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(71) Applicant: UNIVERSITE DE LIEGE [BE/BE]; Place du
XX Aout, 7, 4000 Liege (BE).

(72) Inventors: SCHRIJNEMAKERS, Audrey; Universite De
Liege, LCIS - GreenMAT, Quartier Agora, Allée du six
Août 13, 4000 Liege (BE). BOSCHINI, Frédéric; Uni-
versité de Liège, LCIS - GreenMAT, Quartier Agora, Allée
du six Août 13, 4000 Liege (BE). CLOOTS, Rudi; Uni-

versité de Liège, LCIS - GreenMAT, Quartier Agora, Allée
du six Août 13, 4000 Liege (BE).

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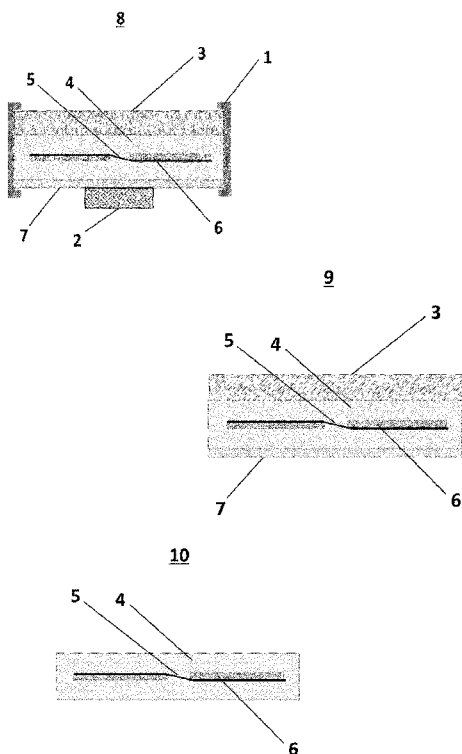


FIG.1

(57) Abstract: A method for recycling/recovering a core (9) of a silicon solar cells module (8) in its raw components comprising: d) providing a core (9) of a silicon solar cells module wherein the cells (6) are interconnected by connection ribbons (5) and embedded in an encapsulation layer (4) said encapsulation layer (4) being sandwiched between a back sheet (7) and a front glass plate (3); e) introducing the core (9) of the silicon solar cells into a reactor; f) dismantling the solar cells core (9) by hydrothermal treatment under subcritical atmosphere to generate recovered clean glass component and a residual laminate (10).



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Method for recycling photovoltaic solar cells module.

The present invention relates to a method for recycling/recovering

- 5 photovoltaic(PV) cells module by hydrothermal treatment , particularly the method comprise a one step dismantling of photovoltaic cells core of the module into its raw components under hydrothermal subcritical conditions preferably under oxidant hydrothermal subcritical conditions.

- 10 Photovoltaic modules production has considerably increased during the last decades and we are now in a stage of end-of-life modules. Moreover there are also a significant number of wastes generated during the production process or resulting from mechanical damages in the module during transport, delivery and / or placement.

- 15 Consequently it is becoming essential to recycle photovoltaic cells modules in order to reduce a negative environmental impact. European Union has even issued a guideline called European WEEE directive to fix rules about end of live photovoltaic modules. According to such guideline, the entire photovoltaic module in terms of its raw components should be recovered.

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A photovoltaic module contains components such as glass, aluminum, organic material, silicon and metallic contacts that may be recovered and reused, either in new photovoltaic modules or in other products.

- 25 Typically, a photovoltaic module is made of silicon solar cells, also called silicon wafers ; metal contacts between the cells; an encapsulation layer that encloses the cells and the contacts; a front glass plate and a back-side foil for isolation or alternatively a second glass plate on the back side. The back-side foil is a polymeric layer generally made of halogenated-polymers such as for example

polyvinylidene fluoride (PVDF) whereas the encapsulation layer is generally made of polyethylene vinyl acetate (EVA). The metallic contacts between the cells are generally made of silver/tin/lead alloys.

The photovoltaic module is generally framed with aluminum and contains a
5 junction box.

Recycling/recovery starts by a primary manual dismantling at room temperature of the aluminum frame and the metallic contacts. Such primary dismantling is induced by a mechanical strain on the glass plate generating small defects in
10 glass that may lead to cracking and/or swelling of the PV module. As the encapsulation layer sticks hardly to the photovoltaic cells and to the glass plate, breakage of the photovoltaic silicon cells cannot be avoided and reuse of all photovoltaic cells is difficult.

15 Currently, the most common way to separate the raw components of a photovoltaic cell module consists in burning the encapsulation layer in a conveyor belt furnace at a temperature from 450°C to 600°C .By this burning method, organic materials of the photovoltaic module cannot be reused but inorganic fractions such as glass, metallic ribbons, silicon wafers are recovered.

20 Nevertheless the burning method has significant drawbacks:

- combustion of halogenated-polymers makes waste gas treatment necessary;
- metallic contacts components are melting and diffusing at high temperature into other photovoltaic components such as glass and silicon wafers. It makes purification steps necessary for recovery of high purity silicon;
- 25 -vaporization of heavy metals such as tin, lead, silver during burning of the encapsulation layer makes waste gas treatment necessary;
- poor separation of inorganic fraction due to the metallic contamination affects quality of recovered components.

- Yamashita Katsuya from Sharp Corp describes in JP 2006093336 a method of taking out silicon material from solar cells modules enclosed into polyethylene vinyl acetate (EVA). He uses a multi steps process. Sharp teaches to immerse first the modules in a chemical solution such as nitric acid to promote a
- 5 decomposition of EVA. After the immersion step; the module is washed with pure water and then introduced into a reactor as a third step. In the reactor the module is exposed to supercritical atmosphere so that EVA is decomposed in a jelly-like state. The decomposition reaction of EVA is linked to such prior immersion step that should not be too short .If such immersion step is not long
- 10 enough further cracking of solar cells occurs. Sharp also reports that the EVA is solidified again when decreasing temperature from supercritical or subcritical atmosphere and the solar cells are encapsulated in the EVA again. The resolidified EVA should therefore be cut mechanically in a fourth step to obtain the solar cells .
- 15 Sharp method is complex and requires an immersion step in chemical solution to avoid the solar cells to be embedded in the encapsulating layer (EVA) again when decreasing the temperature of the reactor. The modules extracted from the reactor should be cut to provide the solar cells.
- 20 There is therefore a need to develop a new, easier, preferably greener recycling method providing recycled/recovered raw components of a photovoltaic cells module without metallic contamination and keeping/recovering their initial electrical property such as semiconductor conductivity.
- 25 We have now found a method for photovoltaic cells module recycling/recovering comprising a dismantling in one step of the core of the module in water under subcritical preferably low subcritical condition. The method is performed, preferably in oxidant condition that allows to degrade and remove organic compounds, reduces mass and volume of the waste photovoltaic module and to

recover valuable components with a low percentage of metallic contamination. Clean glass component is also generated by such one-step method of dismantling.

