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(54) Method of providing methanol for a heat treatment atmosphere in furnace

(57) The present invention relates to a Method of providing methanol for a heat treatment atmosphere in a furnace, comprising the following steps:
- Providing liquid methanol (110) in a container (100),
- Passing nitrogen through the liquid methanol (110) provided in the container (100), in order to generate a gaseous atmosphere (112) above the liquid methanol (110) comprising gaseous methanol and nitrogen, and
- Delivering the atmosphere containing gaseous methanol and nitrogen into a furnace (160).

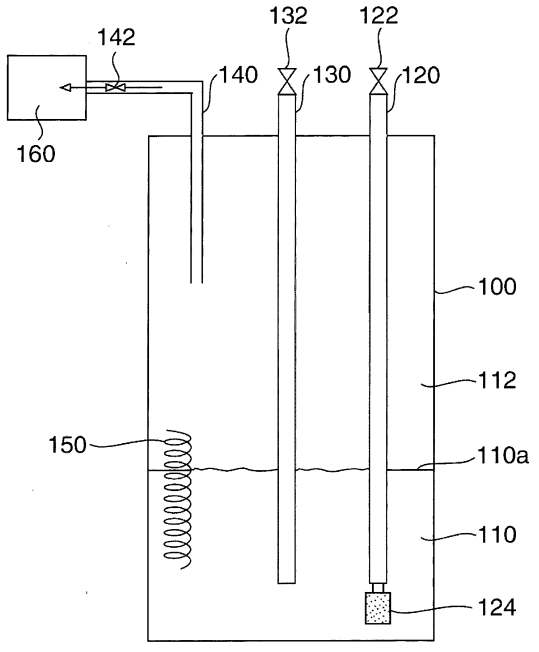

Fig. 1

EP 2 806 241 A1

Description

[0001] The invention relates to a method of providing methanol for a heat treatment atmosphere in a furnace.

[0002] In furnaces, for example industrial heat treatment furnaces for sintering or carburizing, comprising a heating zone and a cooling zone, it is necessary, for numerous applications, to provide CO together with other gases in the heat treatment atmosphere.

[0003] In the prior art there are heat treatment processes known, which involve the use of a reactor for generating i.a. CO from methanol, which is placed inside the heat treatment furnace. For example, US patent US 5,160,380 relates to a process and apparatus for preparation of treatment gas used in heat treatments, whereby the treatment gas is produced in a furnace disposed catalyst retort at a temperature of that of the furnace in which the retort is positioned.

[0004] From EP 2 487 442 A1 there is known a method to provide a heat treatment atmosphere in a furnace comprising a heating zone and a cooling zone, wherein methanol is supplied to a gas generator, and wherein said methanol is dissociated in said gas generator to produce CO and H_2, and wherein CO and H_2 are introduced into said furnace, wherein the gas generator is installed in the contact area of the heating zone and the cooling zone, and the gas generator is heated by the atmosphere within the furnace.

[0005] However, such equipment is often complex and requires intensive maintenance.

[0006] It is also known to directly inject liquid methanol into a furnace and to let the methanol dissociate. However, for example in sintering furnaces, this method is not practical since due to the structure of the sintering furnace with ceramic and metal retorts or muffles drilling holes to employ proper nozzles proves impractical. There is also a risk that liquid methanol could reach the furnace components or the sintered parts and damage them. Further, when liquid methanol sits on the components it could improperly dissociate and generate unwanted atmosphere constituents. Another disadvantage of direct injection of liquid methanol is the endothermic character of the dissociation reaction which takes away heat and could cause issues in the sintered components, e.g. decarburization or partial oxidation.

[0007] It is also known to directly inject CO into a furnace. Such CO is provided from cylinders. However, CO is a toxic gas and is dangerous to handle, especially indoors, from such cylinders.

[0008] The invention serves to provide a method for producing methanol for a heat treatment atmosphere in a furnace.

