



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
08.06.2022 Bulletin 2022/23

(21) Application number: **21020605.8**

(22) Date of filing: **01.12.2021**

(51) International Patent Classification (IPC):
C23C 8/02 ^(2006.01) **C23C 8/10** ^(2006.01)
C23C 8/16 ^(2006.01) **C23C 8/18** ^(2006.01)
C23C 8/24 ^(2006.01) **C23C 8/26** ^(2006.01)
C23C 8/30 ^(2006.01) **C23C 8/32** ^(2006.01)
C23C 8/80 ^(2006.01) **F27B 5/16** ^(2006.01)
F27B 7/16 ^(2006.01) **F27D 7/02** ^(2006.01)
F27D 7/06 ^(2006.01)

(52) Cooperative Patent Classification (CPC):
F27B 7/16; C23C 8/02; C23C 8/10; C23C 8/16;
C23C 8/18; C23C 8/24; C23C 8/26; C23C 8/30;
C23C 8/32; C23C 8/80; F27B 5/16; F27D 7/02;
F27D 7/06

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

(30) Priority: **02.12.2020 EP 20020584**

(71) Applicant: **Linde GmbH**
82049 Pullach (DE)

(72) Inventor: **Aström, Anders**
82049 Pullach (DE)

(74) Representative: **Gellner, Bernd**
Linde GmbH
Intellectual Property EMEA
Dr.-Carl-von-Linde-Straße 6-14
82049 Pullach (DE)

(54) **METHOD OF AND APPARATUS FOR OXIDATIVE POST-PROCESSING OF A NITRIDED OR NITROCARBURIZED ARTICLE**

(57) The invention relates to a method (200) of oxidative post-processing of a nitrided or nitrocarburized article (125), comprising providing (210) the article (125) in a furnace (120), preparing (230) a fluid mixture containing at least water and one or more of carbon dioxide

and nitrogen, providing (230) the fluid mixture in and/or to the furnace (120), and heating (220, 240) the furnace (120) to a temperature level, particularly in the range of 400 °C to 600 °C. Further, the invention provides an apparatus (100) for carrying out the method (200).

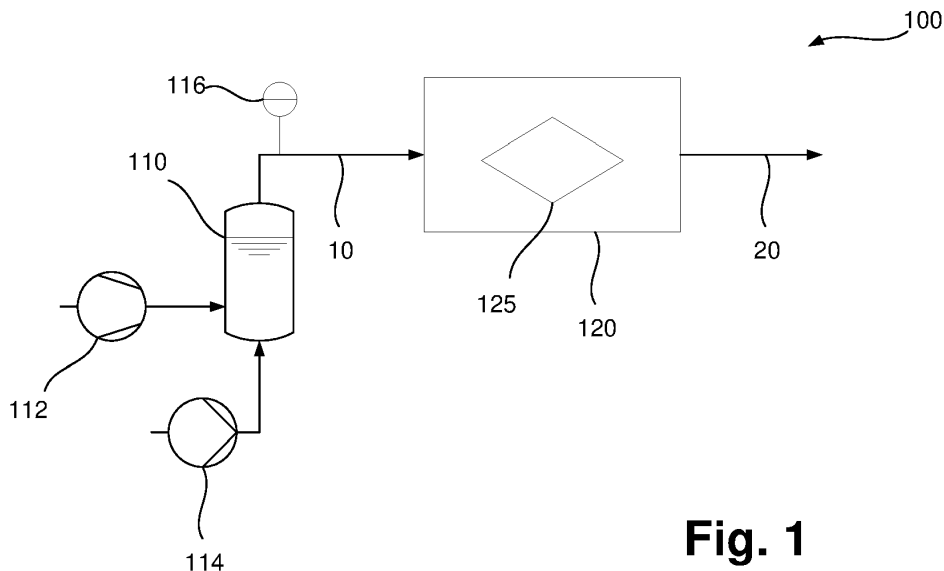


Fig. 1

Description

[0001] The present invention relates to a method of oxidative post-processing of a nitrided or nitrocarburized article (or workpiece or another object) and to an apparatus for carrying out such a method

Background of the invention

[0002] Nitrocarburizing and nitriding of steel or other iron based metal objects produces a hard and smooth surface on the treated objects. Post-treatment oxidation of the surface can further enhance corrosion resistance and the visual appearance of the object's surface.