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According to a first embodiment, the method according to the invention comprises a dismantling in a reactor of the solar cell module in order to separate glass component from the other components of the module by using subcritical hydrothermal conditions.

10

Water is environmentally the safest material and the cheapest of all solvents. It can act as a mineralizer or a catalyst under elevated pressure-temperature conditions. Thermodynamic and transport properties of subcritical water are remarkably different from those of ambient water or from water in supercritical condition. A method using water in subcritical condition has the advantage to work under pressure and temperature that are lower than water in supercritical state and is therefore safer and economic on an energetic point of view. Moreover water in subcritical water condition is more easily processed at industrial level for large quantity of modules.

15

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Under water subcritical conditions, solubility of nonpolar species increases, whereas the solubility of ionic and polar compounds decreases. As a result, there is a drop of polarity of water, molecular mobility increases due to a decrease in solvent viscosity (η). Drastic changes of ionic hydration are brought about by a decrease in dielectric constant (ϵ) and density (ρ).

25

The term "hydrothermal treatment" has been defined in the art as "any heterogeneous chemical reaction in presence of a solvent (whether aqueous or non-aqueous) above room temperature and at pressures greater than 1 atm (or

0.1 MPa) in a closed system. However in the present invention, hydrothermal treatment refers to a method involving dismantling reactions carried out in water facilitated by high temperatures and high pressures conditions.

- 5 Water plays an important role in hydrothermal photovoltaic modules recycling treatment wherein it does not only act as solvent, but is also a main reactant for degradation of organic components. Indeed, at high pressure-temperature conditions usually employed in hydrothermal processes, water has a high reactivity and is able to break chemical bonds in complex molecules like
- 10 polymers and convert them into simpler compounds. Water used in hydrothermal treatment is able to depolymerize the back-side foil and to generate organic flakes.

- Hydrothermal treatment in subcritical conditions involves a combination of a
- 15 temperature and a pressure that allows water to remain liquid at a temperature above its boiling point.

- Typically in subcritical conditions, temperature of water varies between its atmospheric boiling point and its critical temperature (374°C), preferably between 200 and 220°C and the pressure has to be raised between 0.1 and 21.8
- 20 MPa preferably 2 MPa. Low subcritical conditions corresponds to a temperature between 120 and 250 °C and a pressure between 0.1 and 5.0 MPa.

- Regarding water autogenous pressure temperature between 120 and 220°C and pressure between 0.1 and 2.2 MPa is preferred. Such conditions are particularly attractive at an industrial level.

25

Hydrothermal treatment are carried out in a reactor specially designed to resist to such high temperature and pressure conditions, either in a vertically or an horizontally position such as drum reactor.

When photovoltaic solar cells cores are submitted to hydrothermal treatment in subcritical conditions, glass peeling occurs off the core. Simultaneously the back foil sheet also peels off from the core and may be partly depolymerized. Organic flakes and clean glass are generated after one step of hydrothermal treatment. It also remains a residual laminate wherein the silicon solar cells and its metal contacts needs subsequent treatment to be recovered.

Hydrothermal treatment may be repeated several times on the residual laminate provided from a previous hydrothermal treatment to obtain further residual fragments and to further eliminate organic compounds.

According to another embodiment, the method according to the invention comprises a dismantling in a reactor of the solar cell module in order to separate glass component from the other components of the module by using oxidant subcritical hydrothermal conditions.

Oxidant subcritical conditions can be generated by using water with a liquid or gaseous oxidizing agent.

A Liquid oxidizing agent is an oxidant acid particularly inorganic or organic oxacid such as nitric acid; peroxyntic acid, chromic acid, manganic acid, hydrogen peroxide, halogenated oxacid, and the like or a combination thereof; or a compound generating ozone or oxygen. Practically nitric acid and hydrogen peroxide or a mixture thereof are preferred because they exhibit lower toxicity for environment and they are not damaging reactor vessel.

Gaseous oxidizing agents are for example oxygen, ozone, fluor, chlore, brome, iode, protoxyde of nitrogen and the like. The most preferred gaseous oxidizing agent is oxygen.

When photovoltaic solar cells cores are submitted to hydrothermal treatment in oxidant subcritical conditions, glass peeling occurs off the core and residual fragment are generated. Simultaneously the back foil sheet is also peeling and de-polymerization of the encapsulant layer progress more quickly than with
5 water in subcritical conditions. The back foil sheet is totally eliminated from the core of the module.

Oxidant hydrothermal treatment may be repeated several times on residual fragments resulting from a previous dismantling step and allows to recover most components of the PV module, particularly silicon and the metal components.
10

In a preferred embodiment, an oxidant hydrothermal treatment under subcritical condition of the method according to the invention comprises an oxidant acid, preferably an acid selected from the group comprising or consisting of nitric acid,
15 hydrogen peroxide or a combination thereof.

Oxidant hydrothermal treatment in subcritical conditions such as with nitric acid, allows advantageously to improve de-polymerization of the back sheet in the core or to improve de-polymerization of the encapsulation layer in the laminate. Oxidant hydrothermal treatment in subcritical conditions allows to recover
20 silicon. Selective recovery of metals are carried out by precipitation and/or electrolysis treatments.

The subcritical conditions using nitric acid in water are performed at a
25 temperature between 107°C and 374°C, preferably 130°C and 180°C, most preferably at 150°C.

Preferably the subcritical conditions are maintained in the reactor during several hours at an autogenous pressure of 0.5 to 2.5 MPa.

In another preferred embodiment, the oxidant hydrothermal treatment under subcritical condition of the method according to the invention comprises a supply of oxidant gas in the reactor. The most preferred oxidant gas is oxygen.