[0009] This object is achieved by a method comprising the features of claim 1.

[0010] The invention provides a simple cost effective way of providing methanol in gaseous form for a heat treatment atmosphere in a furnace. By providing methanol in gaseous form, the disadvantages described above in connection with providing the liquid methanol can be avoided. Furthermore, the method according to the present invention is highly cost effective.

[0011] Advantageous embodiments of the method according to the invention are the subject matter of the dependent claims.

[0012] According to a preferred embodiment, the atmosphere containing gaseous methanol and nitrogen is delivered from the container, in which nitrogen is passed through the liquid methanol, directly into the furnace. Hereby, the construction of the furnace can be significantly simplified in relation to previous designs.

[0013] It is also possible, according to a further embodiment of the method of the invention, to pass the atmosphere containing gaseous methanol and nitrogen into the furnace via a gas generator, for example a gas generator as described in EP 2 487 442 A1.

[0014] According to a preferred embodiment of the invention, the method comprises monitoring the CO content in the heat treatment atmosphere in the furnace and controlling the temperature in the container containing the liquid methanol in accordance with said monitored CO content. Hereby, it is easily and effectively possible to adjust and control the CO content in the heat treatment atmosphere in the furnace, merely by raising or lowering the temperature in the container. A raising of the temperature in the container will lead to enhanced gaseous methanol content in the atmosphere in the container, which is then delivered to the furnace. An enhanced content of gaseous methanol will lead to an enhanced generation of CO within the furnace. As soon as a desired CO content or level in the heat treatment atmosphere in the furnace is reached, it is, for example, possible to maintain the temperature within the container at a constant level.

[0015] Preferably, the temperature in the container is variable between room temperature, especially 25°C and 100°C, especially 80°C. Such temperatures can easily and cost effectively be provided and allow variation of the content of gaseous methanol over a wide range.

[0016] The method according to the invention it is advantageously usable for furnaces comprising a heating zone and a cooling zone, and/or wherein the furnace is used for sintering applications, especially sinter hardening, carburizing applications and neutral heating applications.

[0017] Preferably, the passing of nitrogen through the liquid methanol comprises bubbling the nitrogen through the liquid methanol. Various devices can be used to effect such a bubbling, for example bubbling devices at the distal end of a tubing for supplying nitrogen formed with a multitude of holes or openings, or in form of a mesh.

[0018] The invention as well as further details and embodiments thereof shall now be described with reference to the attached drawings.

Figure 1 schematically shows a preferred embodiment of a container for use with the method

according to the invention.

[0019] Figure 1 schematically shows a container 100 for holding liquid methanol 110.

[0020] The container 100 is provided with a first piping 120 for passing (gaseous) nitrogen from a nitrogen source (not shown) into and through liquid methanol 110.

[0021] The tubing 120 can be provided with a control valve 122 at its end proximal to the nitrogen source.

[0022] The distal end of piping 120 terminates below the surface of the liquid methanol. Advantageously, it can be provided with a bubbling device 124 at its distal end. The bubbling device 124 can be provided for example with a number of holes or openings, or in form of a mesh. Such a bubbling device 124 can serve to create a diffuse entrance of nitrogen into the liquid methanol. It is e.g. also possible to provide the nitrogen via a mesh in the lower side of the container 100.

[0023] A further piping 130 for passing liquid methanol into the container 100 is provided. This piping 130 can also be provided with a control valve 132.

[0024] Container 100 is provided with a further piping 140, by means of which the gaseous atmosphere 112 above the surface 110a of the liquid nitrogen 110 can be extracted and passed or delivered into a furnace 160 (schematically shown). This piping 140 can also be provided with a control valve 142.

[0025] The temperature within container 100 is adjustable, preferably between room temperature and 100°C, more preferably between 25°C and 80°C. Herefore, the container 100 is provided with a heating device, schematically shown and designated 150. This heating device serves especially to control the temperature of the gaseous atmosphere 112, but can also or alternatively serve to control the temperature of liquid methanol 110.