Disclosure of the invention

[0003] The present invention proposes a method of oxidative post-processing of a nitrided or nitrocarburized article and an apparatus for carrying out the same with the features of the independent claims. Advantageous embodiments are subject-matter of the dependent claims and the description herein below.

[0004] The invention makes use of water vapor as an oxidant and uses otherwise gases which are generally present at heat treatment facilities as further oxidizing agents and/or dilutants for the water vapor. Thereby, the oxidative post-treatment can be carried out in a controlled manner with high precision with less expected furnace wear and maintenance resulting in improved furnace lifetime.

[0005] A method according to the invention comprises providing the article in a furnace, preparing a fluid mixture containing at least water and one or more of carbon dioxide and nitrogen, controlling the water content of the fluid mixture, providing the fluid mixture to the furnace, and heating the furnace, preferably to a temperature level in the range of 400 °C to 600 °C. Under these process conditions, water vapor as well as carbon dioxide serve as oxidizing agents with respect to the nitrided or nitrocarburized surface, respectively.

[0006] The diluting effect of the admixed gas minimizes the negative effects a moist furnace could have on subsequent processes and abolishes or at least reduces the need for drying steps between subsequent processes.

[0007] As mentioned, nitrocarburizing and nitriding are processes used to harden iron based metal objects. Typical examples of objects or articles, to which such processes are applied, include, without limitation, gun or rifle barrels and slides, bearings, drills, spindles, gears, dies, hydraulic pistons and other parts which during use generally come into dynamic contact with other similarly hard surfaces and are therefore prone to friction induced wear.

[0008] US 2007/0251605 A1 proposes a process for producing highly corrosion-resistant articles made of steel by subjecting the surface of a nitride steel article to an oxidizing heat treatment. The heat treatment atmosphere contains for example air and steam at a volume

ratio of 50:50. However, such an oxidizing process is hard to control since the air has an undefined water content.

[0009] Therefore, the invention proposes to control the water content and in particular the dew point of the fluid mixture before it is introduced into the furnace. The dew point depends on the moisture content of the gases which are blended to produce the fluid mixture and it is independent of the temperature contrary to the relative humidity which is temperature dependent.

[0010] By the inventive control of the water content or dew point prior to introducing the fluid mixture into the furnace it is possible to achieve well-defined oxidizing conditions in the furnace. The degree of oxidation is a result of the moisture inside the furnace which is controlled by means of the dew point measurement and of the furnace temperature.

[0011] Advantageously, the fluid mixture is prepared such that a dew point of the mixture under a pressure in the range of 1 - 50 Pa gauge (above atmospheric pressure) that is present in the furnace during heating is in the range of 0 °C to 50 °C, preferably in the range of 10 °C to 30 °C. Under such conditions, the furnace is left dry enough directly after the treatment of the articles, which results in faster conditioning and shorter overall production cycle duration.

[0012] Preferably, preparing the fluid mixture comprises flowing/ducting a gas containing one or more of carbon dioxide and nitrogen through a vessel containing liquid water at a temperature level in the range of 20 to 100°C, preferably between 20 and 50 °C. Gas flow rates and water temperatures are adjusted and preferably controlled with respect to the respective furnace and process in question. This is a very cost-effective and highly controllable method of providing vapor in predefined quantities. Particularly, control parameters like mass flow rate of the gas, dispersion of the gas within the water vessel and water temperature can be easily controlled and have a significant effect on the resulting composition and dew point of the fluid mixture.

[0013] The furnace is preferably kept in a heated state for a period of time chosen such that a thickness of an oxide layer afforded by the method on the article reaches or exceeds 1 µm but does not exceed 3 µm. Heat treatment duration is a major factor influencing the quality of the final product, thereby enabling precise control by adjusting this duration.

[0014] In another aspect, the invention proposes an apparatus for carrying out all the steps discussed in relation to the proposed method. The apparatus, therefore, profits from the same advantages as the method.

[0015] Such an apparatus comprises a furnace configured to accommodate at least one nitrided or nitrocarburized article and to be heated to a temperature level preferably in the range of 400 to 600 °C, a fluid mixture providing device, configured to provide a fluid mixture containing at least water and one or more of carbon dioxide and nitrogen to the furnace and means for determining

the water content or dew point of the fluid mixture before it is provided to the furnace. The apparatus preferably comprises means connecting the fluid mixture providing device to the furnace to transport the fluid mixture into the furnace while the furnace is heated.