- 5 The subcritical conditions using oxygen as oxidant are performed at a temperature between 150°C and 374°C, preferably between 150 and 250°C, most preferably at 190°C.

Preferably the subcritical conditions are maintained during several hours with a permanent supply of oxygen.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention may be more completely understood in consideration of the following detailed description of embodiments according to the invention with the accompanying drawings, in which:

- 5 FIG. 1 illustrates a schematic view of a photovoltaic module (8) , its core (9) and its laminate (10) that can be dismantled according to the invention.

FIG.2 illustrates a schematic view of a reactor that implements the method according to the invention.

- Fig.3 illustrates a temperature-pressure diagram of water up to its supercritical
10 state. Various filling volumes of the reactor are illustrated corresponding to different T-P conditions of the diagram.

- In figure 1, a photovoltaic module (8) is schematically illustrated. The module (8) comprises a laminate (10) made of a photoactive material such as silicon solar cells (6) that are connected together with metal contacts (5) between the cells
15 (6). The silicon solar cells (6) are generally made silicon and are encapsulated in a polymeric layer also called encapsulation layer (4). The encapsulation layer (4) may be polyethylene vinyl acetate also called EVA or PEVA.

- The laminate (10) is protected by a front glass plate (3) and a back side foil (7) made of a polymeric layer comprising halogenated polymers, for example
20 polyvinylidene fluoride. Such an assembly (9) is called core of photovoltaic module. The core is generally framed with aluminum (1). The module still contains a junction box (2) at the back side of the module(8).

- In figure 2, a reactor is schematically illustrated. The reactor is made of stainless
25 steel. and comprises the following elements :

A pressure gage (11) connected at the top of the reactor to measure ambient pressure inside the reactor

A gas inlet valve (12) and a gas release valve (13) to respectively introduce gas into the reactor or to release it.

- 5 A liquid sampling valve (14) allows to collect sample from the reactor during the hydrothermal treatment.

A safety rupture disc assembly (15) allows to drop the pressure to 1 atm (or 0.1 MPa) in case of emergency.

- 10 A head with cooling coil (16) is used to adjust temperature during hydrothermal treatment and to cool the reaction medium at the end of the treatment

A sealing clamp(17) allows to seal the reactor during treatment at high temperature and pressure

A cooling coil serpentine (18) is located inside the reactor and used to control temperature. The reactor is partially located inside a furnace (19)

- 15 A dip tube (20) allows to extract samples from inside of the reactor during hydrothermal treatment

A stirrer (21) allows to homogenize the oxidant reaction medium

- 20 Inside diameter and height of the reactor are 140 mm and 385 mm respectively. Its total capacity is approximatively 5.9l. The real content volume with stirrer, cooling coil and dip tube system is around 5.6l.

The reactor allows the treatment of piece of PV panel with one solar cell height and three solar cells length to be dismantled. Samples made of core of PV modules of about (10cm x 10cm) are used

- 25 During treatment samples are slipped horizontally between the loops of the cooling serpentine. Hydrothermal treatment in subcritical conditions

($180^{\circ}\text{C} < T < 374^{\circ}\text{C}$) in pure water for a period less than or equal to 6 hours are performed. Time processing may be reduced by addition of a base such as sodium hydroxide.

- 5 In figure 3, the reactor autogenous pressure is illustrated versus temperature of water medium for various filling volume of the reactor.

DETAILED DESCRIPTION

The following detailed description should be read with reference to the figures. The detailed description and the figures, which are not necessarily to
10 scale, discloses embodiments according to the invention and are not intended to limit the scope of the invention.

Example 1: method of dismantling with water under subcritical atmosphere

First, the junction box (2) (approximately 2 wt.% of the total weight of the module) and aluminum frame (1) (approximately 16 wt.% of the total weight of
15 the module) are mechanically removed from an out-of-order photovoltaic module (8) during a primary dismantling.

After this primary dismantling, the core of the panel remains. The core of the panel is then introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) together with de-ionized water and exposed to
20 low subcritical atmosphere.

The low subcritical atmosphere is formed by water as medium. An autogenous pressure is generated in the reactor and is directly correlated to temperature and filling volume. The table 1 gives the autogenous pressure generated into the reactor (Parr instruments model 4580 hydrothermal bomb) in function of the
25 temperature for a filling volume between 32 and 80 %.

Temperature ($^{\circ}\text{C}$)	Autogeneous Pressure (MPa)*
100	0.07

150	0.4
170	0.7
180	0.9
200	1.5
220	2.2
250	5.0
*for 32 % < filling level of the reactor < 80 %	

Table 1 Autogenous pressure versus temperature of water medium for various filling volume of the reactor (Parr instruments model 4580 hydrothermal bomb). Experimental values

5

As shown on figure 3, the curve between the triple point, where the gaseous, liquid and solid phase coexist, and the critical point (C), where the density and others properties of liquid and gas are identical), corresponds to the saturated vapor curve (dash dot line on the graph of figure 3). The saturated vapor curve corresponds to the conditions where the liquid and gaseous phases coexist. At pressure value below the pressure value corresponding to the saturated vapor curve, the liquid phase is absent and vapor phase is not saturated whereas, at pressure value above the pressure value corresponding to the saturated vapor curve, the liquid phase is under compression and vapor phase is absent.

15

In the method according to the invention, the dismantling step is performed in the reactor under conditions that the critical temperature and pressure (critical point C on the graph figure 3) are never reached , nor the supercritical state.

Isochores (black curves on the graph figure 3) give the pressure inside the heated close reactor as a function of the filling volume.

20

When the filling volume is lower than 32 %, the liquid-gas interface decreases and for a given temperature the reactor is completely filled with the gaseous phase. In these conditions, fractions cannot be released from the core of photovoltaic module.

25

When the filling volume is greater than 32 %, the density of the liquid phase decreases whereas the density of gaseous phase increases and, the liquid-gas

interface increases with temperature. In this case, the pressure increases in function of the temperature in the reactor. Higher is the filling volume, lower is the temperature at which the reactor is completely filled with the liquid phase. Exposed to these conditions, protective glass (3) and halogenated-polymers from the backsheet or the entire backsheet (7) versus its composition peel off from the core of photovoltaic module. Recovered glass is clean and can directly reintegrate a glass production line. The residual laminate (10) constituted of silicon solar cells and its connection ribbon embedded between encapsulation layers, needs subsequent treatment to recover the other components. It is possible to use the same water medium several times. Identical results were obtained when keeping the same water medium for five consecutive badge treatments.

