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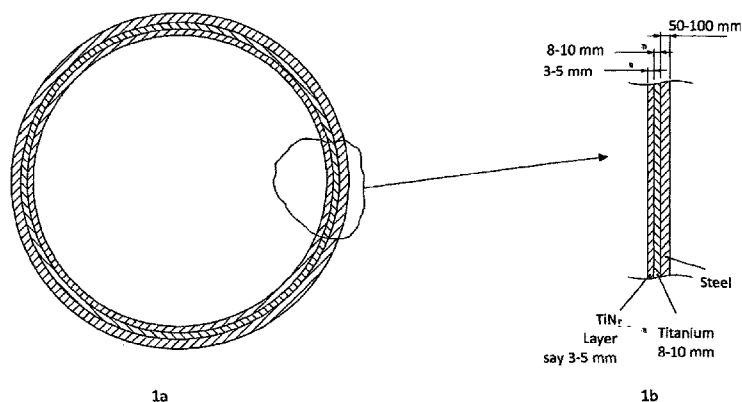
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
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(54) **Title:** AUTOCLAVE FOR PRESSURE OXIDATION

Figure 1



(57) **Abstract:** The present invention relates to TiN coated autoclaves for pressure oxidation of slurried ores and concentrates and provides an autoclave for pressure oxidation of slurried ores and/or concentrates comprising a main shell having an interior layer composed of titanium or titanium alloy having a TiN layer on its surface, the TiN layer coming into contact with the slurried ores/or concentrates and oxygen and preventing exposure of titanium to oxygen.

AUTOClave FOR PRESSURE OXIDATION

FIELD OF THE INVENTION

The invention relates to autoclaves for pressure oxidation (POX) of slurried ores and concentrates, in particular to brickless POX autoclaves.

5 BACKGROUND OF THE INVENTION

Autoclaves utilized in leaching operations of slurried ores and concentrates requiring elevated temperatures and pressures are subject to highly corrosive and erosive environment. Examples of such processes include pressure oxidation (POX) of sulfide ores and concentrates and high pressure acid
10 leaching (HPAL) of nickel laterites. In many processes, maintenance and downtime associated with autoclave wear and failure can be substantial.

In pressure oxidation (POX) of sulphide ores and concentrates silicate based bricks are used to provide wear protection in the autoclave while lead, furan or alloys like Inconel provide corrosion resistance between the carbon steel shell and the bricks. However, failure of bricks is common and the
15 wear-course of the bricks need frequent replacement at high cost. For gold POX autoclave the top-course of the vapour phase bricks require replacement every 2 to 5 years and with the slurry phase every 5 to 7 years.

In addition to regular replacement the bricks are also very sensitive
20 to pressure induced failure and it is not uncommon for whole sections of brick work to be lost during an accidental de-pressurization of an autoclave. Hence accidental brick failure and planned brick repairs are major causes of autoclave downtime.

In high pressure acid leaching (HPAL) of nickel laterites, the use of
25 bricks has been successfully substituted by constructing the autoclaves using plates of titanium-clad steel. The titanium and steel plates are positioned one adjacent to another and welded together. However, in the POX autoclaves the use of titanium is limited mainly to the slurry phase. Bricks are still used for the main shell lining due to the risk of titanium fire which would lead to serious failure of the shell if ignited.
30

BRIEF DESCRIPTION OF THE INVENTION

It is thus an object of the present invention to provide a brickless autoclave for pressure oxidation of slurried ores and concentration having a TiN layer on the interior surface of the shell so as to overcome the above prob-

lems. The objects of the invention are achieved by an autoclave which is characterized by what is stated in the relevant independent claims. The preferred embodiments of the invention are disclosed in the dependent claims.

The invention is based on the realization that autoclaves composed
5 of plates of titanium-clad steel can be utilized in leaching operations of slurried ores and concentrates requiring elevated temperatures and pressures if the titanium surface which comes to contact with the slurried ores and/or concentrates and oxygen is converted into a thick, tenacious and hard titanium nitride (TiN) layer. This will provide a POX autoclave with enhanced wear resistance
10 without the risks associated with non-coated titanium. A TiN layer on the interior surface of the autoclave provides enhanced wear-resistance and hardness while TiN does not ignite and burn like titanium. In order to ignite titanium fire a fresh surface of titanium is required. When the inner surface of an autoclave is coated with a thick layer of TiN, there is no pure titanium that could become
15 exposed and ignite as all titanium is converted into titanium nitrides.

