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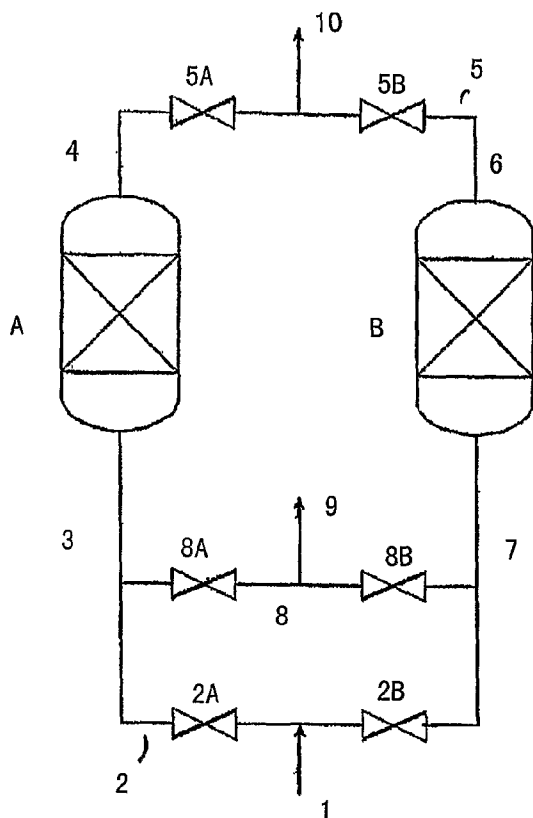
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[Continued on next page]

(54) Title: GAS PURIFICATION PROCESSES



(57) Abstract: Methods for separating acid gases from gas streams are disclosed herein. The gas streams, such as methane, containing the acid gases contact a separation means, such as a monolith substrate, porous membrane, or pellets and/or beads that has been coated, impregnated, or filled with an ionic liquid or mixtures of ionic liquids. The ionic liquids are exemplified by imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, sulphonium and/or guanidinium-based ionic liquids.

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PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

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GAS PURIFICATION PROCESSES

BACKGROUND OF THE INVENTION

The present invention provides for processes for purifying gas streams. More particularly, the present invention relates to processes for removing acid gases from feed gas streams using adsorption and/or absorption means prepared with ionic liquids.

Hydrogen sulfide and carbon dioxide can form acids when they contact water. These acids will be in the form of gas in many industrial processes whereby the hydrogen sulfide and carbon dioxide are by-products of the process. Acid gases are not a desirable component, particularly when the process involved is the production or recovery of a particular gas or mixture of gases. The acid gases can be deleterious to the industrial processes and can cause corrosion and interference in other aspects of the operation.

Accordingly the acid gases must be removed so that the twin benefit of improved end product quality and improved equipment life are achieved. Typically acid gases are removed by absorption, membrane permeation or adsorption processes. Absorption is desirable when the acid gas partial pressure is high. Membrane permeation may be used to remove carbon dioxide from a high pressure gas. Adsorption is a viable alternative when acid gas concentration is small and the gas contains the heavier sulfur compounds such as mercaptans and carbon disulfide.

The present inventors have discovered a process whereby ionic liquids are employed in a manner such that a variety of removal techniques may be utilized for removing acid gas from gas streams such as natural gas.

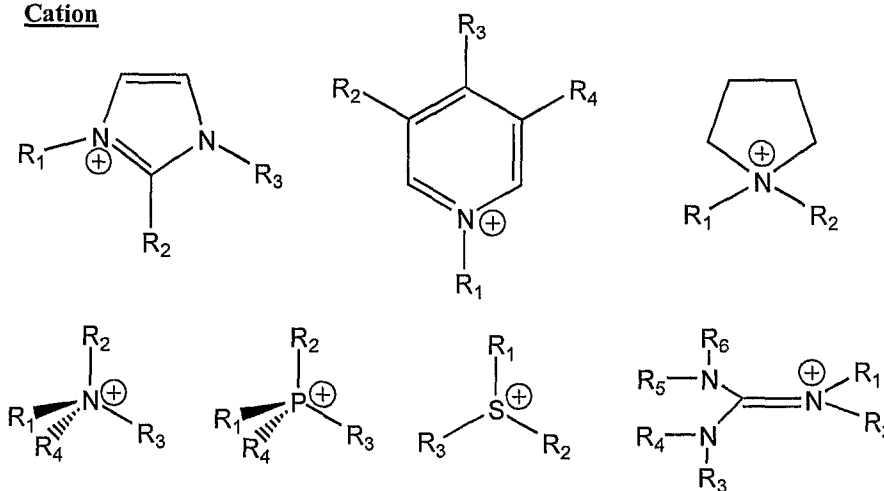
SUMMARY OF INVENTION

The present invention provides for the use of ionic liquids which are applied to a variety of materials and substrates for use in removing acid gases from gas streams.

