Title: METHOD OF PREPARATION FOR TITANIA PHOTO-CATALYST BY OXYGEN PLASMA AND RAPID THERMAL ANNEALING

Abstract: Provided is a process for preparing a titania photocatalyst. The process comprises plasma-treating titanium to oxidize a surface of titanium into titania andsubjecting the titania to rapid thermal annealing. The photocatalyst prepared according to the present invention has a high purity and a nano size of a crystal particle, wherein the crystal has an anatase structure. Therefore, the photocatalyst of the present invention exhibits excellent photocatalytic properties and can be used for various applications such as water treatment apparatus, metal membranes, photocatalysts for decomposition of various organic materials and for hydrogen production, electrodes of electrochemical cells for hydrogen production via water decomposition, and the like.
METHOD OF PREPARATION FOR TITANIA PHOTO-CATALYST BY OXYGEN PLASMA AND RAPID THERMAL ANNEALING

The present invention relates to a titania photocatalyst and preparation thereof. More specifically, the present invention relates to a photocatalyst with excellent photocatalytic properties and a process for preparing the same.

Titanium dioxide (TiO₂, titania) used as a photocatalyst is an n-type semiconductor material, and generates electrons and holes with UV irradiation. The thus-generated electrons and holes migrate to the semiconductor surface, and then combine with oxygen (O₂) and hydroxyl (OH⁻), respectively, thereby forming hydroxy radicals and superoxide anions having strong oxidizing power which oxidize and decompose organic materials into water and carbon dioxide.

The titania photocatalyst can decompose a variety of pollutants and is therefore an environmentally friendly material. The titania photocatalyst can be used in the decomposition reaction of various organic materials, for example decomposition and sterilization of toxic substances or malodorous substances dissolved in water or suspended in air. Further, titania can be applied to
practical realization of environmental purification, and quarantine
and epidemic control.

Further, titania has been used in optical applications (such
as coating of chemical lens) and fabrication of solar reflective
glass, via formation of a titania thin film on a surface of a
substrate such as a ceramic material (e.g. glass, tile, or the like)
or an inorganic fiber. Titania is also expected to be used for
preparation of solar cells which can achieve inexpensive solar
photovoltaic power generation.

Generally, when it is desired to employ titania as a
photocatalyst, titania is used in the form of a fine powder.
Therefore, it is difficult to separate and recover titania, when it
is used in water treatment.

In order to overcome the above-mentioned problems, a great
deal of study and research has been actively made to find and
develop an immobilization method of titania.

Immobilization of titania may be carried out by a variety of
conventional methods known in the art, such as powder mixing, metal
oxidation, spin coating, spray pyrolysis, a sol-gel method, and
chemical vapor deposition.

The powder mixing is a method of immobilizing titania by
mixing of a titania powder with a binder and applying the mixture to
a support medium. The thus-immobilized titania exhibits a decreased
catalytically active area on the titania surface, due to the
presence of the binder, thereby resulting in deterioration of the
photocatalytic performance. Further, the binder undergoes
degradation of performance due to strong oxidant species produced by
the photocatalytic action of titania, and separation of the titania powder therefore occurs, resulting in damage to the catalyst.

The metal oxidation is a method of oxidizing a surface of a target object with titania by heating metallic titanium in the air or subjecting it to anodization, but suffers from disadvantages such as expensiveness and low specific surface area of metallic titanium.

The sol-gel method is currently the most widely used method of preparing a titania film by applying an organotitanium compound or a titanium sol material to a support material, followed by heat treatment. As a typical example, Korean Patent Application Publication No. 2000-63580 A1 discloses a process for preparing a photocatalyst including coating a thin film of a titanium alkoxide precursor on various materials such as glass, metal, fibers, paper, or the like by a dip-coating or spray method, heating the coated film at a temperature increasing rate of 1 to 20°C/min in a range of 50 to 700°C to form a titania photocatalyst thin film. However, this method suffers from various disadvantages such as the presence of a residual impurity (such as acid or an organic material) in a starting material, thus making it impossible to obtain a pure titania film, expensiveness of the starting material, and non-usability upon occurrence of damage in the film.