15 Example 1bis: method of dismantling with nitric oxide or (nitric acid + hydrogen peroxide) subcritical atmosphere

The method of dismantling is performed according to example 1 but the core of the panel is introduced into the reactor together with nitric acid at a concentration 32wt.% in de-ionized water and exposed to an oxidant subcritical atmosphere. Regarding this example, the oxidant subcritical atmosphere is formed by nitric acid 32 wt.% as medium but nitric acid concentration can be halved by hydrogen peroxide 30 wt.% in a 2:1 molar ratio. In such a latter case, the medium is made of nitric acid or nitric acid/hydrogen peroxide mix in de-ionized water with quantity of 2.4l.

25 Inside the reactor, the temperature is set at 150°C. The autogenous pressure is controlled and measured with value around 0.5 MPa. These atmosphere conditions were maintained for a holding time of 3 hours.

Further to the 3 hours oxidant subcritical atmosphere treatment in the reactor, two fractions are generated in one step from the core of the photovoltaic

module. The solid fraction is made of glass/silicon fragments mix and a tin precipitate (which represents approximately 70 wt.% of total weight of the module) while the liquid fraction contains dissolved metallic ribbons (also called metal connections) and metallic grid contact (which represents approximately 1 wt.% of total weight of the module) are leached from the silicon solar cells. The liquid fraction also contains organic residues resulting from the backsheet oxidation and encapsulation layer oxidation (approximately 11 wt% of total weight of the module). A tin precipitate can be removed from the solid fraction by leaching with a slight basic solution NH_4OH 1M. Glass/silicon fragments mix could be separated by a mechanical process. Further treatment is still needed to go on with the recovery of raw metal component. Selective recovery of metals are carried out by precipitation and/or electrolysis treatment. Metals oxidation by nitric acid releases a huge volume of NO_x gas (particularly NO_2 and NO) and pressure rises sharply during the oxidation reaction to reach a pressure value higher than 2.5 MPa.

Example 2: method with water in subcritical atmosphere- no influence of CO_2

First process consisting in removing mechanically the junction box (2) and aluminum frame (1) from the out-of-order photovoltaic module (8) is identical to the primary dismantling described in example 1. After this first dismantling, the core of the panel is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding this example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity is identical than previously described in example 1. Regarding the present example, the medium is made of water with quantity of 2.4l.

Before heating the reactor, the air volume above the liquid water media is substituted by a pressure of 0.1 MPa of carbon dioxide gas (CO_2). Inside this reactor, the atmosphere temperature was set to 200°C. The autogenous

pressure was controlled and measured with value around 1.6 MPa. These atmosphere conditions were maintained for holding time of 6 hours. Exposed to the subcritical atmosphere of the reactor, fractions cannot be released from the core of photovoltaic module. Only protective glass (3) and halogenated-polymers from the backsheet peel off slightly from the core of photovoltaic module.

Example 3: method with water in subcritical atmosphere- no influence of nitrogen

First process consisting in removing mechanically the junction box (2) and aluminum frame (1) from the out-of-order photovoltaic module (8) is identical to the primary dismantling described above in the example 1. After this first process, the core of the panel is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity is identical than previously described in example 1. Regarding the present example, the medium is made of water with quantity of 2.4l. Before heating the reactor, the air volume above the liquid water media is substituted by a pressure of 0.1 MPa of nitrogen gaz (N_2). Inside this reactor, the atmosphere temperature was set to 200°C. The autogenous pressure was controlled and measured with value around 1.6 MPa. These atmosphere conditions were maintained for holding time of 6 hours. Exposed to the subcritical atmosphere of the reactor, fractions cannot be released from the core of photovoltaic module. Only protective glass (3) and halogenated-polymers from the backsheet peel off slightly from the core of photovoltaic module.

Example 4: method with water in subcritical atmosphere- influence of water quantity -no influence of air

First process consisting in removing mechanically the junction box (2) and aluminum frame (1) from the out-of-order photovoltaic module (8) is identical to the primary dismantling described above in the example 1. After this first process, the core of the panel is introduced into the reactor (Parr instruments
5 model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity is identical than previously described in example 1. Regarding the present example, the medium is made of water with quantity of 1.4l. Before heating the reactor, the gas
10 volume (approximatively 4l) above the liquid water media is composed of air (approximatively 78 mol.% N₂ and 21 mol.% O₂). Inside this reactor, the atmosphere temperature was set to 200°C. The autogenous pressure was controlled and measured with value around 1.5 MPa. These atmosphere conditions were maintained for holding time of 6 hours. Exposed to the
15 subcritical atmosphere of the reactor, fractions cannot be released from the core of photovoltaic module.

Example 5: method with water in subcritical atmosphere- influence of air (21 mol. % O₂)

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First process consisting in removing mechanically the junction box (2) and aluminum frame (1) from the out-of-order photovoltaic module (8) is identical to the primary dismantling described above in the example 1. After this first process, the core of the panel (9) is introduced into the reactor (Parr instruments
25 model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1. Regarding the present example, the medium is made of water with quantity of 2.4l. Here, it is possible to use the same water

medium several times. Identical results were obtained when keeping the same water medium for five consecutive badge treatments. Before heating the reactor, the gas volume (approximately 3l) above the liquid water media is composed of air (approximately 78 mol.% N₂ and 21 mol.% O₂). Inside this reactor, the atmosphere temperature was set to 200°C. The autogenous pressure was controlled and measured with value around 1.5 MPa. These atmosphere conditions were maintained for holding time of 6 hours. Exposed to the subcritical atmosphere of the reactor, protective glass (3) and halogenated-polymers from the backsheet or the entire backsheet (7) versus its composition peel off from the core of photovoltaic module. Recovered glass is clean and can directly reintegrate a glass production line. The residual laminate (10) constituted of silicon solar cells and its connection ribbon embedded between encapsulation layers, needs subsequent treatment to recover the other components. It could be the process described in the example 1 or in the example 6.

Example 6: method with water in subcritical atmosphere- influence of O₂

First process consisting in removing mechanically the junction box (2) and aluminum frame (1) from the out-of-order photovoltaic module (8) is identical to the primary dismantling described above in the example 1. After this first process, the core of the panel is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1.