[0016] Preferably, the apparatus further comprises means for carrying out a method as set out above. For example, such means can comprise a water vessel equipped with piping to introduce a gas stream below the surface of water within the vessel in order to enrich introduced gas in water content. The water vessel may also be provided with a heating device to controllably heat water contained within the vessel to a desired temperature. Further, the apparatus comprises a device to measure water content within the fluid mixture. For example such devices may include one or more of a dew point measuring device, a partial water vapor pressure measuring device, a hygrometer, or another suitable instrument.

[0017] The furnace may be provided with any suitable type of heater, including but not limited to a burner, an electric heater based on resistive heating, a heat exchanger or combinations thereof. Preferably, an inner wall of the furnace comprises a moisture resistant material, such as (non-porous) ceramics, stainless steel, titanium or similarly suitable materials. Brick and/or fiber insulated furnaces are optional but generally less suited where moist processes are combined with drier processes. For such cases the invention offers a small but controllable process window.

[0018] Further advantages and embodiments of the invention will be discussed in connection with the appended drawings and the description thereof.

[0019] It is to be understood that the features mentioned and discussed herein are not only useable in the combinations explicitly mentioned, but can also be used in different combinations thereof or alone, without departing from the scope of the present invention as defined in the appended claims.

[0020] The invention is described in further detail herein below with reference to an exemplary embodiment that is illustrated schematically in the drawings.

Description of the drawings

[0021]

Figure 1 shows an advantageous embodiment of an apparatus according to the invention in the form of a simplified block diagram.

Figure 2 shows an advantageous embodiment of a method according to the invention in a schematic flow diagram.

Figure 3 schematically shows alternative advantageous embodiments of an apparatus according to the invention.

[0022] In Figure 1, an advantageous embodiment of an apparatus according to the invention is illustrated in the form of a simplified block diagram and collectively referred to with 100.

[0023] The apparatus 100, in the depicted example, comprises a water vessel 110, which is provided with water via a pump 114. A gas stream comprising carbon dioxide and/or nitrogen is introduced into the water vessel 110, particularly making use of the gas pressure originating from a source of supply 112 (e.g. tank with vaporizer, bundle or similar, gas regulators for keeping the pressure stable). The introduction is effected on a geodetic level which is sub-surface with respect to the water in the vessel 110, such that the introduced gas forms bubbles within the water in the vessel 110 in order to increase a contact surface area between the gas and the water to enhance water uptake into the gas.

[0024] One or more pipes 10 connect the water vessel 110 to a furnace 120 of the apparatus 100. A sensor 116 is arranged in fluid contact with the one or more pipes 10 and monitors a composition of a gas water mixture running through the pipe(s) 10. The sensor 116 may, for example, comprise a dew point measuring device, such that the water content in the mixture running through pipe(s) 10 is determined.

[0025] The furnace 120 comprises a heater and is configured to accommodate at least one article 125 to be treated. One or more exhaust pipes 20 lead from the furnace to an external atmosphere. The exhaust pipe(s) 20 may be equipped with pilot flames, filters, condensers, washers or other after-treatment devices, e.g. to comply with environmental protection regulations, and/or heat exchangers in order to recuperate excessive heat at least partially from exhaust gases leaving the furnace 120.

[0026] In Figure 3, alternative embodiments of such an apparatus 100 are shown. Like reference signs are used for like components and not necessarily all of them are repeatedly discussed, for reasons of conciseness. Compared to the apparatus 100 as depicted in Figure 1, here, two different alternatives for preparing the fluid mixture are illustrated. One alternative, corresponding to a preparation as described in relation to Figure 1, is illustrated with solid lines for the connection of the different components.

[0027] The apparatus 100 as illustrated in Figure 3 comprises a water supply unit 101, a nitrogen supply unit 102 and a carbon dioxide supply unit 103. In some embodiments, only one of nitrogen 102 and carbon dioxide 103 supply units may be present. The supply units 102, 103 for supplying gas(es) may be provided in the form of conventional gas cylinders, storage tanks or devices for producing such gas(es), e.g. air separation units, gas generators or other suitable devices. In the first alternative, the media from supply units 101, 102 and 103 are transported to the water vessel 110, which may be controlled regarding temperature by a control unit 130, which, in this embodiment, also includes the sensor 116 for determining the water content of the fluid mixture 10

before its introduction into the furnace 120. In addition, the water content or dew point of the atmosphere inside the furnace may also be determined (117). The procedure for preparing the fluid mixture according to this embodiment has already been described in detail in connection with Figure 1.