[0026] When nitrogen is passed into and through the liquid methanol 110 via piping 120 and bubbling device 124, it will rise to the surface 110a of the liquid methanol 110 and enter the gaseous atmosphere above surface 110a. At the same time, presence and passing through of nitrogen in liquid methanol leads to an enhanced phase transition of liquid methanol into gaseous methanol, which will also pass into the gaseous atmosphere 112 above surface 110a.

[0027] By means of controlling the temperature within the container 100, the composition of the gaseous atmosphere 112 may be varied. For example, by raising the temperature by means of heating device 150, the partial pressure of gaseous methanol can be increased, while the partial pressure of nitrogen can be lowered. Lowering the temperature, vise versa, can increase the partial pressure of the nitrogen, and lower the partial pressure of gaseous methanol.

[0028] The gaseous atmosphere 112, containing gaseous methanol, can be extracted from container 100 by means of piping 140 and passed into the furnace 160. In this furnace, the gaseous methanol will react to CO and H_2. For various furnace settings, a partial pressure for CO in the furnace atmosphere (heat treatment atmosphere) should lie in the region of 2%. By varying the temperature within container 100 and thus, as explained above, the content of gaseous methanol in the gaseous atmosphere 112, this CO content within the furnace atmosphere can be reliably provided. A temperature of 27°C has been shown to render possible such a methanol content within gaseous atmosphere 112.

[0029] The method according to the invention can be used in most kinds of industrial heat treatment furnaces for most heat treatment applications. It is especially useful when used in connection with sintering (sinter hardening), carburizing and neutral heating applications, where homogeneous surface modifications are decisive quality determining factors.

Claims

1. Method of providing methanol for a heat treatment atmosphere in a furnace (160), comprising the following steps:

   - Providing liquid methanol (110) in a container (100),
   - Passing nitrogen through the liquid methanol (110) provided in the container (100), in order to generate a gaseous atmosphere (112) above the liquid methanol (110) comprising gaseous methanol and nitrogen, and
   - Delivering the atmosphere containing gaseous methanol and nitrogen into the furnace (160).

2. Method according to claim 1, wherein the atmosphere comprising gaseous methanol and nitrogen is passed from the container (100) directly into the furnace (160).

3. Method according to claim 1, wherein the atmosphere comprising gaseous methanol and nitrogen is passed into the furnace (160) via a gas generator.

4. Method according to any one of the preceding claims, comprising monitoring the CO content of the heat treatment atmosphere within furnace (160) and controlling the temperature in the container (100) in accordance with said monitored CO content.

5. Method according to any one of the preceding claims, wherein the temperature within the container (100) is variable between room temperature, especially 25°C, and 100°C, especially 80°C.

6. Method according to any one of the preceding claims, wherein the furnace (160) comprises a heating zone and a cooling zone, and/or the furnace is used for sintering applications, especially sinter hardening, carburizing applications and neutral

heating applications.

7. Method according to any one of the preceding claims, wherein the passing of nitrogen through the liquid methanol comprises bubbling the nitrogen trough the liquid methanol.