Regarding the present example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 200°C. The autogenous pressure was controlled and measured with value around 1.5 MPa. When temperature reaches 200°C inside the reactor, a pressure of 0.1 MPa of dioxygen gas (O₂) was added to the subcritical atmosphere. As oxygen was

consumed, reactor was continuously fed with oxygen by step of 0.1 MPa. These atmosphere conditions were maintained for holding time of 6 hours. Exposed to the oxidant subcritical atmosphere of the reactor, all fractions can be released from the core of photovoltaic module. The solid fraction contains protective glass (3), solar cells (6) fragments partially released from the encapsulant, encapsulant scrap and connection ribbons (5). The solution contains organic residues resulting from backsheet and encapsulant layer oxidation (approximately 11 wt% of total weight of the module). Gas chromatography coupled to mass spectroscopy measurement was made on the residual solution and are reported in table 2. After the dismantling of the core of photovoltaic module, the water medium contains branches alkanes with various chains length and some ketones due to the breakage of esters functional group from the EVA (ethylene vinyl acetate) encapsulation layer.

The gaseous phase (reactor residual pressure approximately 0.25 MPa) contains carbon dioxide formed by complete oxidation of a part of polymers materials. Connection ribbons/glass/solar cells fragments mix could be separated by subsequent mechanical process.

Molecule	Retention time	Hexane extraction	Dichloromethane extraction
2,4-pentanedione	5.41	No	Yes
nonane	8.89		
2,2dihydroxy-1-phenyl-ethanone	11.10	No	Yes
decane	12.10		
3-penten-2-one	14.23	No	Yes
undecane	15.24		
dodecane	18.24		
1,3-bis(1,1-dimethyl)benzene	19.66	No	Yes
tridecane	21.09		
tetradecane	23.75		
pentadecane	26.26		
hexadecane	28.67		
heptadecane	30.94		
octadecane	33.10		
nonadecane	35.14		

eicosane	37.11		
heneicosane	38.99		
docosane	40.77		
tricosane	42.50		
tetracosane	44.16		
pentacosane	45.75		
hexacosane	47.30		
heptacosane	48.77		
octacosane	50.20		
nonacosane	51.58		
triacontane	52.93		

Table 2 : molecules identified by Gas chromatography coupled to mass spectroscopy measurement on the residual solution

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Example 7: method with water in subcritical atmosphere- under permanent O₂ supply

First process consisting in removing mechanically the junction box (2) and aluminum frame (1) from the out-of-order photovoltaic module (8) is identical to the primary dismantling described above in the example 1. After this first process, the core of the panel is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical than previously described in example 1. Regarding the present example, the medium is made of water with quantity of 2.4l. Inside the reactor, the atmosphere temperature was set to 190°C. The autogenous pressure was controlled and measured with value around 1.2 MPa. When temperature reaches 190°C inside the reactor, a pressure of 0.1 MPa of dioxygen gaz (O₂) was added to the subcritical atmosphere. As oxygen was consumed, reactor was continuously fed with oxygen by step of 0.1 MPa. These atmosphere conditions were maintained for holding time of 4 hours. Exposed to the oxidant subcritical atmosphere of the

reactor, protective glass (3) almost completely peel off from the core of photovoltaic module (figure 3) and backsheet (7) almost totally breaks up due to oxidation of polymers materials. The residual laminate (10) constituted of photoactive material and its connection ribbons embedded between encapsulant layers, needs subsequent treatment to recover the other components. It could be the process described in the example 1 or in the example 6 or 7.

Example 8: Residual laminate treatment with water in subcritical atmosphere-under permanent O₂ supply

- 10 The residual laminate (10) constituted of solar cells and its connection ribbons embedded between encapsulant layers, is obtained by one of the process described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present
- 15 example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1. Regarding the present example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 170°C. The autogenous pressure was controlled and measured with value around 0.7 MPa.
- 20 When temperature reaches 170°C inside the reactor, a pressure of 0.1 MPa of dioxygen gaz (O₂) was added to the subcritical atmosphere. As oxygen was consumed, reactor was continuously fed with oxygen to keep total pressure 0.1 MPa above the autogeneous pressure. These atmosphere conditions were maintained for holding time of 2 hours. Exposed to the oxidant subcritical
- 25 atmosphere of the reactor, de-polymerization of the encapsulation layer in the laminate doesn't occur. The solar cells and its connection ribbons cannot be released from the residual laminate.

Example 9: Residual laminate treatment with water in subcritical atmosphere-under permanent O₂ supply

The residual laminate (10) constituted of solar cells and its connection ribbons embedded between encapsulant layers, is obtained by one of the process described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1.

Regarding this example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 190°C. The autogenous pressure was controlled and measured with value around 1.2 MPa. When temperature reaches 190°C inside the reactor tank, a pressure of 0.1 MPa of dioxygen gaz (O₂) was added to the subcritical atmosphere. As oxygen was consumed, reactor was continuously fed with oxygen to keep total pressure 0.1 MPa above the autogeneous pressure. These atmosphere conditions were maintained for holding time of 4 hours. Exposed to the oxidant subcritical atmosphere of the reactor, de-polymerization of the encapsulation layer in the laminate begins. The medium takes a light yellow color but, the solar cells and its connection ribbons cannot be released from the residual laminate.

Example 10: Residual laminate treatment with water in subcritical atmosphere-under permanent O₂ supply

The residual laminate (10) constituted of solar cells and its connection ribbons embedded between encapsulant layers, is obtained by one of the process described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1.

Regarding the present example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 190°C. The autogenous pressure was controlled and measured with value around 1.2 MPa. When temperature reaches 190°C inside the reactor, a pressure of 0.3 MPa of
5 dioxygen gaz (O_2) was added to the subcritical atmosphere. As oxygen was consumed, reactor was continuously fed with oxygen to keep the total pressure 0.3 MPa above the autogeneous pressure. These atmosphere conditions were maintained for a holding time of 4 hours. Exposed to the oxidant subcritical atmosphere of the reactor, de-polymerization of the encapsulation layer in the
10 laminate begins. The medium takes a yellow brown color but and, the solar cells and its connection ribbons are partially released from the residual laminate.

