4),
    - a mixer (16),
    - a deposition device (17), and
    - a lighting system (18).

15. The manufacturing plant (10) according to claim 14, further comprising:
    - a fourth storage tank (14) of at least one powdered fuel (6).

16. The manufacturing plant (10) according to claim 14 or 15, further comprising:
    - a fifth storage tank (15) of at least one additive (7).

17. The manufacturing plant (10) according to any claims 14 to 16, wherein the mixer (16) is a device equipped with mechanical agitators capable of making the product homogeneous and with sealing systems to prevent contamination of the mixture (5).

18. The manufacturing plant (10) according to any claims 14 to 17, wherein the

deposition device (17) is a system equipped with a dispenser having definite shape and dimensions with suitable continuous supply apparatus of the mixed product, which supply may occur by piston system, worm screw or other similar system, the deposition device (17) preferably being an extruder or a laminator.

19. The manufacturing plant (10) according to any claims 14 to 18, wherein the lighting system (18) is an ultraviolet or visible radiation lighting system and it is positioned together with the deposition device (17) for obtaining the immediate crosslinking of the mixture (5) and, consequently, the composite solid propellant (1).

20. A composite solid propellant (1) for a chemical rocket motor (50) comprising:
- at least one oxidising solid component (2),
- at least one polymeric liquid component (3),
- at least one photo-initiator (4),

obtained by the manufacturing process according to any claims 1 to 13 or produced in the manufacturing plant according to any claims 14 to 19.

21. The composite solid propellant (1) according to claim 20, wherein said composite solid propellant (1) is a grain, said grain having a diameter ranging between 1 cm and 500 cm, preferably between 10 cm and 350 cm, with a length/diameter ratio ranging between 0.1 and 50, preferably between 1 and 15.

22. The composite solid propellant (1) according to claim 20 or 21, having visual properties of an opaque solid, having a white colouring if formed without the use of metal powders and additives, or a light grey colouring if enriched with metal powders, or a different colouring depending on the possible additive used and on its natural colouring; to the touch it is a compact and homogeneous solid with a gummy-tending consistency; its mechanical characteristics has a tensile failure strength ranging between 0.3 and 0.9 MPa and a compression failure strength ranging between 7 and 17 MPa.

23. The composite solid propellant (1) according to any claims 20 to 22, wherein said at least one oxidising solid component (2) is chosen from ammonium perchlorate, ammonium nitrate, ammonium dinitramide, 1,3,5-Trinitroperhydro-1,3,5-triazine, 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane, 2,2-Dinitroethene-1,1-diammine, guanylurea

dinitramide, Hexanitrohexaazaisowurtzitane, potassium nitrate, potassium perchlorate, sodium and nitroguanidine perchlorate, preferably it is a crystalline oxidiser.

24. The composite solid propellant (1) according to any claims 20 to 23, wherein said at least one polymeric liquid component (3) is chosen from diacrylate polybutadiene, hydroxyl polybutadiene, carboxylic polybutadiene, polypropylene glycol, polyethylene glycol, polybutadiene acrylonitrile and similar acrylates, polyalkylene oxide, polycaprolactone, adipate polyglycol, glycidyl azide polymer, polyglycidyl nitrate, biazidomethyloxethane in copolymer with other polymeric or monomeric substances or with catalysts, preferably it is a monomer or a prepolymer.

25. The composite solid propellant (1) according to any claims 20 to 24, wherein said at least one photo-initiator (4) is chosen from the compounds of the ketone family capable of activating radical polymerization reactions and, preferably, from the compounds capable of activating the Norrish reactions.

26. The composite solid propellant (1) according to any claims 20 to 25, further comprising:
   - at least one powdered fuel (6); and/or
   - at least one additive (7).

27. The composite solid propellant (1) according to claim 26, wherein said at least one powdered fuel (6), having micrometric or nanometric size, is chosen from metal or metal alloys powders of beryllium, aluminium, boron, zirconium or magnesium, even mixed together, it is preferably an aluminium metal powder.

28. The composite solid propellant (1) according to claim 26 or 27, wherein said at least one additive (7) is chosen from metal oxides (preferably of iron, lead, zirconium, copper, silicon or magnesium), their combinations at a level both atomic and in mechanical mixture, and fluorides (preferably of lithium).

