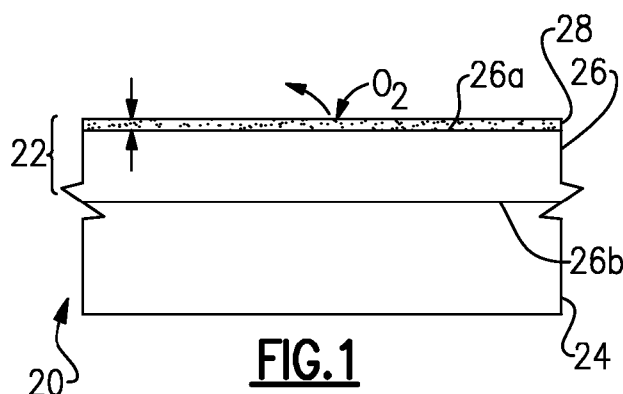




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(54) **Title:** SILICON OXYCARBIDE-BASED ENVIRONMENTAL BARRIER COATING



(57) **Abstract:** An article includes a silicon oxycarbide-based layer that has Si, O, and C in a covalently bonded network. The silicon oxycarbide-based layer has first and second opposed surfaces. A calcium-magnesium aluminosilicate-based layer is interfaced with the first surface of the silicon oxycarbide-based layer.

SILICON OXYCARBIDE-BASED ENVIRONMENTAL BARRIER COATING

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application No. 61/927,079, filed January 14, 2014.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under contract number N00014-09-C-0201 awarded by the United States Navy. The government has certain rights in the invention.

BACKGROUND

[0003] This disclosure relates to composite articles, such as those used in gas turbine engines.

[0004] Components, such as gas turbine engine components, may be subjected to high temperatures, corrosive and oxidative conditions, and elevated stress levels. In order to improve the thermal and/or oxidative stability, the component may include a protective ceramic barrier coating.

SUMMARY

[0005] An article according to an example of the present disclosure includes a silicon oxycarbide-based layer having Si, O, and C in a covalently bonded network, the silicon oxycarbide-based layer having first and second opposed surfaces, and a calcium-magnesium alumino-silicate-based layer interfaced with the first surface of the silicon oxycarbide-based layer.

[0006] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer further includes SiO₂.

[0007] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer includes, by volume, 5-65% of the SiO₂ with a remainder of silicon oxycarbide.

[0008] In a further embodiment of any of the foregoing embodiments, the SiO₂ is a continuous matrix phase with regions of the silicon oxycarbide dispersed there through.

[0009] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer further includes a dispersed phase of barium-magnesium alumino-silicate.

[0010] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer includes, by volume, 1-30% of the dispersed phase of barium-magnesium alumino-silicate.

[0011] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer further includes a continuous matrix phase of SiO₂ and a dispersed phase of barium-magnesium alumino-silicate.

[0012] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer further includes a continuous matrix phase of barium-magnesium alumino-silicate and a dispersed phase of SiO₂.

[0013] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer further includes a continuous matrix phase of SiO₂ or barium-magnesium alumino-silicate, the silicon oxycarbide-based layer including, by volume, 5-65% of the continuous matrix phase, and 1-30% of a dispersed phase of the other of the SiO₂ or barium-magnesium alumino-silicate, with a remainder of silicon oxycarbide.

[0014] In a further embodiment of any of the foregoing embodiments, the calcium-magnesium alumino-silicate-based layer partially penetrates into the silicon oxycarbide-based layer such that at least a central core of the silicon oxycarbide-based layer is free of calcium-magnesium alumino-silicate-based material.

[0015] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer has a composition SiO_xM_zC_y, where M is at least one metal, $x < 2$, $y > 0$ and $z < 1$ and x and z are non-zero.

[0016] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer is thicker than the calcium-magnesium alumino-silicate-based layer.

[0017] In a further embodiment of any of the foregoing embodiments, the calcium-magnesium alumino-silicate-based layer has an average thickness of 1 micrometer to 3 millimeters.