Furthermore, TiN is chemically inert under the leaching conditions of slurried ores and concentrates requiring elevated temperatures and pressures. TiN layer formed by diffusion process from existing titanium material is 100% dense and defect free and metallurgically bonded to the substrate. This is a
20 significant advantage over e.g. spray coatings that always contain porosity and are only mechanically anchored to the substrate preventing their use in protecting load-bearing structures. TiN layer is metallurgically bonded to the substrate meaning that it is not possible for the layer to be detached from the surface under any conditions.

25 BRIEF DESCRIPTION OF THE DRAWINGS

In the following the invention will be described in greater detail by means of preferred embodiments with reference to the attached [accompanying] drawings, in which

Figure 1 shows a cross section of an autoclave of the present invention;
30 Figure 2 shows a TiN layer etched with Kroll's reagent to reveal the extension of the diffusion layer;

Figure 3 shows hardness value (HV) measured from the cross-section of TiN coated titanium sheet;

Figure 4 shows wear test results of a TiN layer as compared to titanium and conventional autoclave coatings.
35

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to an autoclave for pressure oxidation of slurried ores and/or concentrates comprising a main shell having an outer layer and an interior layer. The inner side of the autoclave, i.e. the interior layer, which is exposed to the slurried ores and/or concentrates and oxygen, is composed of titanium or titanium alloy and a titanium nitride (TiN) layer, whereby the TiN layer is formed on the surface of the titanium or titanium alloy so that the TiN layer covers the surface of the titanium or titanium alloy and only the TiN layer comes into contact with the slurried ores and/or concentrates and oxygen. Thus the TiN layer prevents the exposure of metallic titanium to oxygen while the TiN layer itself comes into contact with the slurried ores and/or concentrates and oxygen.

The present invention accordingly provides an autoclave for pressure oxidation of slurried ores and/or concentrates, wherein the interior layer of the autoclave is composed of titanium or titanium alloy having a TiN layer on its surface, the TiN layer coming into contact with the slurried ores and/or concentrates and oxygen and preventing exposure of titanium to oxygen.

Figure 1 shows an example of an autoclave of the present invention. 1a illustrates a cross-section of the autoclave and 1b shows a detail of the different layers of the main shell of the autoclave. The outer layer of the main shell of the autoclave is in this example composed of steel. The thickness of the steel layer is typically from 50 to 100 mm. The steel layer is covered by a titanium layer which is bonded through the use of chemical explosives, i.e. explosion welded, to the steel layer. The titanium layer is further covered by a TiN layer formed on the surface of the titanium or titanium alloy so that the TiN layer covers the surface of the titanium layer and only the TiN layer comes into contact with the slurried ores and/or concentrates and oxygen. The thickness of the titanium layer is typically from 8 to 10 mm. The thickness of the TiN layer is from 3 to 5 mm.

The TiN layer may be formed by nitriding the surface of the titanium or titanium alloy. The TiN layer may be formed e.g. by welding. Nitrogen absorbed on the surface of the interior layer during the nitriding process diffuses into the titanium or titanium alloy. It forms a TiN compound layer and a so called diffusion zone where nitrogen exists as an interstitial solution in the titanium phase. The resulting TiN layer is thus metallurgically bonded to the substrate and will not be detached. This is an advantage over spray coatings that

rely on mechanical anchoring and can be detached from the surface under some conditions.

The TiN layer prevents exposure of titanium to oxygen and thus ignition of titanium fire. Exposure of metallic titanium by abrasion or scratching of the protective layer is possible when spray coatings are utilized or in applica-
5 tions where the thickness of the coating layer is small e.g. TiO₂ coatings. This can be avoided with the TiN layer.