To cope with such problems as mentioned above, there has been proposed a method of forming titania in the form of a thin film, other than powder. Even though the titania thin film may be formed by a conventional method such as ion plating, sputtering, or the like, it is difficult to form a thin film on a substrate having a
large area or to form a uniform thin film on a surface of a substrate having a complicated shape.

Further, in order to exhibit excellent properties as the photocatalyst, titania preferably has an anatase structure. For this purpose, a conventional method involves heat treatment of the titania in a range of 400 to 500°C for 1 to 3 hours. However, such a long-term heat treatment of titania suffers from continuous growth of a crystal structure, thus leading to a decreased surface area of titania, and poor economic efficiency of manufacturing processes.

[Disclosure]

[Technical Problem]

Therefore, the present invention has been made in view of the above problems, and it is an object of the present invention to provide a process for preparing titania, which is more economical and provides excellent photocatalytic properties.

It is another object of the present invention to provide a photocatalyst prepared by the aforesaid process.

[Technical Solution]

In accordance with an aspect of the present invention, the above and other objects can be accomplished by the provision of a process for preparing a photocatalyst, comprising:

- plasma-treating titanium to oxidize a surface of titanium into titania; and

subjecting the titania to rapid thermal annealing.
The plasma treatment is carried out by supplying a gas selected from the group consisting of oxygen, nitrous oxide ($N_2O$), oxygen-containing air and a mixture thereof at a flow rate of 5 to 15 cm$^3$/min (seem) and at a temperature of less than 350°C, preferably 25 to 350°C. Preferably, pure oxygen gas is used. Further, in the above-mentioned treatment step, plasma is made by applying to the gas an electric power of at least 100 W, preferably 150 to 300 W under a pressure of 7.5$x10^{-2}$ to 8.5$x10^{-2}$ mbar for 5 to 10 min.

Thereafter, titania is subjected to rapid thermal annealing at a temperature of 400 to 500°C for 1 to 3 min.

In accordance with another aspect of the present invention, there is provided a photocatalyst prepared by the aforesaid process.

[Advantageous Effects]

A photocatalyst prepared according to the process of the present invention has a high purity, an anatase crystal structure and a nanoscale crystal particle size, thereby exhibiting excellent photocatalytic properties. Further, the process of the present invention involves a relatively brief thermal annealing process and is therefore more economical, as compared to a conventional art.

[Description of Drawings]

FIG. 1 is a process flow chart illustrating manufacturing steps of a titania photocatalyst in accordance with one embodiment of the present invention;

FIG. 2a is a sectional view illustrating a structure of a photocatalyst in accordance with one embodiment of the present
invention, and FIG. 2b is a schematic view illustrating manufacturing steps of the photocatalyst;

FIG. 3a is a sectional view illustrating a structure of a photocatalyst in accordance with another embodiment of the present invention, and FIG. 3b is a schematic view illustrating manufacturing steps of the photocatalyst;

FIG. 4 is a photograph showing a reaction vessel employed in a humic acid removal test of Test Example 1;

FIG. 5 is a graph showing results of Test Example 1;

FIGS. 6a and 6b are photographs showing results of Test Example 2;

FIG. 7 is a graph showing results of Test Example 3; and

FIGS. 8a to 8c are graphs showing results of Test Example 4.

[Best Mode]

Hereinafter, the present invention will be described in more detail.

The process for preparing a photocatalyst according to the present invention provides production of high-purity titania using titanium as an environmentally friendly material, without use of an additional medium. Titania has an anatase crystal structure, and a nanoscale crystal particle size, thereby exhibiting excellent photocatalytic properties.

FIG. 1 is a process flow chart illustrating a process for preparing a photocatalyst in accordance with one embodiment of the present invention.
Referring to FIG. 1, the process for preparing a photocatalyst in accordance with one embodiment of the present invention comprises a) oxidizing a surface of titanium using plasma, and b) subjecting the oxidized titanium to rapid thermal annealing. Hereinafter, individual steps will be illustrated in more detail.

a) Plasma-treatment

In Step a), a surface of titanium is oxidized into titania via plasma treatment.

Titanium used in Step a) may be in the form of bulk titanium or thin film titanium. Even though there is no particular limit to kinds of titanium in the present invention, titanium preferably has a purity of 99.0% to 99.9%.