[0028] The media from supply units 101, 102 and 103 are directly supplied to the furnace 120 and injected thereto. In such a case, the water content of the atmosphere in the furnace 120 may be controlled by adjusting regulating valves in a flow path between the individual supply units 101, 102, 103 and the furnace 120. These regulating valves may, for example, be controlled by the control unit 130, particularly electronically, pneumatically, hydraulically or in any other suitable manner, including a combination of the mentioned possibilities. The media from supply units 101, 102 and 103 are united or mixed upstream of the furnace 120 to prepare the fluid mixture which is then introduced into the furnace 120. Sensor 116 is used to determine the water content of the fluid mixture 10. Further, an additional sensor 117 may be arranged inside the furnace 120 or downstream thereof, in order to analyze the actual composition of the atmosphere within the furnace 120 and/or to verify the result of the dew point measurement of sensor 116.

[0029] Independent of the specific design of apparatus 100, a desired water content of the furnace atmosphere for oxidative post treatment may be in the range of 2.5% to 10% by volume in a cold state, i.e. in wet conditions. During operation of the furnace, therefore, the water content may dramatically increase regarding volume, since at elevated temperatures, all the water contained within the atmosphere in furnace 120 is in gaseous or vapor state. For more precisely reproducible results, the water content is therefore expressed as dew point of the furnace atmosphere lying preferably in the range of 10 °C to 30 °C. The dew point can either be determined by simultaneous measurement of relative humidity and temperature, capacity thin-film polymer sensor or directly, for example, using a reflectivity of a periodically cooled mirror. The determined dew point may be used to adjust the water content in the furnace atmosphere to a desired specification, as described above.

[0030] In Figure 2, an advantageous embodiment of a method according to the invention is illustrated in a schematic flow diagram and generally referred to as 200.

[0031] References regarding components of an apparatus refer to the apparatus 100 described above in connection with figures 1 and 3.

[0032] In a first step 210 of the method 200, an article 125 to be oxidatively post-treated is placed in the furnace 120. The furnace may then be heated to a desired treatment temperature level in a heating step 220.

[0033] It may be possible, in some embodiments, that the furnace 120 is used not only for the oxidative post-treatment, but also for the previously performed nitridization or nitrocarburization treatment of the article 125. In such cases, one or both of steps 210 and 220 may be

omitted, as the article 125 may already be in the furnace 120 and the furnace may already have the desired temperature or a higher (or lower) temperature, so that, for example, only cooling down, or heating up, to the desired temperature may be required, instead of the described steps 210, 220.

[0034] In a step 230, a fluid mixture comprising water and a gas, particularly nitrogen and/or carbon dioxide, is provided. In the exemplary embodiment of an apparatus 100, depicted in figure 1, the composition of such a mixture may be regulated by adjusting a gas flow rate and/or a temperature of water within the vessel 110. Therefore, e.g. a pressure of the gas may be set or adjusted to a desired value by controlling the gas regulator or compressor 112. It may also be advantageous to provide for a control mechanism for bubble size and/or amount, for example by providing several sets of perforated gas pipes inside the vessel 110, such that each set of pipes may be individually fed with the gas. By feeding more sets of pipes, more and potentially smaller bubbles may be formed, whereas feeding gas to fewer (sets of) pipes may result in larger and/or fewer bubbles. The more bubbles are formed in step 230 and the smaller the formed bubbles are, the larger the relative amount of water that is taken up by the gas. A similar observation will hold for the water temperature: the higher the temperature, the higher the saturation pressure, leading to increasing relative amounts of water in the mixture with increasing water temperature within the vessel 110.

[0035] Preferably, the water amount is adjusted or regulated according to an actual composition of the mixture as determined by the sensor 116. Step 230 may therefore include measuring the momentary composition and adjusting the mentioned influencing parameters like, for example, pressure and/or temperature and/or bubble size and number.

[0036] The so prepared fluid mixture, in which water may be present in vapor and/or liquid form, particularly in the form of mist droplets, is then transported to the furnace 120 via pipe(s) 10.