Preferably the TiN layer has a thickness of 1 to 5 mm, more preferably from 3 to 4 mm. A thickness of at least 1 mm is sufficient for providing protection against scratching. The thickness of the TiN layer may be determined
10 for example by optical microscopy of a cross-section of the treated material. Herein the thickness refers to the total thickness of the TiN compound layer and the diffusion zone. Figure 2 shows a TiN layer on a titanium sheet etched with a Kroll's reagent to reveal the extension of the diffusion layer. Black arrow
15 shows the metallurgical bond between the TiN/diffusion layer and titanium substrate.

Furthermore, the TiN layer has high wear resistance under high temperature erosion-corrosion conditions owing to its hardness. Hardness measurements of Figure 3 show that the hardness of the surface of a TiN coating is about 600 HV, which is almost double compared to the hardness of a
20 super duplex stainless steel. Hardness was measured according to the Vickers hardness test (ASTM E384-11e1). The initial hardness of titanium and titanium alloys varies usually between 100 and 250 HV depending on the chemical composition of the material. Various techniques known in the art can be utilized for measuring the wear resistance of the TiN layer.
25

In accordance with the present invention the hardness value (HV) of the TiN layer is preferably at least 300 HV, more preferably from 450 to 1800 HV, most preferably from 550 to 800 HV. The hardness of the TiN layer can be controlled by changing the different processing parameters depending on the
30 type of nitriding.

In accordance with an aspect of the present invention the outer layer of the main shell of the autoclave is preferably composed of carbon steel. The interior layer composed of titanium or titanium alloy is preferably bonded to the outer layer by explosion welding. Alternatively it can be bonded by any
35 other similar technique giving sufficiently high quality metallurgical bond. In an further example of the present invention the main shell of the autoclave com-

prises: an outer layer composed of steel; a titanium layer explosion welded to the steel layer; and a TiN layer formed on the surface of the titanium layer so that the TiN layer covers the surface of the titanium layer and only the TiN layer comes into contact with the slurried ores and/or concentrates.

5 An autoclave for pressure oxidation of slurried ores and/or concentrates comprising a main shell having an interior surface composed of titanium or titanium alloy having a TiN layer on its surface, the TiN layer coming into contact with the slurried ores and/or concentrates and oxygen and preventing exposure of titanium to oxygen can be provided by the steps of: providing a
10 plate of carbon steel; providing a thin sheet of titanium or titanium alloy; explosion welding the plate of carbon steel to the thin sheet of titanium or titanium alloy to obtain a titanium carbon steel plate; forming a TiN layer on the surface of the titanium or titanium alloy layer of the titanium carbon steel plate using a nitriding method to obtain a TiN coated titanium steel plate; and fabricating the
15 autoclave form a plurality of obtained TiN coated titanium steel plates. The obtained TiN coated titanium steel plates can be fabricated into a final autoclave assembly by for example welding the plates together by the welding methods especially developed for welding TiN coated titanium.

EXAMPLES

20 Erosion resistance of several interior surfaces (Ti Gr. 2, Ti Gr. 12 TiO₂ and TiN) was tested by exposing the interior surface of a slurry port testing device to quartz sand slurry (125 to 180 microns). The weight loss of the surface was measured after 40 min exposure by weighing the samples before and after the test and calculating the weight change. Results of the test are
25 shown in Figure 4. TiN surface demonstrated best wear properties as only minor weight loss was observed.

 It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above
30 but may vary within the scope of the claims.