[0018] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based layer includes discrete regions of silicon oxycarbide-based material, the discrete regions having an average maximum dimension of 1-75 micrometers.

[0019] In a further embodiment of any of the foregoing embodiments, the calcium-magnesium alumino-silicate-based layer sealing the silicon oxycarbide-based layer from oxygen diffusion and steam recession into the silicon oxycarbide-based layer.

[0020] A composite according to an example of the present disclosure includes a silicon oxycarbide-based material having Si, O, and C in a covalently bonded network, the silicon oxycarbide-based material having a surface, and a calcium-magnesium alumino-silicate-based material interfaced with the surface of the silicon oxycarbide-based material.

[0021] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based material further includes a dispersed phase of barium-magnesium alumino-silicate.

[0022] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based material includes, by volume, 1-30% of the dispersed phase of barium-magnesium alumino-silicate.

[0023] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based material further includes a continuous matrix phase of SiO_2 or barium-magnesium alumino-silicate, and a dispersed phase of the other of barium-magnesium alumino-silicate or SiO_2 .

[0024] In a further embodiment of any of the foregoing embodiments, the silicon oxycarbide-based material has a composition $\text{SiO}_x\text{M}_z\text{C}_y$, where M is at least one metal, $x < 2$, $y > 0$ and $z < 1$ and x and z are non-zero.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] The various features and advantages of the present disclosure will become apparent to those skilled in the art from the following detailed description. The drawings that accompany the detailed description can be briefly described as follows.

[0026] Figure 1 illustrates a portion of an example article that includes a silicon oxycarbide-based layer and a calcium-magnesium alumino-silicate-based layer.

[0027] Figure 2 illustrates a covalently bonded network of Si, O, and C atoms.

[0028] Figure 3 illustrates a portion of another example article that includes a silicon oxycarbide-based layer and a calcium-magnesium alumino-silicate-based layer.

[0029] Figure 4 illustrates a portion of another example article that includes a silicon oxycarbide-based layer and a calcium-magnesium alumino-silicate-based layer.

[0030] Figure 5 illustrates a portion of another example article that includes a silicon oxycarbide-based layer and a calcium-magnesium alumino-silicate-based layer.

[0031] Figure 6 illustrates a micrograph of a silicon oxycarbide-based layer and a calcium-magnesium alumino-silicate-based layer.

DETAILED DESCRIPTION

[0032] Figure 1 schematically illustrates a representative portion of an example article 20 that includes a composite material 22. The article 20 can be a gas turbine engine component, such as but not limited to an airfoil, a combustor liner panel, a blade outer air seal, or other component that would benefit therefrom. In this example, the composite material 22 is used as an environmental barrier coating system to protect an underlying substrate 24 from environmental conditions, as well as thermal conditions. As will be appreciated, the composite material 22 of the coating system can be used as a stand-alone environmental barrier coating, as an outermost/topcoat with additional underlying layers, or in combination with other coatings, such as, but not limited to, ceramic thermal barrier coatings.

[0033] In this example, the composite material 22 of the article 20 includes a silicon oxycarbide-based layer 26 that extends between first and second opposed surfaces 26a/26b and a calcium-magnesium alumino-silicate-based layer 28 interfaced with the first surface 26a of the silicon oxycarbide-based layer 26. The calcium-magnesium alumino-silicate-based layer 28 can be deposited using known coating deposition techniques, such as but not limited to thermal spraying. In other examples, at least a portion of the calcium-magnesium alumino-silicate-based layer 28 can be deposited *in-situ* during use of the article 20, with purposeful exposure to calcium-, magnesium-, aluminum-, and silicon-containing materials at temperatures that can cause at least partial liquefaction and wetting to a coating with at least partial adhesion to the underlying layer.