[0037] In a step 240, the furnace 120 is kept at the desired processing temperature level for a predefined period of time, which may be chosen according to a required layer thickness of an oxide layer produced by the method 200. In some embodiments, a temperature program may be followed, i.e. one or more predefined temperature ramps may be provided and the temperature of the furnace 120 may be adjusted to follow the one or more temperature ramps.

[0038] A step 250 may follow for cooling down or quenching the article 125 and removing it from the controlled atmosphere within the furnace 120.

[0039] The method 200 may then return to step 210 to go through a subsequent treatment cycle for one or more other articles 125.

[0040] It should be noted, that the steps described above are not necessarily performed in the order mentioned or in the form of distinct steps altogether. Some

of these steps may, by way of example, be performed in a different, e.g. reversed, order or simultaneously. Some steps may be performed combined as an integrated step or even be omitted without departing from the scope of the present invention. The stepwise description of the method 200 was chosen for readability and illustration purposes only and is in no way to be understood in a limiting manner.

Claims

1. Method (200) of oxidative post-processing of a nitrated or nitrocarburized article (125), comprising

providing (210) the article (125) in a furnace (120),
 preparing (230) a fluid mixture containing at least water and one or more of carbon dioxide and nitrogen,
 controlling the water content, and in particular the dew point, of the fluid mixture and
 providing (230) the fluid mixture to the furnace (120), and
 heating (220, 240) the furnace (120) to a predetermined temperature.

2. Method (200) according to claim 1, wherein the predetermined temperature is in the range of 400 °C to 600 °C, particularly 450 °C to 580 °C.

3. Method (200) according to claim 1 or 2, wherein the fluid mixture is prepared such that a dew point of the mixture under a pressure that is present in the furnace (120) during heating (220, 240) is in the range of 0 °C to 50 °C, preferably in the range of 10 °C to 30 °C.

4. Method (200) according to any one of claims 1 to 3, wherein preparing (230) the fluid mixture comprises flowing a gas containing one or more of carbon dioxide and nitrogen through a vessel (110) containing liquid water at a temperature level in the range of 20 to 100 °C, preferably between 20 and 50 °C.

5. Method (200) according to any one of the preceding claims, wherein the furnace (120) is kept in a heated state (240) for a period of time chosen such that a thickness of an oxide layer on the article (125), afforded by the method (200), reaches or exceeds 1 μm, but does not exceed 3 μm.

6. Apparatus (100) for oxidative post-processing of a nitrated or nitrocarburized article (125), comprising

- a furnace (120) configured to accommodate at least one nitrated or nitrocarburized article (125) and to be heated to a predetermined tempera-

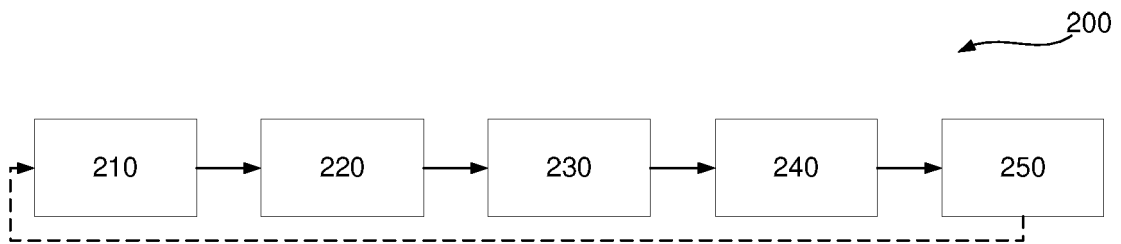
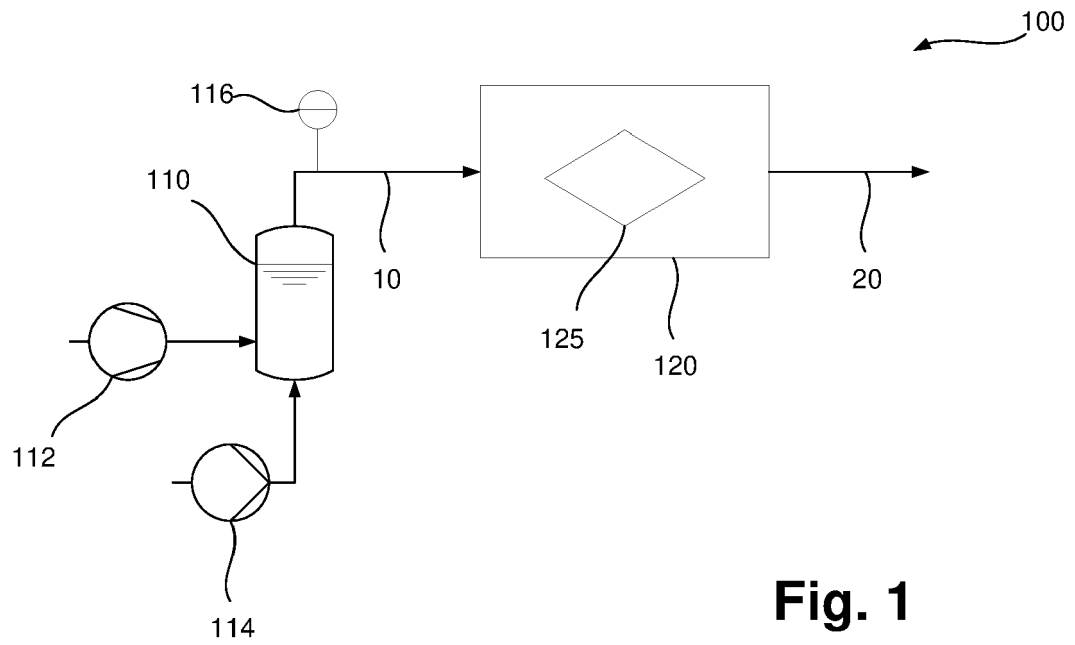
ture,