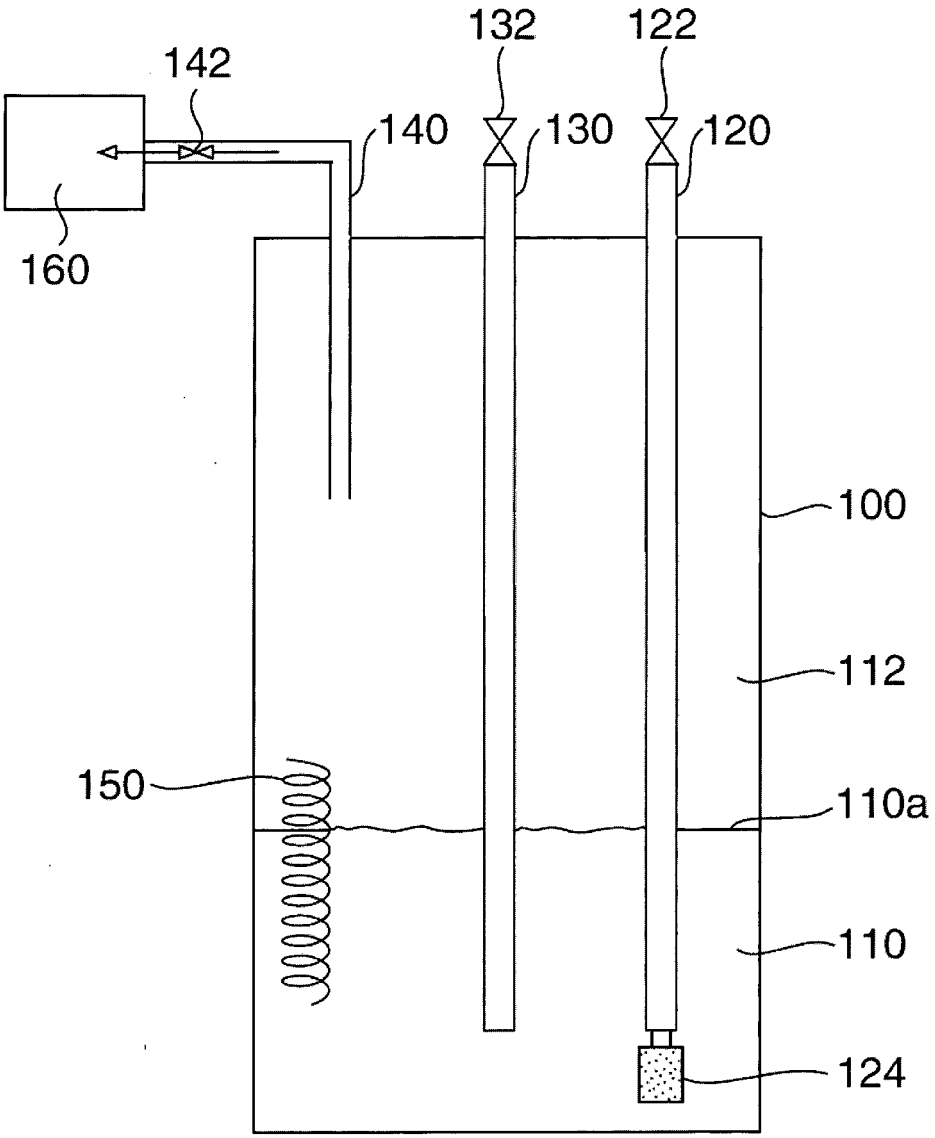

Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 13 00 2697

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	EP 0 027 649 A1 (AIR PROD & CHEM [US]) 29 April 1981 (1981-04-29) * page 3, line 30 - page 4, line 6 * * page 6, line 26 - page 7, line 36 * -----	1-7	INV. F27D7/06 B01D1/14 C21D1/74 B01B1/00

TECHNICAL FIELDS SEARCHED (IPC)

C21D
F27D
B01D
F27B
B01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	22 October 2013	Peis, Stefano

CATEGORY OF CITED DOCUMENTS

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22-10-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0027649 A1	29-04-1981	AR 222104 A1	15-04-1981
		BR 8006801 A	28-04-1981
		CA 1147634 A1	07-06-1983
		EP 0027649 A1	29-04-1981
		ES 8200926 A1	16-02-1982
		ES 8200927 A1	16-02-1982
		JP S5665920 A	04-06-1981
		MX 152840 A	18-06-1986
		US 4359351 A	16-11-1982
		ZA 8006460 A	28-10-1981

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 5160380 A **[0003]**
- EP 2487442 A1 **[0004] [0013]**