[0034] As shown in the example in Figure 2, the silicon oxycarbide-based layer 26 has Si, O, and C atoms in a covalently bonded network 30. The network 30 is amorphous and thus does not have long range crystalline structure. The illustrated network 30 is merely one example in which at least a portion of the silicon atoms are bonded to both O atoms and C atoms. As can be appreciated, the bonding of the network 30 will vary depending upon the atomic ratios of the Si, C, and O. In one example, the silicon oxycarbide-based layer 26 has a composition $\text{SiO}_x\text{M}_z\text{C}_y$, where M is at least one metal, x is less than two, y is greater than zero, z is less than one, and x and z are non-zero. The metal can include aluminum, boron,

transition metals, refractory metals, rare earth metals, alkaline earth metals or combinations thereof.

[0035] While calcium-magnesium alumino-silicate material is normally expected to debit the durability of ceramic thermal barrier coatings, the calcium-magnesium alumino-silicate based layer 28 serves in the composite material 22 to seal the silicon oxycarbide-based layer 26 with respect to the combustion environment, including oxygen and steam, thus protecting the chemical composition of the silicon oxycarbide-based layer 26 and the underlying substrate 24 from oxidative attack and steam recession. In this regard, the calcium-magnesium alumino-silicate-based layer 28 in one example can have average thickness of 1 micrometer to 3 millimeters, with a preferred range of 1 – 254 micrometers, to provide a sealing functionality. In some examples, the calcium-magnesium alumino-silicate-based layer 28 can protect the silicon oxycarbide-based layer 26 and underlying substrate 24 from oxidation and steam attack at temperatures of up to about 2700°F (1482°C), and potentially greater than 3000°F (1648°C). In this case, although calcium-magnesium alumino-silicate material typically normally serves to destroy thermal barrier coatings, the composition of the silicon oxycarbide-based layer 26 is not readily infiltrated by the calcium-magnesium alumino-silicate material and, at high temperatures, the material does not substantially penetrate into the silicon oxycarbide-based layer 26.

[0036] Figure 3 illustrates another example article 120 that is similar to the article 20 of Figure 1 with the exception that a calcium-magnesium alumino-silicate based layer 128 penetrates partially, as represented at P, into the silicon oxycarbide-based layer 26. At least a central core 26c of the silicon oxycarbide-based layer 26 is free of calcium-magnesium alumino-silicate-based material. In this example, the penetration of the calcium-magnesium alumino-silicate material partially into the silicon oxycarbide-based layer 26 can occur at elevated temperatures at which the calcium-magnesium alumino-silicate material may soften or liquefy and penetrate into macro- or micro-pores of the silicon oxycarbide-based layer 26. However, due to the similar chemistry between the calcium-magnesium alumino-silicate based layer 128 and the silicon oxycarbide-based layer 26, the driving force for diffusion is relatively low. The thermomechanical behavior between the calcium-magnesium alumino-silicate based layer 128 and the silicon oxycarbide-based layer 26 is also similar because of the similar chemistry, thus reducing thermal expansion mismatches that could otherwise serve to initiate and propagate cracks.

[0037] Figure 4 illustrates another example article 220 that includes a silicon oxycarbide-based layer 226. In this example, the article 220 is somewhat similar to the article

20 of Figure 1, with the exception that the silicon oxycarbide-based layer 226 includes discrete regions 232 of silicon oxycarbide-based material that is dispersed within a continuous matrix phase 234. For example, the continuous matrix phase 234 is silicon dioxide (SiO_2) or barium-magnesium alumino-silicate. In one example, the silicon oxycarbide-based layer 226 includes, by volume, 40% of the silicon dioxide or barium-magnesium alumino-silicate, with a remainder of silicon oxycarbide, and the discrete regions 232 of silicon oxycarbide-based material have an average maximum dimension, represented at D, of 75 micrometers or less, which facilitates blocking the diffusion of oxygen. In one further example, the continuous matrix phase 234 is the barium-magnesium alumino-silicate and there is also a dispersed phase of SiO_2 .

[0038] Figure 5 illustrates another example article 320 that is somewhat similar to the article 220 of Figure 4 with the exception that a silicon oxycarbide-based layer 326 additionally includes a dispersed phase of barium-magnesium alumino-silicate 336. In one example, the silicon oxycarbide-based layer 326 includes, by volume, 25% of the silicon dioxide, 4% of the dispersed phase of barium-magnesium alumino-silicate 336 and a remainder of silicon oxycarbide.