- a fluid mixture providing device (110) configured to provide a fluid mixture containing at least water and one or more of carbon dioxide and nitrogen,
 - means for determining the water content of the fluid mixture and
 - means for providing the fluid mixture to the furnace (120).

7. Apparatus (100) according to claim 6, further comprising means (10) connecting the fluid mixture providing device (110) to the furnace (120) to transport the fluid mixture into the furnace (120) while the furnace (120) is heated.

8. Apparatus (100) according to any of claims 6 or 7, wherein the fluid mixture providing device comprises a water vessel and at least one of a carbon dioxide supply and a nitrogen supply connected to said water vessel.

9. Apparatus (100) according to one of claims 6 to 8, further comprising means (112, 114, 116) configured to carry out a method (200) according to any of claims 1 through 5.



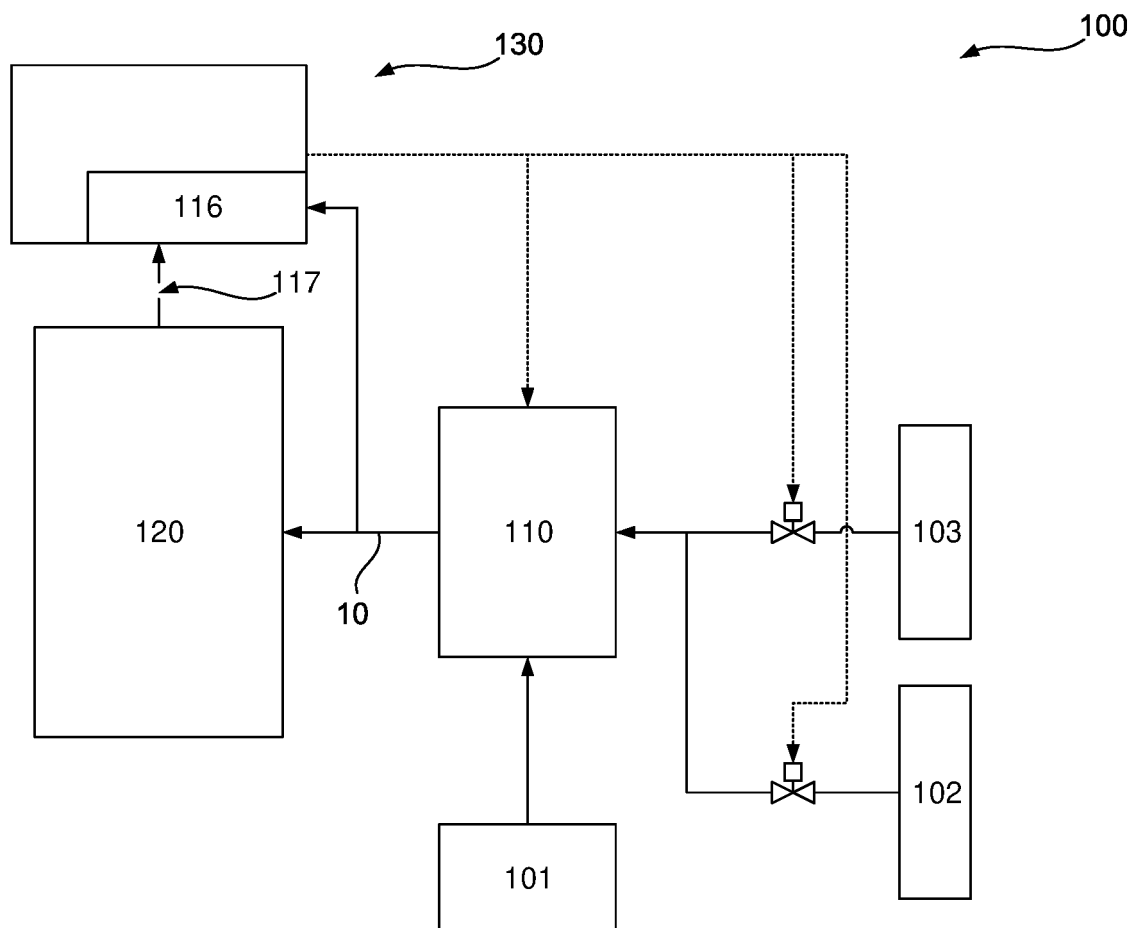


Fig. 3



EUROPEAN SEARCH REPORT

Application Number

EP 21 02 0605

5

10

15

20

25

30

35

40

45

50

55

1

EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2007/251605 A1 (KIM YOUNG HEE [KR]) 1 November 2007 (2007-11-01)	1-5	INV. C23C8/02
A	* paragraphs [0033] - [0036]; claims 1-4; example 2 *	6-9	C23C8/10 C23C8/16 C23C8/18
X	WO 2014/002120 A1 (CAVINA FULVIO FABRIZIO [IT]; ROVETTO GUIDO [IT]) 3 January 2014 (2014-01-03) * claims 1-10; figure 1 *	6-9	C23C8/24 C23C8/26 C23C8/30 C23C8/32 C23C8/80
X	EP 0 299 625 A2 (LUCAS IND PLC [GB]) 18 January 1989 (1989-01-18) * columns 1-2; claims 1-12 *	1-9	F27B5/16 F27B7/16 F27D7/02 F27D7/06