The bulk titanium is processed and used in the form of spherical or pellet-like particles during a preparation process or otherwise may be commercially available. Further, titanium in the form of a thin film is prepared by a conventional vapor deposition method. For example, vapor deposition is carried out by any method selected from the group consisting of sputtering, ion beam deposition, chemical vapor deposition and plasma deposition. A thickness of the titanium thin film is not particularly limited in the present invention, and is appropriately adjusted depending upon desired applications of the photocatalyst.

According to the present invention, bulk titanium or thin film titanium is oxidized using plasma. Plasma is generated by a conventional plasma generator with injection of oxygen-containing
gas. Preferably, the plasma treatment is carried out by supplying a gas selected from the group consisting of oxygen, nitrous oxide ($N_2O$), oxygen-containing air and a mixture thereof at a flow rate of 5 to 15 seem and at a temperature of less than 350°C, preferably 25 to 350°C. Preferably, the plasma treatment is carried out by a supply of pure oxygen alone.

If an amount of injected gas is lower than the above-specified range, an amount of generated plasma decreases, thus requiring a longer period of time in the plasma treatment. On the other hand, if an amount of injected gas is higher than the above-specified range, a high pressure is required, thus resulting in a problem associated with generation of high-temperature plasma. The injection volume of gas may be sufficiently adjusted depending upon a size of a reaction chamber, a capacity of a vacuum pump, and the like.

Further, if the plasma treatment is carried out below the above-specified temperature range, it is difficult to achieve sufficient amounts of plasma generation. On the other hand, if the plasma treatment is carried out above the above-specified temperature range, it is not economical in terms of a manufacturing process, due to requirement of high energy and it may result in deterioration of surface properties such as surface damage, arising from generation of high-temperature plasma.

In another embodiment of the present invention, the plasma treatment may be carried out by mixing the oxygen-containing gas with nitrogen, argon or a mixed gas thereof to enhance effects of the plasma treatment.
The plasma treatment is carried out under a pressure of $7.5 \times 10^{-2}$ to $8.5 \times 10^{-2}$ mbar. If the plasma treatment pressure is lower than the above-specified range, it is difficult to generate plasma. On the other hand, if the plasma treatment pressure is higher than the above-specified range, this may result in generation of high-temperature plasma, thereby consuming large amounts of energy.

For generation of plasma, electric power of at least 100 W, preferably 150 to 300 W is applied for 5 to 10 min. If the applied electric power is lower than the above-specified range, an amount of generated plasma decreases, thus resulting in difficulty of oxidation. On the other hand, if the applied electric power is higher than the above-specified range, it is inefficient in terms of a manufacturing process. Further, if the plasma treatment time is shorter than the above-specified range, a sufficient amount of titania is not formed. On the other hand, if the plasma treatment time is longer than the above-specified range, it is not economical in terms of a manufacturing process.

A titania layer is formed on the surface of titanium which was plasma-treated under the above-specified conditions, and a crystal structure of the thus-formed titania becomes amorphous. The titania, which is formed according to an oxidation process of titanium using plasma, can be formed on the titanium surface and up to a position of a certain depth from the surface of titanium, so the present invention has an advantage in that it is possible to adjust the thickness of titania by a process condition.

b) **Rapid Thermal Annealing (RTA)**
Titanium, which forms titania by the above-mentioned process, is then subjected to rapid thermal annealing, and then a titania photocatalyst is prepared.

Titania exhibits poor photocatalytic properties in the amorphous state, so photocatalytic properties should be enhanced by converting a crystal structure of titania into crystalline anatase titania through a thermal annealing process. In a conventional art, thermal annealing was carried out at a temperature of 400 to 500°C for 1 to 3 hours. However, in titania of the present invention formed by plasma treatments of titanium, it is possible to obtain a sufficient anatase crystal structure even with thermal annealing at a temperature of 400 to 500°C for 1 to 3 min.

If the rapid thermal annealing is carried out at a temperature lower than the above-specified range, insufficient oxidation of titanium leads to formation of crystalline Ti$_2$O$_3$ or Ti$_2$O. On the other hand, if the thermal annealing is carried out at a temperature higher than the above-specified range, the crystalline phase of titania converts into rutile TiO$_2$, thereby resulting in deterioration of photocatalytic efficiency.