[0039] Figure 6 shows an example micrograph of the composite material. In this example, the composite material includes regions of the silicon oxycarbide 232 dispersed through a continuous or semi-continuous matrix phase of silicon dioxide 234, with the calcium-magnesium alumino-silicate-based layer 28 interfaced with the surface of the silicon oxycarbide-based material.

[0040] Although a combination of features is shown in the illustrated examples, not all of them need to be combined to realize the benefits of various embodiments of this disclosure. In other words, a system designed according to an embodiment of this disclosure will not necessarily include all of the features shown in any one of the Figures or all of the portions schematically shown in the Figures. Moreover, selected features of one example embodiment may be combined with selected features of other example embodiments.

[0041] The preceding description is exemplary rather than limiting in nature. Variations and modifications to the disclosed examples may become apparent to those skilled in the art that do not necessarily depart from the essence of this disclosure. The scope of legal protection given to this disclosure can only be determined by studying the following claims.

CLAIMS

What is claimed is:

1. An article comprising:
 - a silicon oxycarbide-based layer having Si, O, and C in a covalently bonded network, the silicon oxycarbide-based layer having first and second opposed surfaces; and
 - a calcium-magnesium alumino-silicate-based layer interfaced with the first surface of the silicon oxycarbide-based layer.
2. The article as recited in claim 1, wherein the silicon oxycarbide-based layer further includes SiO₂.
3. The article as recited in claim 2, wherein the silicon oxycarbide-based layer includes, by volume, 5-65% of the SiO₂ with a remainder of silicon oxycarbide.
4. The article as recited in claim 2, wherein the SiO₂ is a continuous matrix phase with regions of the silicon oxycarbide dispersed there through.
5. The article as recited in claim 1, wherein the silicon oxycarbide-based layer further includes a dispersed phase of barium-magnesium alumino-silicate.
6. The article as recited in claim 5, wherein the silicon oxycarbide-based layer includes, by volume, 1-30% of the dispersed phase of barium-magnesium alumino-silicate.
7. The article as recited in claim 1, wherein the silicon oxycarbide-based layer further includes a continuous matrix phase of SiO₂ and a dispersed phase of barium-magnesium alumino-silicate.
8. The article as recited in claim 1, wherein the silicon oxycarbide-based layer further includes a continuous matrix phase of barium-magnesium alumino-silicate and a dispersed phase of SiO₂.
9. The article as recited in claim 1, wherein the silicon oxycarbide-based layer further includes a continuous matrix phase of SiO₂ or barium-magnesium alumino-silicate, the silicon oxycarbide-based layer including, by volume, 5-65% of the continuous matrix phase, and 1-30% of a dispersed phase of the other of the SiO₂ or barium-magnesium alumino-silicate, with a remainder of silicon oxycarbide.
10. The article as recited in claim 1, wherein the calcium-magnesium alumino-silicate-based layer partially penetrates into the silicon oxycarbide-based layer such that at least a

central core of the silicon oxycarbide-based layer is free of calcium-magnesium alumino-silicate-based material.

11. The article as recited in claim 1, wherein the silicon oxycarbide-based layer has a composition $\text{SiO}_x\text{M}_z\text{C}_y$, where M is at least one metal, $x < 2$, $y > 0$ and $z < 1$ and x and z are non-zero.

12. The article as recited in claim 1, wherein the silicon oxycarbide-based layer is thicker than the calcium-magnesium alumino-silicate-based layer.

13. The article as recited in claim 1, wherein the calcium-magnesium alumino-silicate-based layer has an average thickness of 1 micrometer to 3 millimeters.

14. The article as recited in claim 1, wherein the silicon oxycarbide-based layer includes discrete regions of silicon oxycarbide-based material, the discrete regions having an average maximum dimension of 1-75 micrometers.