X	US 4 859 251 A (HAYAMI TOSHITOMO [JP] ET AL) 22 August 1989 (1989-08-22) * claims 1-3; figure 1 * * column 2, lines 51-68 * * column 3, lines 47-68 * * column 4, lines 20-64 *	6-9	TECHNICAL FIELDS SEARCHED (IPC) C23C F27B F27D
X	US 3 655 172 A (INGELS GLENN R) 11 April 1972 (1972-04-11) * claims 1-7; figure 1 *	6-9	
X	EP 0 229 325 A2 (LUCAS IND PLC [GB]) 22 July 1987 (1987-07-22) * page 9; claims 1-6 *	1,2	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 3 January 2022	Examiner Chalaftris, Georgios
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 21 02 0605

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-01-2022

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 2007251605	A1	01-11-2007	CN	101067194 A		07-11-2007
			JP	4639203 B2		23-02-2011
			JP	2007297702 A		15-11-2007
			KR	100761903 B1		28-09-2007
			US	2007251605 A1		01-11-2007

WO 2014002120	A1	03-01-2014	BR	112014032480 A2		27-06-2017
			CN	104603319 A		06-05-2015
			EP	2864520 A1		29-04-2015
			WO	2014002120 A1		03-01-2014

EP 0299625	A2	18-01-1989	DE	3884696 T2		28-04-1994
			EP	0299625 A2		18-01-1989
			ES	2045121 T3		16-01-1994
			GB	2208658 A		12-04-1989
			JP	H0571661 B2		07-10-1993
			JP	S6431957 A		02-02-1989
			US	4881983 A		21-11-1989

US 4859251	A	22-08-1989	CN	88101245 A		23-11-1988
			KR	880011553 A		29-10-1988
			US	4859251 A		22-08-1989

US 3655172	A	11-04-1972	NONE			

EP 0229325	A2	22-07-1987	NONE			

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 20070251605 A1 [0008]