Example 11: Residual laminate treatment with water in subcritical atmosphere-
under permanent O_2 supply

The residual laminate (10) constituted of solar cells and its connection ribbons
15 embedded between encapsulant layers, is obtained by one of the process described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor
20 dimensions and capacity are identical as previously described in example 1. Regarding this example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 190°C. The autogenous pressure was controlled and measured with value around 1.2 MPa. When temperature reaches 190°C inside the reactor, a pressure of 0.5 MPa of
25 dioxygen gaz (O_2) was added to the subcritical atmosphere. As oxygen was consumed, reactor was continuously fed with oxygen to keep the total pressure 0.5 MPa above the autogeneous pressure. These atmosphere conditions were maintained for holding time of 4 hours. Exposed to the oxidant subcritical atmosphere of the reactor, complete de-polymerization of the encapsulation

layer in the laminate occurs. The medium takes a yellow color but and, the solar cells and its connection ribbons are completely released from the residual laminate.

Example 12: Residual laminate treatment with water in subcritical atmosphere-
under permanent O₂ supply

The residual laminate (10) constituted of solar cells and its connection ribbons embedded between encapsulant layers, is obtained by one of the process described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1. Regarding the present example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 190°C. The autogenous pressure was controlled and measured with value around 1.2 MPa. When temperature reaches 190°C inside the reactor, a pressure of 0.5 MPa of dioxygen gaz (O₂) was added to the subcritical atmosphere. As oxygen was consumed, reactor tank was continuously fed with oxygen to keep the total pressure 0.5 MPa above the autogeneous pressure. These atmosphere conditions were maintained for a holding time of 2 hours. Exposed to the oxidant subcritical atmosphere of the reactor, partial de-polymerization of the encapsulation layer in the laminate occurs. The medium takes a yellow color but and, the solar cells and its connection ribbons cannot be released from the residual laminate.

Example 13: Residual laminate treatment with water in subcritical atmosphere-
under permanent O₂ supply

The residual laminate (10) constituted of solar cells and its connection ribbons embedded between encapsulant layers, is obtained by one of the process

described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1. Regarding this example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 170°C. The autogenous pressure was controlled and measured with value around 0.7 MPa. When temperature reaches 170°C inside the reactor, a pressure of 0.5 MPa of dioxxygen gaz (O_2) was added to the subcritical atmosphere. As oxygen was consumed, reactor was continuously fed with oxygen to keep the total pressure 0.5 MPa above the autogeneous pressure. These atmosphere conditions were maintained for holding time of 4 hours. Exposed to the oxidant subcritical atmosphere of the reactor, de-polymerization of the encapsulation layer in the laminate occurs. The medium takes a yellow color and, the solar cells and its connection ribbons are released from the residual laminate but, de-polymerisation of the encapsulant is not complete. Silicon fragments remain sticky.

Example 14: Residual laminate treatment with water in subcritical atmosphere-
under permanent O_2 supply

The residual laminate (10) constituted of solar cells and its connection ribbons embedded between encapsulant layers, is obtained by one of the process described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1. The medium is made of water with quantity of 2.4l. Inside the reactor, the atmosphere temperature was set to 150°C. The autogenous pressure was

controlled and measured with value around 0.4 MPa. When temperature reaches 150°C inside the reactor, a pressure of 1 MPa of dioxygen gaz (O_2) was added to the subcritical atmosphere. As oxygen was consumed, the reactor was continuously fed with oxygen to keep the total pressure 1 MPa above the autogeneous pressure. such atmosphere conditions were guaranteed for a holding time of 4 hours. Exposed to the oxidant subcritical atmosphere of the reactor, de-polymerization of the encapsulation layer in the laminate begins. When extracted from the reactor, the surface of laminate is sticky but, the medium remains colorless. The solar cells and its connection ribbons cannot be released from the residual laminate.

Example 15: Residual laminate treatment with water in subcritical atmosphere-under permanent O_2 supply

The residual laminate (10) constituted of solar cells and its connection ribbons embedded between encapsulant layers, is obtained by one of the process described in the example 5, 6 or 7. After this first process, the residual laminate is introduced into the reactor (Parr instruments model 4580 hydrothermal bomb) (figure 2) and exposed to subcritical atmosphere. Regarding the present example, the subcritical atmosphere is formed by water as medium. Reactor dimensions and capacity are identical as previously described in example 1. Regarding this example, the medium is made of water with quantity of 2.4l. Inside this reactor, the atmosphere temperature was set to 170°C. The autogenous pressure was controlled and measured with value around 0.7 MPa. When temperature reaches 170°C inside the reactor, a pressure of 1 MPa of dioxygen gaz (O_2) was added to the subcritical atmosphere. As oxygen was consumed, reactor tank was continuously fed with oxygen to keep the total pressure 1 MPa above the autogeneous pressure. These atmosphere conditions were guaranteed for holding time of 2 hours. Exposed to the oxidant subcritical atmosphere of the reactor, de-polymerization of the encapsulation layer in the laminate occurs. The medium takes a light yellow color and, the solar cells and its

connection ribbons are released from the residual laminate but, depolymerisation of the encapsulant is not complete. Silicon fragments remain sticky.

CLAIMS

1. A method for recycling/recovering a core of a silicon solar cells module(9)
in its raw components comprising :
 - 5 a) providing a core (9) of a silicon solar cells module wherein the cells (6)
are interconnected by connection ribbons (5) and embedded in an
encapsulation layer (4) said encapsulation layer(4) being sandwiched
between a back sheet (7) and a front glass plate (3) ;
 - b) introducing the core (9) of the silicon solar cells into a reactor;
 - 10 c) dismantling the solar cells core into the reactor by hydrothermal
treatment under subcritical atmosphere to generate recovered clean
glass component and a residual laminate (10);
characterized in that the hydrothermal treatment under subcritical
atmosphere is an oxidant hydrothermal treatment.
- 15
2. A method according to claim 1 further comprising an additional
treatment of the residual laminate to recover silicon.
- 20 3. A method according to claim 2 wherein such additional treatment is a
second oxidant hydrothermal treatment
4. A method according to anyone of claim 1 to 3 wherein the oxidant
hydrothermal treatment comprises an acid selected from nitric acid,
25 hydrogen peroxide or a mixture thereof.
5. A method according to claim 4 wherein a nitric acid atmosphere is
generated from a water medium comprising between 30 and 65 wt.%
nitric acid, preferably between 30 and 35 wt.%, most preferably 32 wt.%.