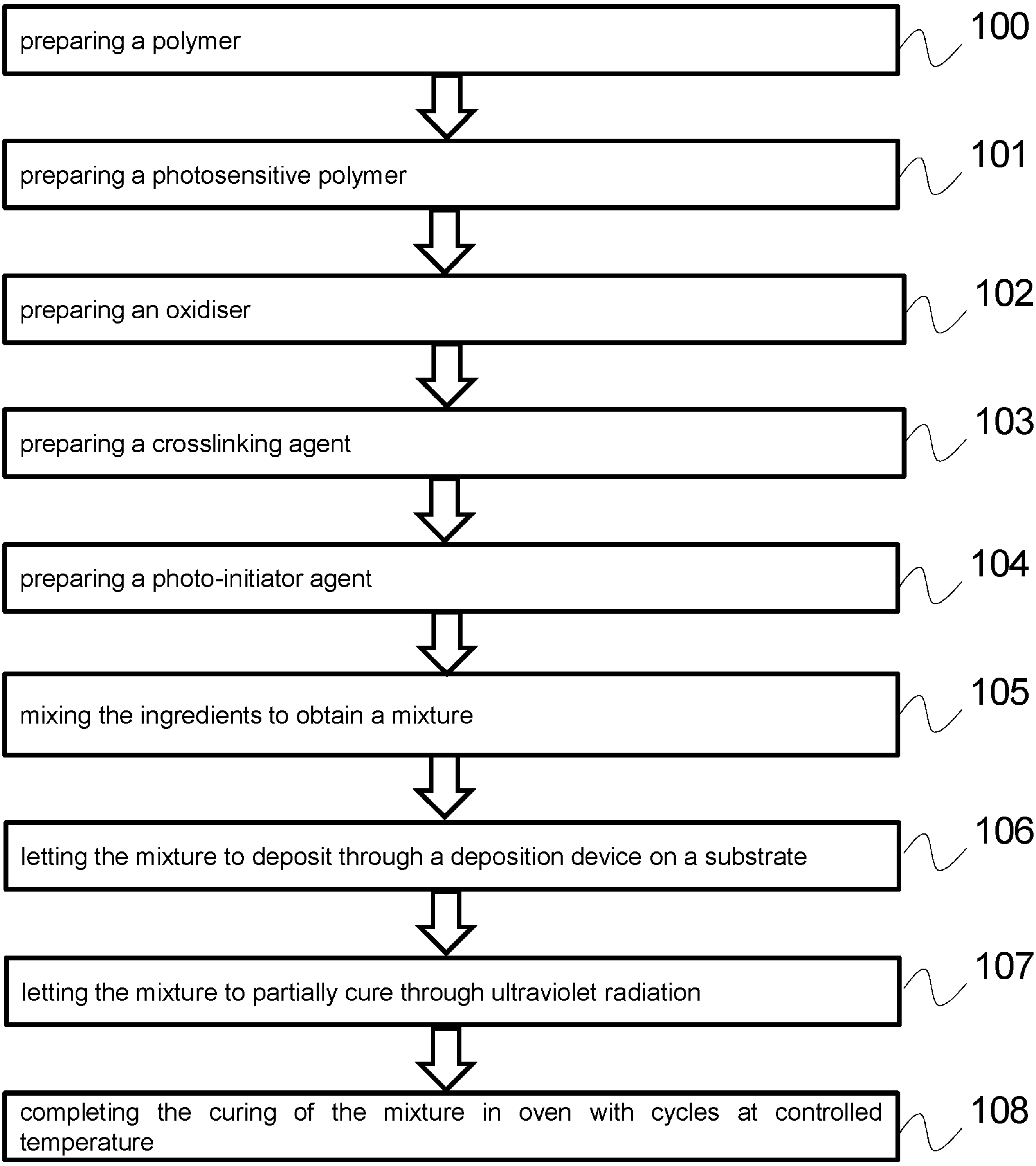


Fig. 1

PRIOR ART

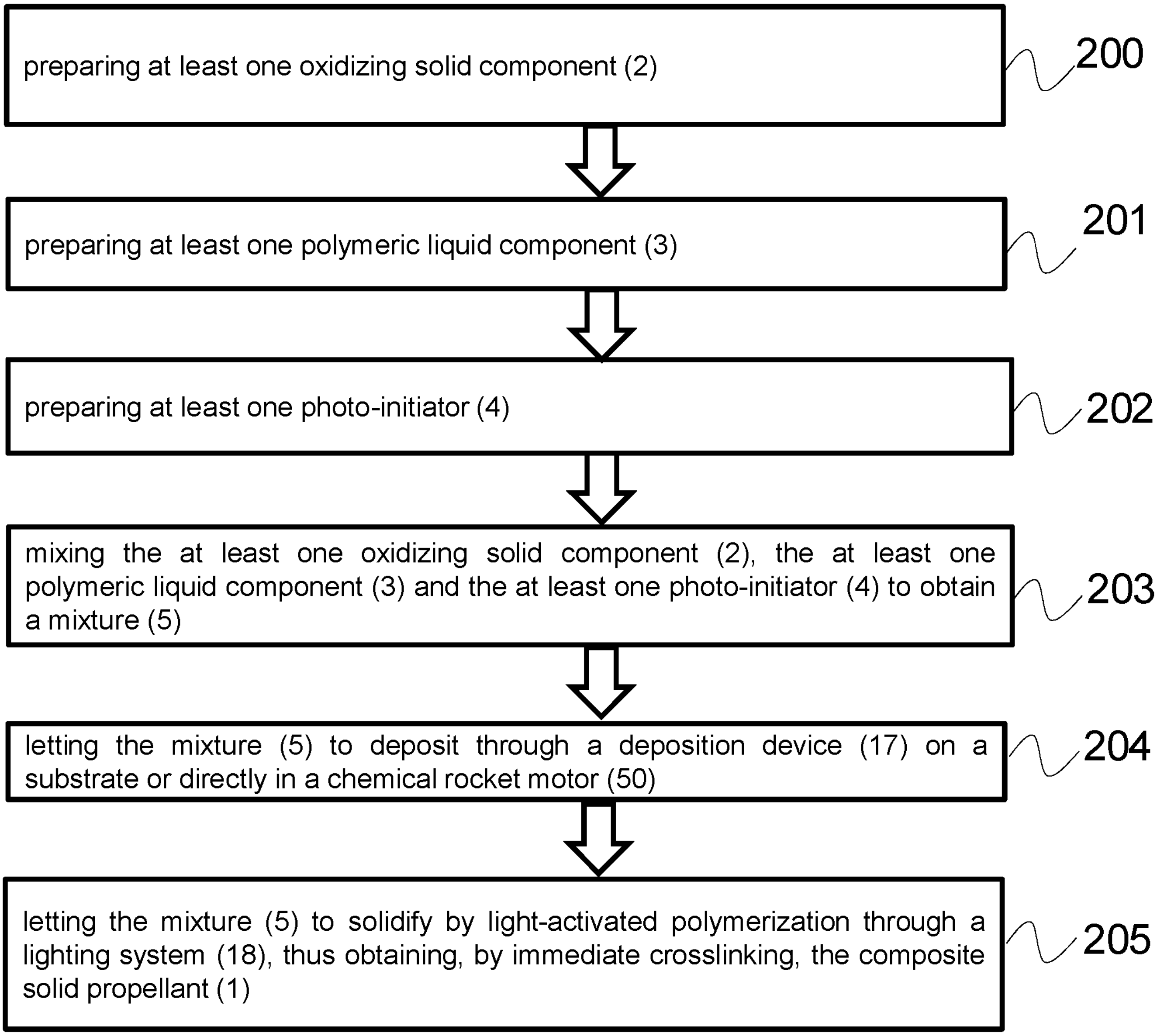
preparing at least one oxidizing solid component (2)
200
preparing at least one polymeric liquid component (3)
201
preparing at least one photo-initiator (4)
202
mixing the at least one oxidizing solid component (2), the at least one polymeric liquid component (3) and the at least one photo-initiator (4) to obtain a mixture (5)
203
letting the mixture (5) to deposit through a deposition device (17) on a substrate or directly in a chemical rocket motor (50)
204
letting the mixture (5) to solidify by light-activated polymerization through a lighting system (18), thus obtaining, by immediate crosslinking, the composite solid propellant (1)
205