CLAIMS

1. An autoclave for pressure oxidation of slurried ores and/or concentrates comprising a main shell having an interior layer composed of titanium or titanium alloy having a TiN layer on its surface, the TiN layer coming into
5 contact with the slurried ores/or concentrates and oxygen and preventing exposure of titanium to oxygen.
2. The autoclave as claimed in claim 1, wherein the interior layer is resistant to corrosion and erosion.
3. The autoclave as claimed in claim 1 or 2, wherein the TiN layer
10 has a thickness of 1 to 5 mm, preferably 3 to 4 mm.
4. The autoclave as claimed in any one of claims 1 to 3, wherein the TiN layer is metallurgically bonded to titanium or titanium alloy.
5. The autoclave as claimed in any one of claims 1 to 4, wherein the interior layer of titanium or titanium based alloy is bonded to the outer layer of
15 the main shell by explosion welding.
6. The autoclave as claimed in any one of claims 1 to 5, wherein the TiN layer is obtained by nitriding surface of the titanium or titanium alloy.
7. The autoclave as claimed in any one of claims 1 to 6, wherein the hardness value (HV) of the TiN layer is preferably at least 300 HV, more preferably from 450 to 1800 HV, most preferably from 550 to 800 HV.
20
8. The autoclave as claimed in any one of claims 1 to 7 wherein the main shell of the autoclave comprises: an outer layer composed of steel; a titanium layer explosion welded to the steel layer and having a thickness from 8 to 10 mm; and a TiN layer formed on the surface of the titanium layer so that
25 the TiN layer covers the surface of the titanium layer and only the TiN layer comes into contact with the slurried ores and/or concentrates and oxygen and wherein the thickness of the TiN layer is from 3 to 5 mm.
9. The autoclave as claimed in any one of claims 1 to 8, wherein the outer layer of the main shell is carbon steel.
- 30 10. The autoclave as claimed in any one of claims 1 to 9, wherein thickness of the outer layer is from 50 to 100 mm.
11. The autoclave as claimed in any one of claims 1 to 10, wherein the thickness of the titanium layer is from 8 to 10 mm.