15. The article as recited in claim 1, the calcium-magnesium alumino-silicate-based layer sealing the silicon oxycarbide-based layer from oxygen diffusion and steam recession into the silicon oxycarbide-based layer.

16. A composite comprising:
 - a silicon oxycarbide-based material having Si, O, and C in a covalently bonded network, the silicon oxycarbide-based material having a surface; and
 - a calcium-magnesium alumino-silicate-based material interfaced with the surface of the silicon oxycarbide-based material.
17. The composite as recited in claim 16, wherein the silicon oxycarbide-based material further includes a dispersed phase of barium-magnesium alumino-silicate.
18. The composite as recited in claim 17, wherein the silicon oxycarbide-based material includes, by volume, 1-30% of the dispersed phase of barium-magnesium alumino-silicate.
19. The composite as recited in claim 16, wherein the silicon oxycarbide-based material further includes a continuous matrix phase of SiO₂ or barium-magnesium alumino-silicate, and a dispersed phase of the other of barium-magnesium alumino-silicate or SiO₂.
20. The composite as recited in claim 16, wherein the silicon oxycarbide-based material has a composition SiO_xM_zC_y, where M is at least one metal, $x < 2$, $y > 0$ and $z < 1$ and x and z are non-zero.

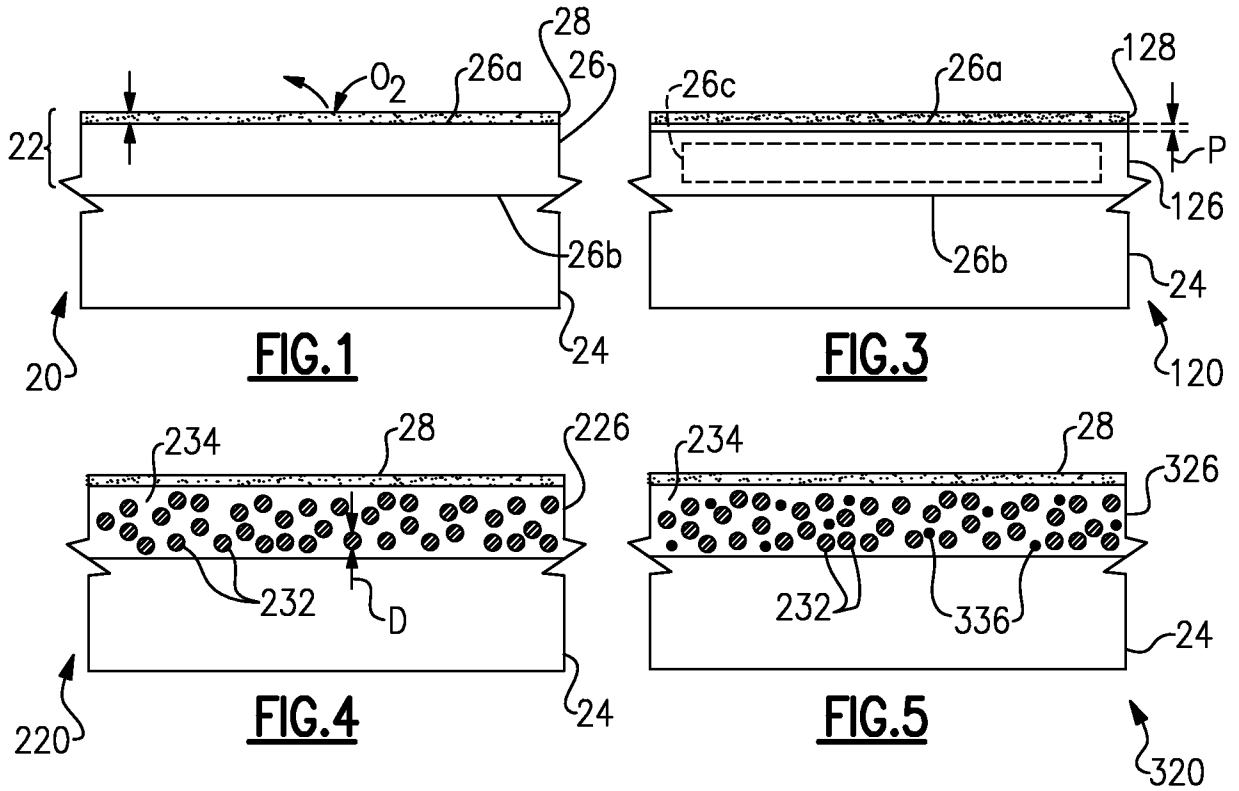


FIG. 6

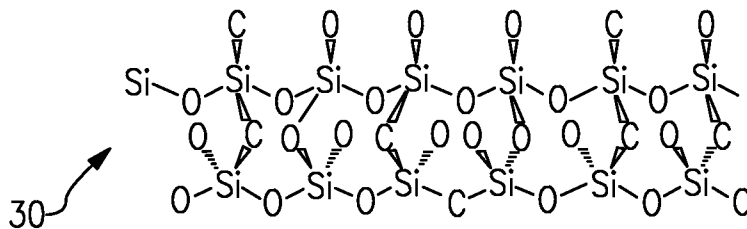


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/010554**A. CLASSIFICATION OF SUBJECT MATTER****B32B 7/02(2006.01)i, B32B 9/00(2006.01)i, B32B 33/00(2006.01)i**

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)

B32B 7/02; B05D 3/02; B32B 15/04; B32B 3/26; B32B 9/04; C23C 16/00; B32B 7/12; F03B 3/12; B32B 9/00; B32B 33/00