If the thermal annealing time is longer than 3 min, the process is not economical. On the other hand, if the thermal annealing time is shorter than 1 min, it is impossible to obtain a sufficient anatase structure.

Through such a rapid thermal annealing process, a photocatalyst with formation of titania on the surface of titanium is prepared. Herein, titania is formed to a thickness of 15 to 20 μ
on the surface of titanium, and has an anatase crystal structure and
a crystal particle size of 10 to 100 nm.

FIG. 2a is a sectional view illustrating a structure of a
photocatalyst in accordance with one embodiment of the present
invention, and FIG. 2b is a schematic view illustrating
manufacturing steps of the photocatalyst;

Referring to FIG. 2a, the photocatalyst prepared by the
preparation process in accordance with the aforesaid embodiment of
the present invention contains a layer 16 of anatase titania on a
surface of a titanium particle 12.

Referring to FIG. 2b, the surface of titanium particle 12 is
oxidized using plasma, thereby forming an amorphous titania layer 14
on the surface of the titanium particle 12. Thereafter, the layer 16
of anatase titania is formed on the surface of the titanium particle
12 by rapid thermal annealing.

FIG. 3a is a sectional view illustrating a structure of a
photocatalyst in accordance with another embodiment of the present
invention, and FIG. 3b is a schematic view illustrating
manufacturing steps of the photocatalyst.

Referring to FIG. 3a, the photocatalyst prepared by the
process in accordance with the aforesaid embodiment of the present
invention has a multi-layered structure in which an anatase titania
thin film 116 of is present on a surface of a titanium thin film
112.

Referring to FIG. 3b, the preparation process in accordance
with a second embodiment of the present invention includes
oxidizing the surface of the titanium thin film 112 using plasma to
thereby form an amorphous titania thin film on the surface of the titanium thin film and then converting the amorphous titania thin film into the anatase titania thin film of by rapid thermal annealing.

[Mode for Invention]

EXAMPLES

Now, the present invention will be described in more detail with reference to the following Examples. These examples are provided only for illustrating the present invention and should not be construed as limiting the scope and spirit of the present invention.

Example 1

A thin film of 99.7% pure titanium was etched with a mixed solution of HF, HNO₃ and H₂O (1:4:5, v/v) to remove a native oxide layer and then stored under vacuum.

The titanium thin film was placed in a PECVD plasma generator to which electric power of 150 W was then applied at 350°C, thereby generating plasma. The titanium thin film was subjected to plasma treatment with introduction of oxygen at a flow rate of 10 sccm for 5 min.

Next, the plasma-treated titanium thin film was subjected to thermal annealing in a rapid thermal annealer at a temperature of 500°C for 1 min, thereby preparing a photocatalyst having titania formed on the surface of the titanium thin film.
Example 2-(1)

A photocatalyst was prepared in the same manner as in Example 1, except that plasma treatment was carried out for 10 min by applying electric power of 300 W;

Example 2-(2)

A photocatalyst was prepared in the same manner as in Example 1, except that plasma treatment was carried out for 5 min by applying electric power of 300 W.

Comparative Example 1

According to a conventional art, a titanium thin film was heated with a thermal spray process to form an oxide film. The thus-oxidized titanium thin film was thermally annealed at 450°C for 1 hour to prepare a photocatalyst.

Comparative Example 2-(1)

A photocatalyst was prepared in the same manner as in Example 1, except that rapid thermal annealing was carried out at 300°C.

Comparative Example 2-(2)

A photocatalyst was prepared in the same manner as in Example 1, except that rapid thermal annealing was carried out at 800°C.

Test Example 1

In order to examine catalytic efficiency of a photocatalyst prepared according to the present invention, a removal test of humic acid (0.01 mg/L, available from Aldrich) was carried out for photocatalysts of Example 1 and Comparative Example 1.
The above-mentioned test was carried out using an apparatus shown in FIG. 4. Specifically, 4 UV bulbs were installed in a reaction vessel, and the bulbs were made of quartz in order to increase UV transmissivity. The bottom surface of a container positioned at the center of the reaction vessel was provided with a photocatalytic layer (area: 2x2 cm) as prepared in Example 1. Then, humic acid was added to an upper part of the photocatalytic layer, followed by UV irradiation. A removal amount of humic acid was periodically measured every 15 minutes.