Figure 1

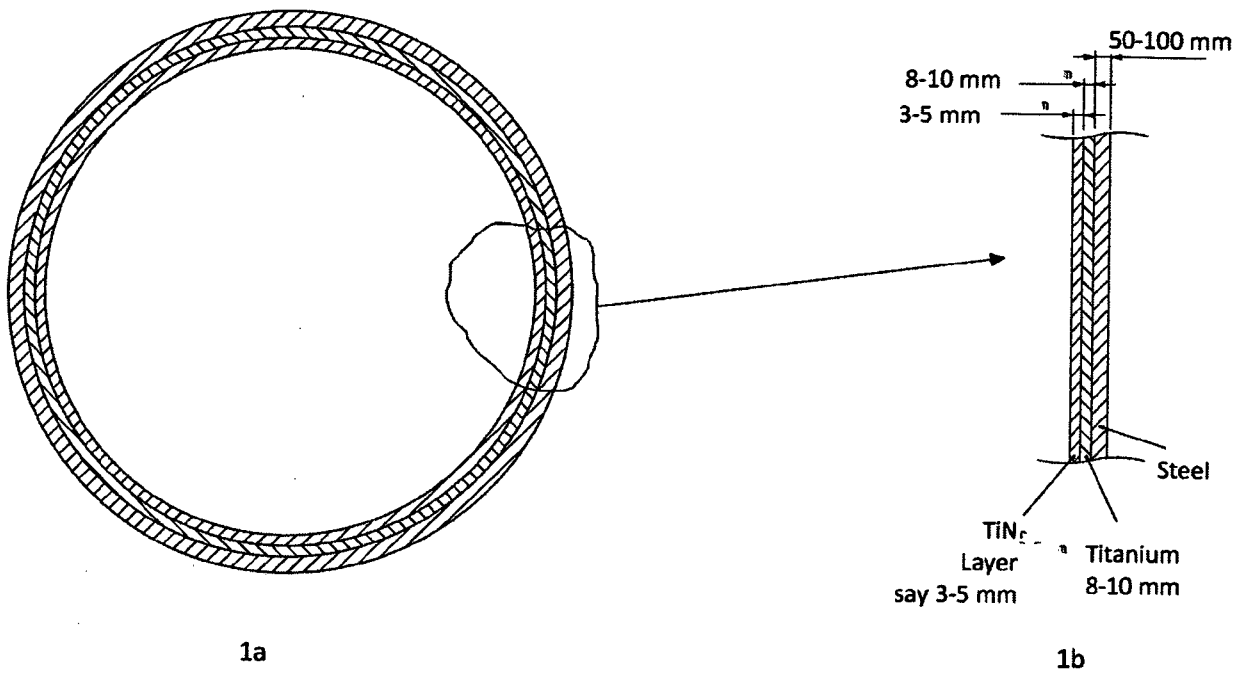


Figure 2

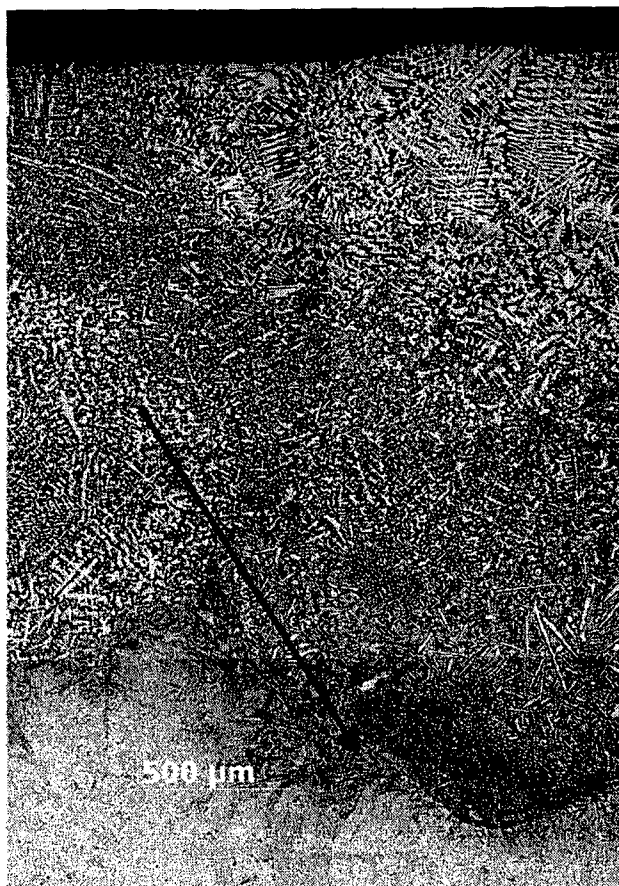


Figure 3

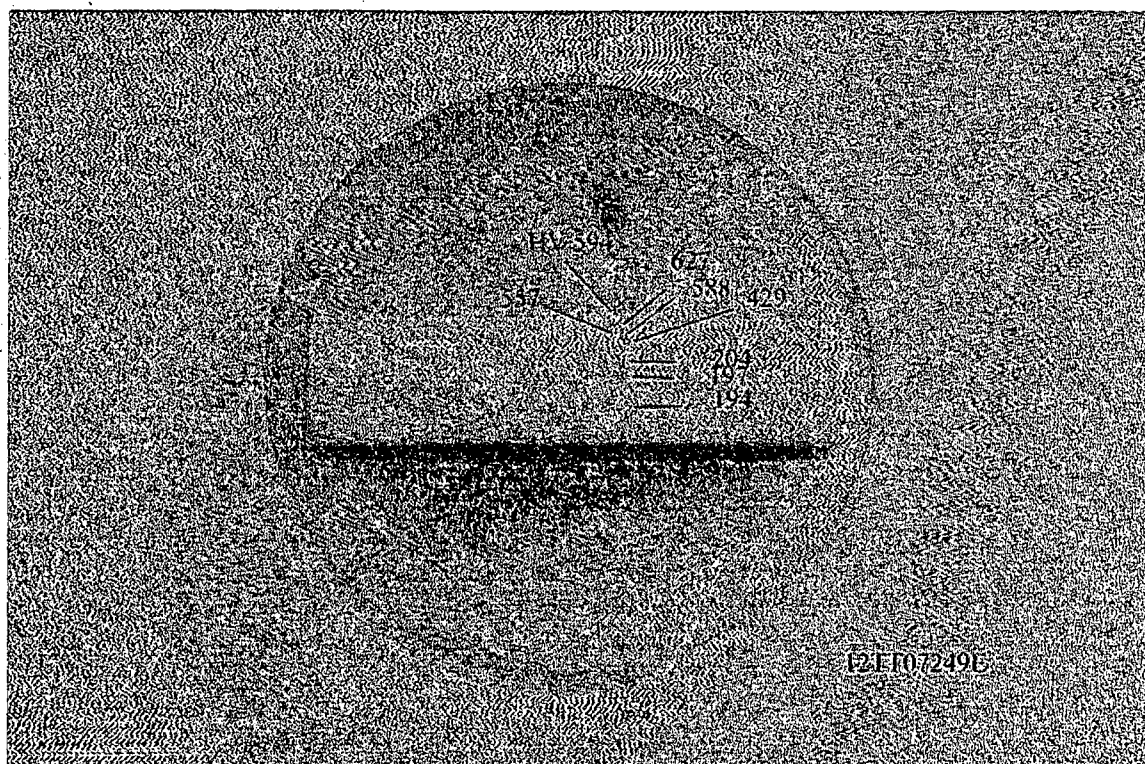
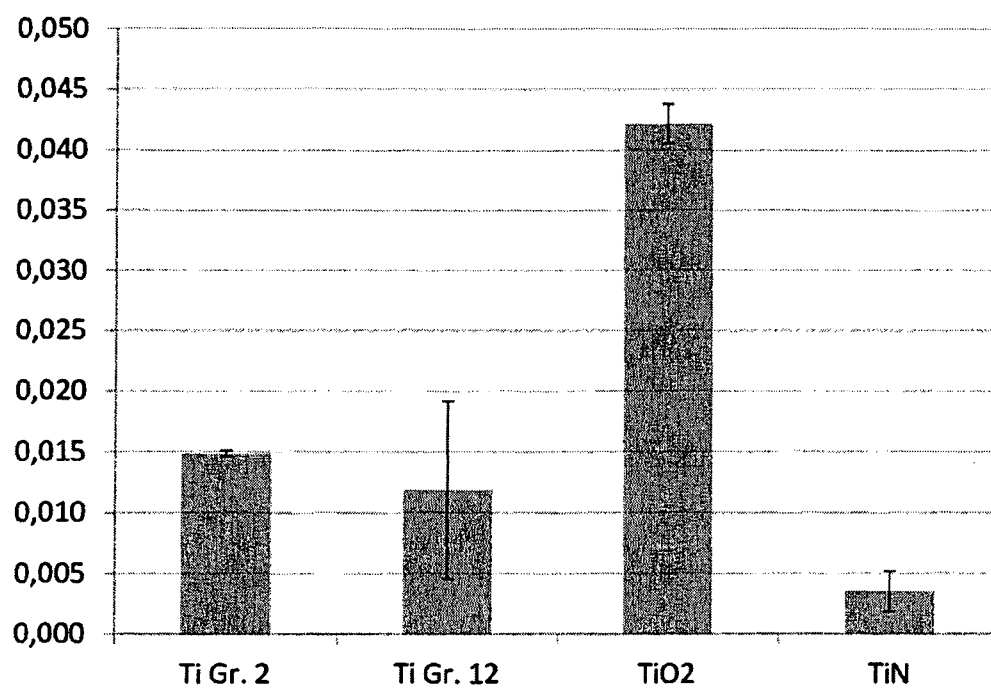


Figure 4



INTERNATIONAL SEARCH REPORT

International application No

PCT/FI2014/050986

A. CLASSIFICATION OF SUBJECT MATTER

INV. C22B3/02 B01J3/04
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)

C22B B01J

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, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2003 082420 A (DOWA MINING CO) 19 March 2003 (2003-03-19) the whole document -----	1-11
Y	US 2008/286180 A1 (JONES DAVID L [CA]) 20 November 2008 (2008-11-20) example 1 -----	1-11
Y	WO 01/83837 A1 (WESTERLAND PTY LTD [AU]; BOSSONG STEVEN MARTIN [AU]; VUKCEVIC RADOMIR) 8 November 2001 (2001-11-08) page 1, line 13 - line 28; claim 23 page 7, line 20 - line 24 -----	1-11
A	US 5 575 981 A (KRAUSE EBERHARD [CA]) 19 November 1996 (1996-11-19) the whole document ----- -/-	1-11

☒ 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

9 March 2015

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INTERNATIONAL SEARCH REPORT

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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.
A	US 4 627 900 A (SHERWOOD WILLIAM G [US] ET AL) 9 December 1986 (1986-12-09) the whole document -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

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