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:coating, silicon oxycarbide, layer, calcium-magnesium alumino-silicate**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A | EP 1726681 A1 (UNITED TECHNOLOGIES CORPORATION) 29 November 2006 See abstract; paragraphs [0009]-[0012]; claims 1, 9, 10; and figure 2. | 1-20 |
| A | US 2009-0324930 A1 (TULYANI, S. et al.) 31 December 2009 See abstract; paragraph [0015]; claims 1, 2, 8, 14, 15; figures 2 and 3. | 1-20 |
| A | US 6607852 B2 (SPITSBERG, I. et al.) 19 August 2003 See abstract; claims 1, 3, 8; and figure 1. | 1-20 |
| A | US 7951459 B2 (TANG, X. et al.) 31 May 2011 See abstract; claims 1, 4, 5; and figure 3. | 1-20 |
| A | US 6902836 B2 (EATON, H. E. et al.) 07 June 2005 See abstract; claims 1, 3; and figure 2. | 1-20 |

 Further documents are listed in the continuation of Box C. See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family


Date of the actual completion of the international search

21 April 2015 (21.04.2015)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/010554

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|----------------------------------------|------------------|-------------------------|------------------|
| EP 1726681 A1 | 29/11/2006 | CN 1868973 A | 29/11/2006 |
| | | CN 1868973 C | 03/09/2008 |
| | | EP 1726681 B1 | 05/05/2010 |
| | | JP 2006-327923 A | 07/12/2006 |
| | | US 2007-0014996 A1 | 18/01/2007 |
| | | US 7374818 B2 | 20/05/2008 |
| US 2009-0324930 A1 | 31/12/2009 | EP 2138477 A2 | 30/12/2009 |
| US 6607852 B2 | 19/08/2003 | US 2003-003328 A1 | 02/01/2003 |
| US 7951459 B2 | 31/05/2011 | EP 1925694 A2 | 28/05/2008 |
| | | EP 1925694 A3 | 02/03/2011 |
| | | JP 2008-127275 A | 05/06/2008 |
| | | US 2008-0187767 A1 | 07/08/2008 |
| | | US 2011-0200759 A1 | 18/08/2011 |
| US 6902836 B2 | 07/06/2005 | EP 1479659 A2 | 24/11/2004 |
| | | EP 1479659 A3 | 08/02/2006 |
| | | EP 1479659 B1 | 28/12/2011 |
| | | JP 2004-345944 A | 09/12/2004 |
| | | US 2004-0234783 A1 | 25/11/2004 |