Fig. 2

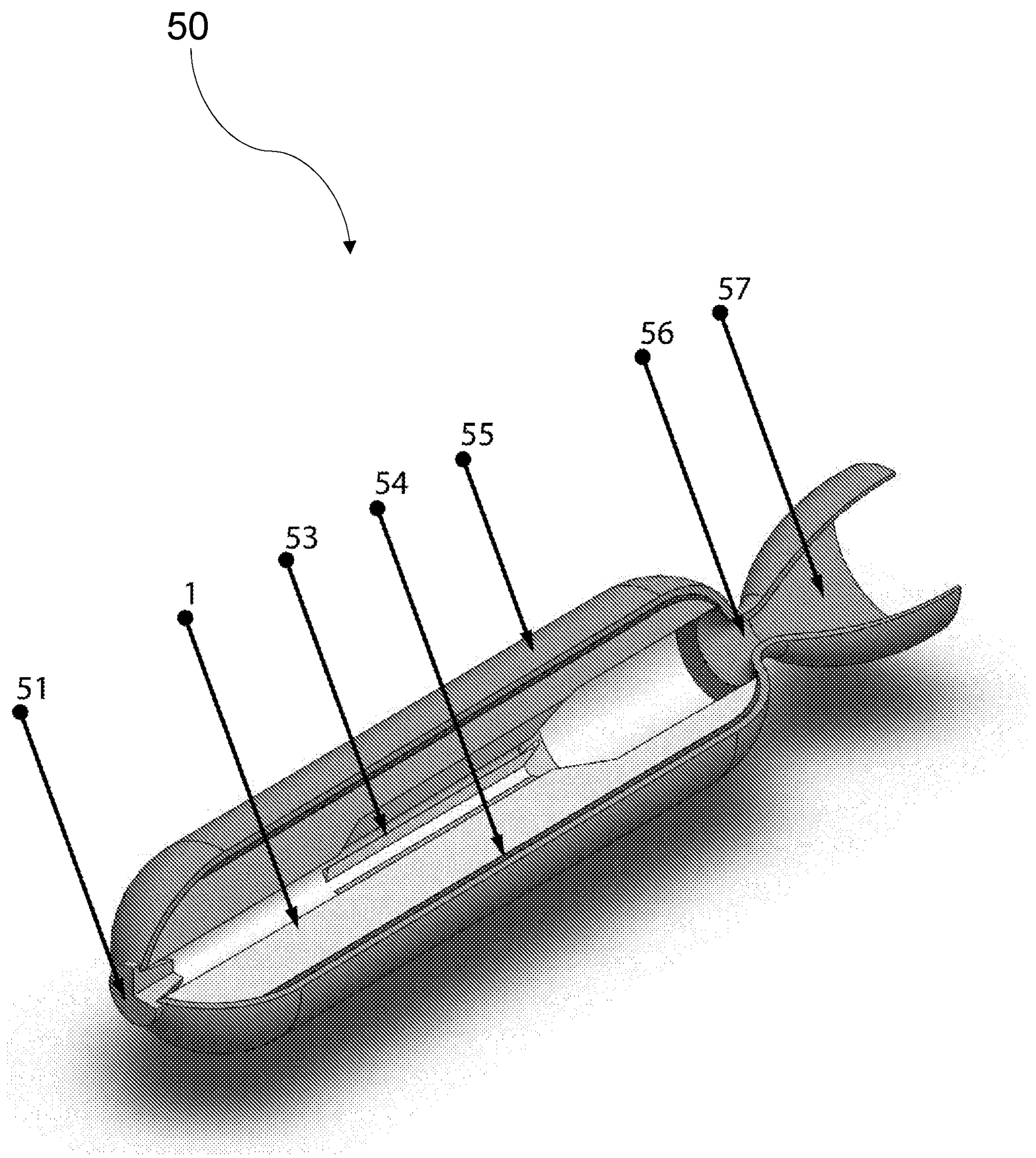


Fig. 3

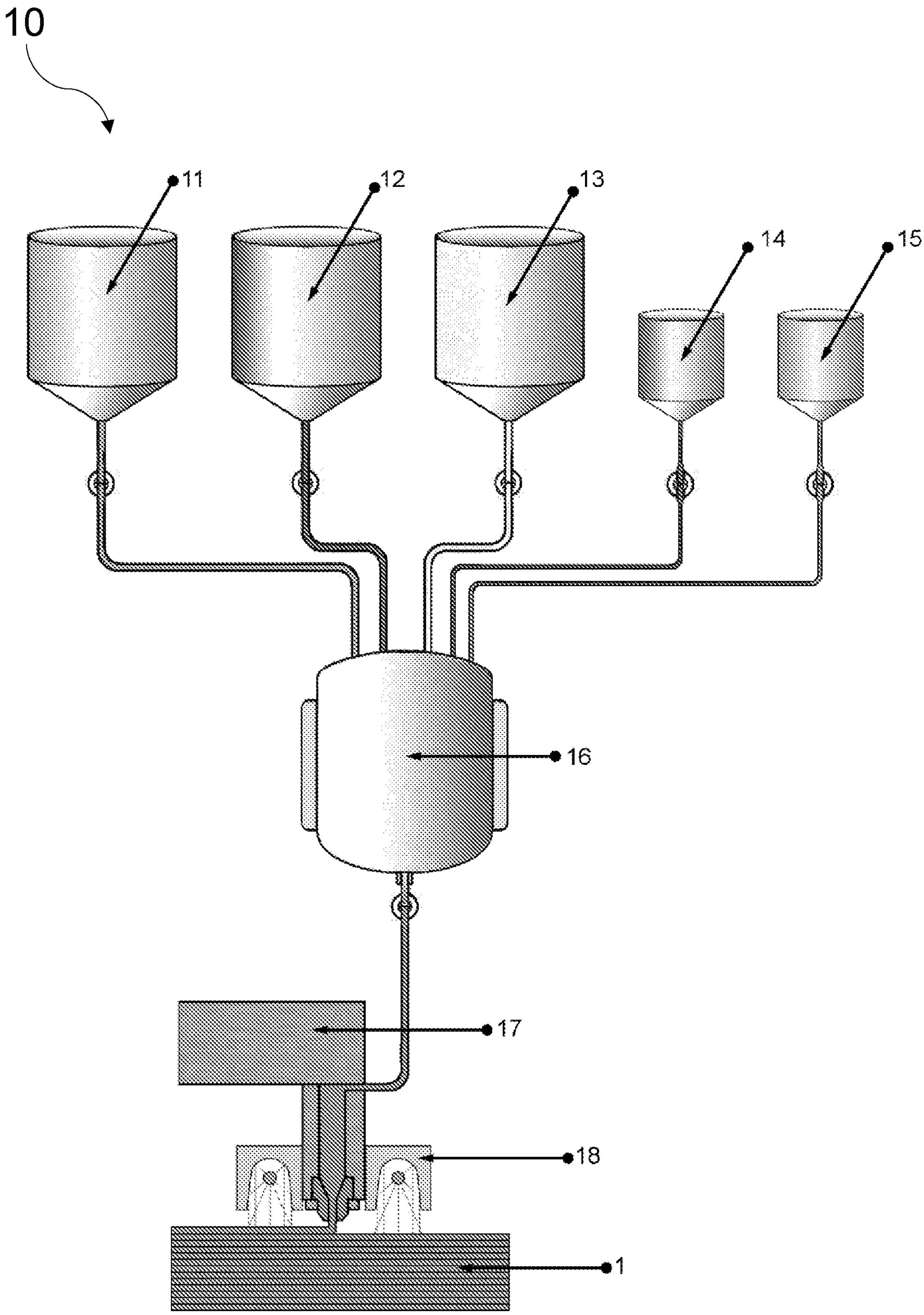


Fig. 4

# INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2020/052947

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C06B21/00 C06B45/10

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)

C06B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | US 2019/055171 A1 (STRAATHOF MICHIEL HANNES [NL] ET AL) 21 February 2019 (2019-02-21) paragraphs [0040], [0041], [0056], [0064]; claims 1, 8, 20, 24 | 1-28 |
| X | US 2018/194699 A1 (SPENCE THEODORE R [US] ET AL) 12 July 2018 (2018-07-12) paragraph [0014]; claims 1, 12, 13, 22-24, 38 | 1-28 |

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

[X] See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 9 July 2020 | 17/07/2020 |

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

# INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2020/052947

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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