Test results for the photocatalysts of Example 1 and Comparative Example 1 are shown in FIG. 5.

Referring to FIG. 5, it can be seen that the titania photocatalyst of Example 1 which was plasma-treated and then thermally annealed for 1 min in the same temperature range is superior in % removal of humic acid, as compared to the titania photocatalyst of Comparative Example 1 which was oxidized by thermal spray and then thermally annealed for 1 hour. In particular, upon reviewing the results after 120 min, the photocatalyst of the present invention exhibited about 70% removal of humic acid, whereas the photocatalyst of Comparative Example 1 exhibited about 45% removal of humic acid, thus representing that the photocatalyst of the present invention is higher in % removal of humic acid. That is, as compared to the titania photocatalyst which was prepared by a conventional process, the titania photocatalyst which was prepared by the process in accordance with the present invention exhibits superior catalytic effects even with brief thermal annealing.
Apart from the removal experiment of humic acid by the photocatalyst, when the same removal experiment of humic acid was carried out by irradiation of UV, it was expected to achieve substantially no removal effects of humic acid, particularly showing a significant difference upon comparison with the removal of humic acid using the photocatalyst of Example 1 of the present invention, simultaneously with UV irradiation.

Test Example 2

Surface morphology of photocatalysts of Example 1 and Example 2-(1) was examined using a scanning electron microscope (SEM). The results thus obtained are given in FIGS. 6a and 6b.

FIG. 6a is an SEM image showing surface morphology of the photocatalyst of Example 1, and FIG. 6b is an SEM image showing surface morphology of the photocatalyst of Example 2-(1).

Referring to FIGS. 6a and 6b, it can be seen that the photocatalyst of Example 2-(1) (FIG. 6b), which was plasma-treated with application of electric power of 300 W for 10 min, exhibits an increased catalytic surface area, as compared to the photocatalyst of Example 1 (FIG. 6a) which was plasma-treated with application of electric power of 150 W for 5 min. Accordingly, it is preferred to carry out the plasma treatment at power of 300 W for 10 min, in terms of surface properties.

Test Example 3

In order to investigate an oxidation state of photocatalysts of Examples 1, 2-(1) and 2-(2), X-ray photoelectron spectroscopy
(XPS) was carried out. The thus-obtained results are given in FIG. 7.

FIG. 7 is a graph showing X-ray diffraction patterns for photocatalysts of Examples 1, 2-(1) and 2-(2). Referring to FIG. 7, the intensity on the Y-axis refers to an oxidation degree of the catalytic surface, so it can be seen that the photocatalyst of Example 2-(1), which was oxygen plasma-treated at the power of 300 W for 10 min, exhibited a higher oxidation degree than the photocatalyst of Example 1 or 2-(2). Further, upon comparing the photocatalysts of Examples 2-(1) and 2-(2), which were plasma-treated at the power of 300 W, it can be seen that the peak of the graph for the photocatalyst of Example 2-(1) exhibits a further chemical shift to the right, as compared to that of Example 2-(2). These results represent that a surface of the photocatalyst of Example 2-(1), which was plasma-treated at the power of 300 W for 10 min, exhibits the higher oxidation degree than the photocatalyst of Example 2-(2) which was plasma-treated at the same power for 5 min.

Test Example 4

In order to investigate changes in a crystalline state of titania catalysts with varying temperatures of rapid thermal annealing, photocatalysts of Example 1 and Comparative Examples 2-(1) and 2-(2) were analyzed using an X-Ray Diffractometer (XRD). The results thus obtained are given in FIGS. 8a to 8c, respectively.

Referring to FIGS. 8a to 8c, a crystalline state of titania which was subjected to rapid thermal annealing at 500°C has an anatase (A) type (FIG. 8a), whereas titania, which was subjected to
thermal annealing at 800°C as shown in the photocatalyst of Comparative Example 2-(2), has a rutile (R) type (FIG. 8c), thus resulting in deterioration of the photocatalytic efficiency. Further, the photocatalyst of Comparative Example 2-(1) with thermal annealing at 300°C suffers from a problem associated with the residual titanium (T) which was not sufficiently oxidized (FIG. 8).
[CLAIMS]

[Claim 1] A process for preparing a photocatalyst, comprising:

plasma-treating titanium to oxidize a surface of titanium into titania; and

subjecting the titania to rapid thermal annealing.