6. A method according to claim 4 wherein nitric acid and hydrogen peroxide are mixed in a ratio from 2:1
- 5 7. A method according to anyone of claim 1-6 wherein the oxidant hydrothermal treatment is generated at a temperature between 130°C and 150°C and a pressure between 0.5 and 2.5 MPa
8. A method according to claim 7 wherein the oxidant hydrothermal
10 treatment is maintained during 3 to 6 hours -
9. A method according to anyone of claim 1 to 3 wherein the oxidant hydrothermal treatment comprises an oxidant gas.
- 15 10. A method according to claim 9 wherein the oxidant gas is oxygen.
11. A method according to claim 10 wherein oxygen is provided in the reactor at a pressure of 0.1 MPa .
- 20 12. A method according to anyone of claim 10 to 11 wherein the oxidant hydrothermal treatment is generated at a temperature between 150°C and 250°C, preferably 190°C and a pressure between 0.5 and 2.5 MPa.
13. A method according to anyone of claim 10 to 12 wherein the oxidant
25 hydrothermal treatment is maintained during 3 to 6 hours with a permanent supply of oxidant gas.

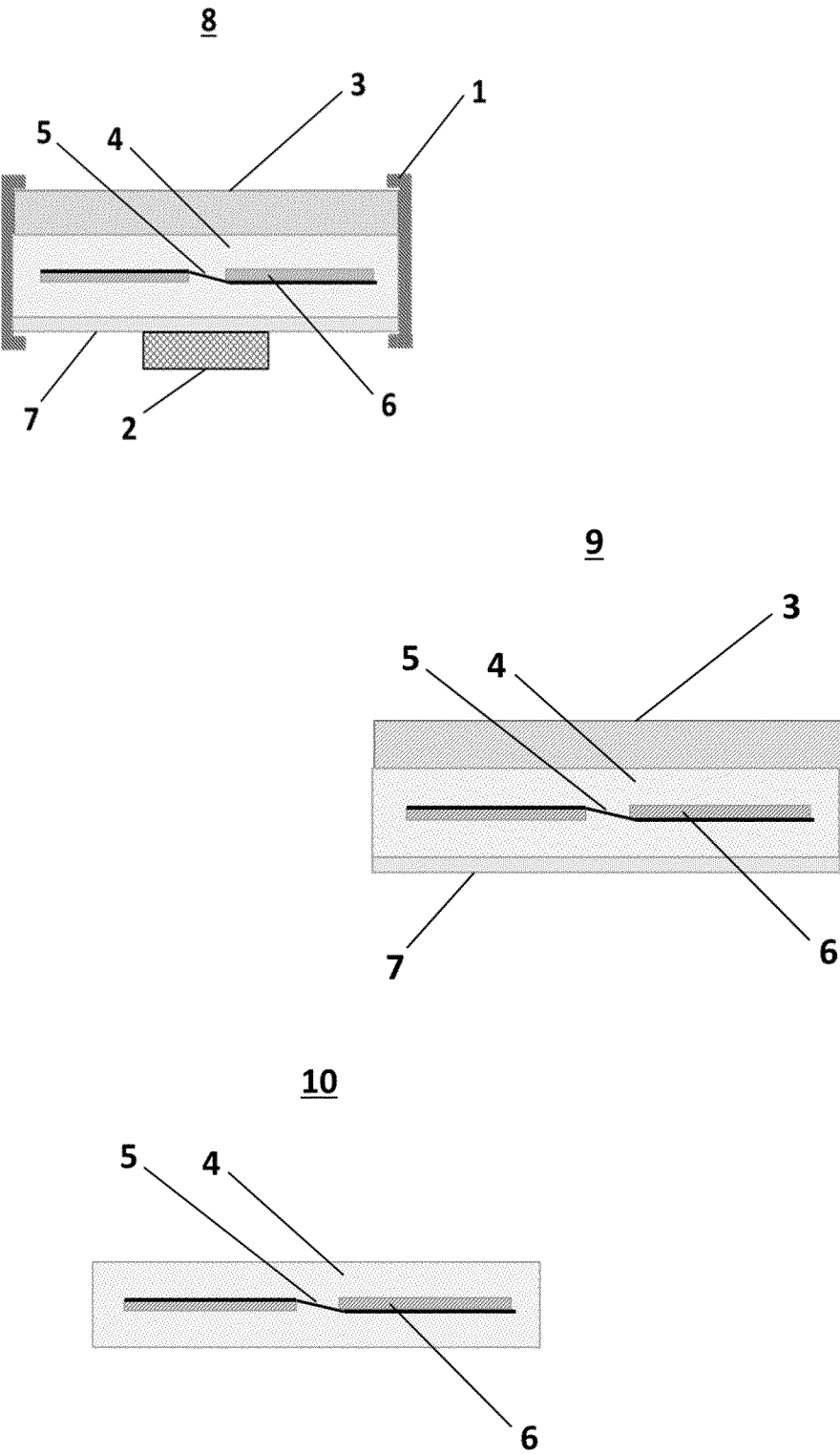


FIG.1

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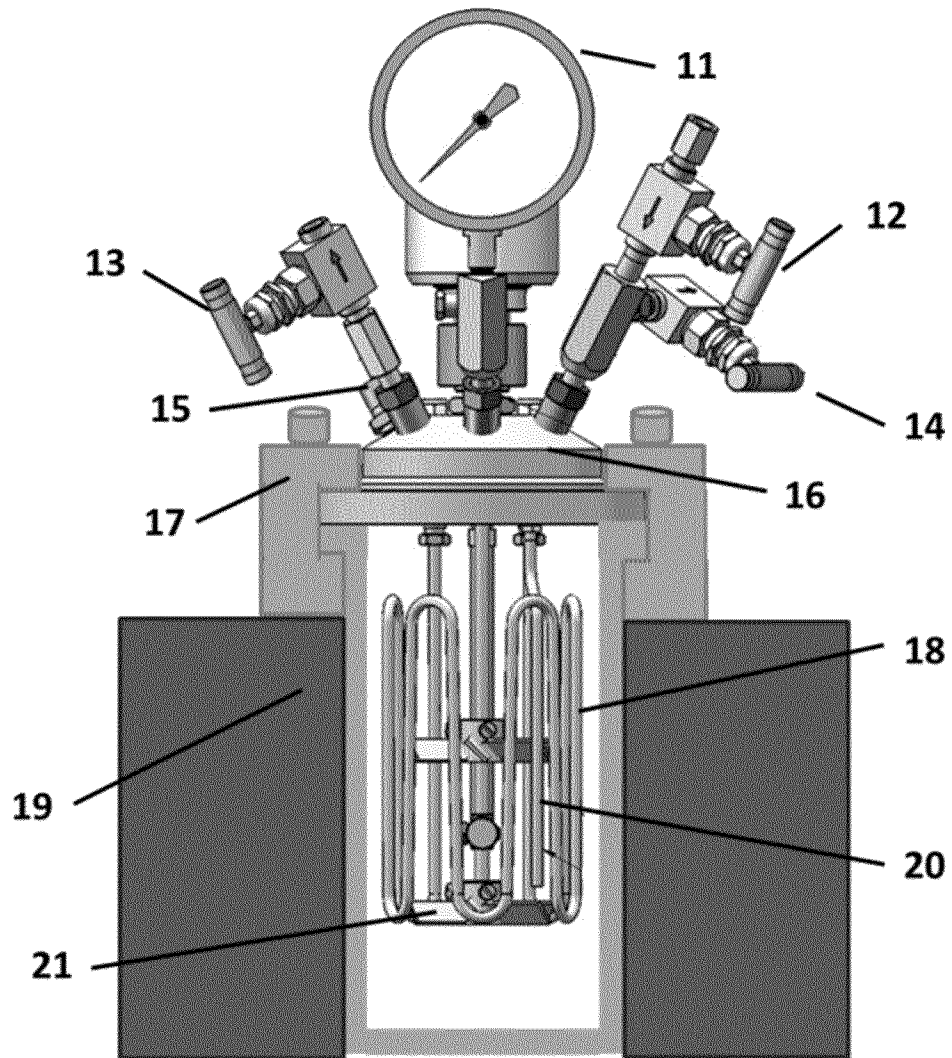


FIG.2

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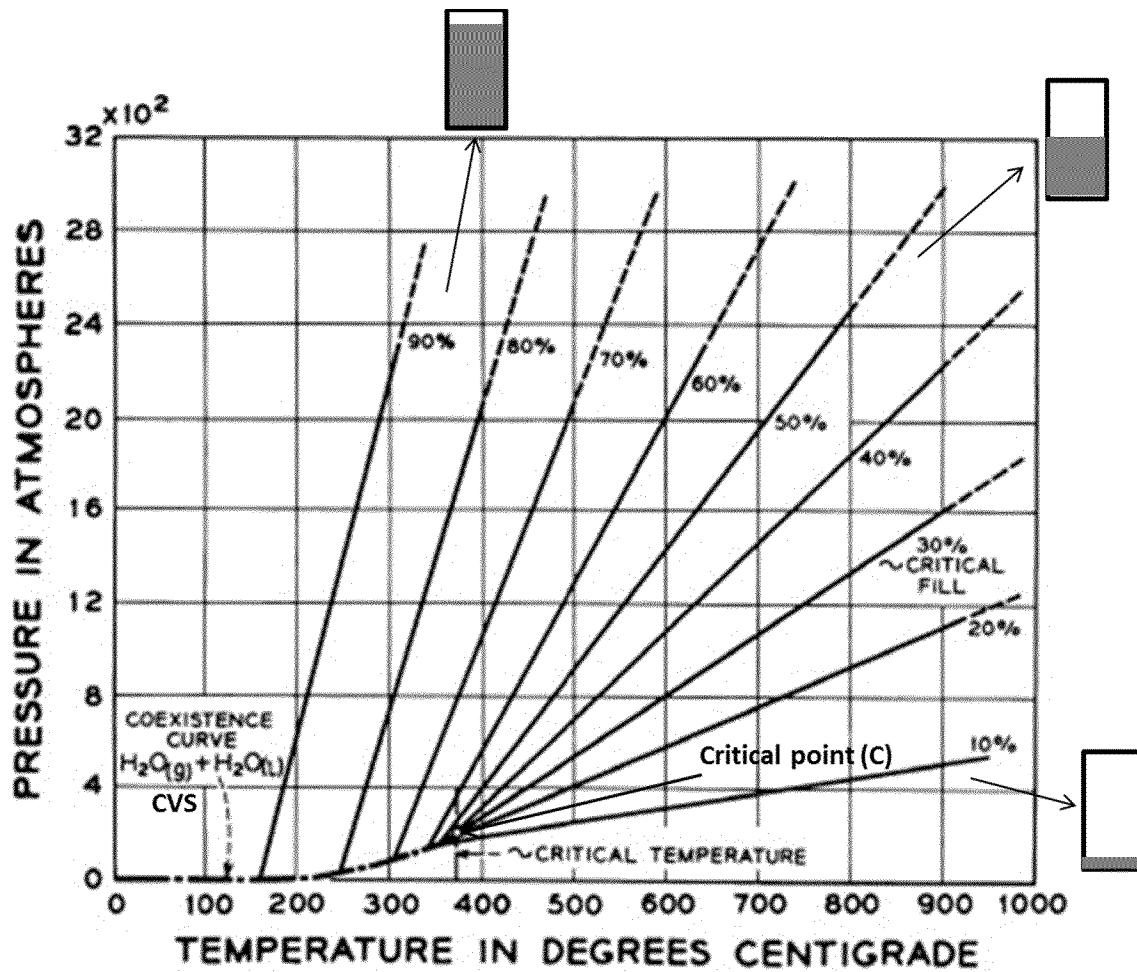


FIG.3

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/065451

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L31/18

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)

H01L C22B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2006 093336 A (SHARP KK) 6 April 2006 (2006-04-06)	1-8
Y	abstract; claims 1-10; figures 1-7 paragraph [0008] - paragraph [0019] paragraph [0026] - paragraph [0051] -----	9-13
Y	EP 0 898 985 A1 (TOSHIBA KK [JP]) 3 March 1999 (1999-03-03) abstract; claims 1-59; figures 1-26 paragraph [0004] - paragraph [0012] -----	9-13
A	JP 2000 061423 A (TOSHIBA CORP) 29 February 2000 (2000-02-29) abstract; claims 1-25; figures 1-14 paragraph [0001] - paragraph [0006] paragraph [0052] ----- -/-	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

15 July 2016

Date of mailing of the international search report

25/07/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Hamdani, Fayçal

INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). 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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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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