[Claim 2] The process according to claim 1, wherein the plasma treatment is carried out at a temperature of less than 350°C.

[Claim 3] The process according to claim 1, wherein the plasma treatment is carried out by supplying a gas selected from the group consisting of oxygen, nitrous oxide (N₂O), oxygen-containing air and a mixture thereof.

[Claim 4] The process according to claim 3, wherein the gas is introduced at a flow rate of 5 to 15 s.e.m.

[Claim 5] The process according to claim 1, wherein the plasma treatment is carried out by applying electric power of 150 to 300 W under a pressure of 7.5*10⁻² to 8.5*10⁻² mbar.

[Claim 6] The process according to claim 1, wherein the plasma treatment is carried out for 5 to 10 min.

[Claim 7] The process according to claim 1, wherein the rapid thermal annealing is carried out at a temperature of 400 to 500°C for 1 to 3 min.

[Claim 8] The process according to claim 1, wherein the titania is in the form of bulk titania or thin film titania.

[Claim 9] A photocatalyst which is prepared by the process of any one of claims 1 to 8 and has titania formed on the surface of titanium.
[Claim 10] The photocatalyst according to claim 9, wherein the titania has an anatase crystal structure.

[Claim 11] The photocatalyst according to claim 9, wherein the titania has a crystal particle size of 10 to 100 nm.

[Claim 12] The photocatalyst according to claim 9, wherein the titania has a thickness of 15 to 20 μm.
Figure 1

a) Plasma treating of titanium

b) Rapid thermal annealing

Titanium/titania photocatalyst
[Figure 7]

![Graph showing intensity vs. binding energy for Ex. 1, Ex. 2-(1), and Ex. 2-(2).]
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

BO1J 21/06(2006.01)1

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)

IPC 8 B01J21/06 B01J23/00 B01J21/00 B01J23/20 B32B 17/6 B5D 1/8 C01G23/00 C01G23/047 C23C4/10 C23C16/40

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 since 1975
Japanese Utility Models and Applications for Utility Models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS(KIPO internal), WPI, USPAT, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US200401 15362A1 2004/06/17 Klaus Hartig Annette J Køsko see the whole documents, claims 1-6</td>
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<tr>
<td>A</td>
<td>US06254940 B1 2001/07/03 University of Cincinnati Pratsims see the whole documents</td>
<td>1-12</td>
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<tr>
<td>A</td>
<td>US07078130 B2 2006/07/18 University of Windsor see the whole documents</td>
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Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents
"A" document defining the general state of the art which is not considered to be of particular relevance
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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
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Date of the actual completion of the international search

20 FEBRUARY 2008 (20 02 2008)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

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Facsimile No 82-42-472-7140

Authorized officer

SHIN, JU CHEOL
Telephone No 82-42-481-5564

Form PCT/ISA/210 (second sheet) (April 2007)
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<tr>
<td></td>
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<td>US2002029955A1</td>
<td>14.03.2002</td>
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<td>US2002029955AA</td>
<td>14.03.2002</td>
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<tr>
<td></td>
<td></td>
<td>US6777374BB</td>
<td>17.08.2004</td>
</tr>
<tr>
<td>US20040115362A1</td>
<td>17.06.2004</td>
<td>AU2002250831AA</td>
<td>30.07.2002</td>
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<tr>
<td></td>
<td></td>
<td>EP1352105A2</td>
<td>15.10.2003</td>
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<td>08.07.2004</td>
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<td>JP2004520484T2</td>
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<td>US20041115362A1</td>
<td>17.06.2004</td>
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<td>US20041115362AA</td>
<td>17.06.2004</td>
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<td>WO2002057508A2</td>
<td>25.07.2002</td>
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<td>WO2002057508A3</td>
<td>03.01.2003</td>
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<td>07.11.2000</td>
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<td>JP2000514870T2</td>
<td>07.11.2000</td>
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<td>03.07.2001</td>
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<td>US6254940BA</td>
<td>03.07.2001</td>
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<td></td>
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<td>W09802241A1</td>
<td>22.01.1998</td>
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<td>US2004077493A1</td>
<td>22.04.2004</td>
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