Ionic liquids are employed in the processes of the present invention. Ionic liquids are defined as purely ionic, salt-like materials that are liquid below 100 °C. Typically ionic liquids have melting points below 0°C. Ionic liquids remain liquid over a wide temperature range of about 300 to 400°C from the melting point to the decomposition temperature.

In the present invention, a variety of ionic liquids can be employed, including but not limited to imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, sulphonium, and guanidinium-based ionic liquids or their mixtures as shown below:

Cation



wherein R_{1-6} = hydrocarbon chains

Anion



The various groups designated R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are H groups and

straight or branched alkyl and alkenyl groups having 1 to 12 carbons. Certain amine groups such as thiourea or amino groups can also be incorporated into the cation of the ionic liquid to improve its sequestration capability for H_2S and CO_2 . Additionally, hydroxyl groups may be incorporated into the cation. For a specific application, consideration for the optimal combination of a cation and an anion is required to achieve high adsorption capacity and high thermal stability of the ionic liquids.

The ionic liquids of the present invention are employed in various gas separation processes for removing the acid gases from the gas stream that is sought to be purified.

The ionic liquids are coated onto the surface of monolith substrates which can be in the shape of a honeycomb, foam or reticulate. These substrates are in the shape of a disc and are loaded into a gas column such that the gas mixture will flow through the fixed bed containing the ionic liquid coated monolith structure. These monolith substrates may also be fabricated by ink-jet printing or robocasting processes.

The ionic liquids are also coated on or impregnated into porous membrane materials. Membranes may be fabricated in a symmetric or asymmetric form with the pore size of the membrane varying radially. The membranes can be coated as one layer or filled with the selected ionic liquid and will work as affinity absorbents or supported liquid membranes. The membranes may be loaded into the gas column as a single tube or as a plurality of tubes whereby the gas mixture to be purified will flow in the tube side of the membrane structures.

The ionic liquids may also be employed by coating on or encapsulated in porous beads and/or pellets. The coated beads and/or pellets may be loaded into a gas column and will be in a fixed, moving or fluidized beds.

The ionic liquids may also be coated onto or encapsulated in porous beads and/or pellets and these can be secured to or impregnated within layered or

laminated sheet materials. The coated sheet materials that contain the coated beads and/or pellets are employed by stacking the sheets together to allow gaps between the sheets when stacked in the gas column. The flow of gas to be purified will be parallel to the sheet surface. When porous beads and/or pellets are employed that contain multiple channels throughout in an adsorber bed, resistance to gas flow would be similar in all directions. Gas flow in these instances may then be at an angle with respect to an individual bead and/or pellet but would be influenced by the engineering design of the adsorber bed. In applications such as packed bed adsorption applications, gas flow will be either axial along the bed or radial in the case of radial bed adsorbers.

If the ionic liquid materials are coated on a monolith substrate, gas flow through the monolith substrate adsorber will be parallel to the channels in the monolith substrate in order to minimize the pressure drop. In certain instances, the monolith adsorbent materials will have parallel channels in one direction and gas flow will be only in the direction parallel to the channels present therein.

The acid gases that can be treated by the methods of the present invention are those typically found in gas streams. The acid gases include but are not limited to hydrogen sulfide, carbon dioxide, nitrogen oxides and sulfur oxides.

BRIEF DESCRIPTION OF DRAWINGS

The figure is a schematic outline of a two-bed process for removing acid gases as practiced by the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides in one embodiment a method for separating acid gases from a feed gas stream containing acid gases comprising contacting said feed gas stream with a monolith substrate that has been coated with an ionic liquid or mixtures of ionic liquids.

The present invention provides in an alternative embodiment a method for separating acid gases from a feed gas stream containing acid gases comprising contacting said feed gas stream with a porous membrane that has been coated or impregnated with an ionic liquid or mixtures of ionic liquids.

The present invention provides in yet another alternative embodiment a method for separating acid gases from a feed gas stream containing acid gases comprising contacting said feed gas stream with porous beads and/or pellets that have been coated or filled with an ionic liquid or mixtures of ionic liquids, or are impregnated within layered or laminated sheet materials, that may also be coated with ionic liquids.

The present invention provides in a further embodiment, a method for separating acid gases from a feed gas stream containing acid gases using pressure swing adsorption (PSA), vacuum-pressure swing adsorption (VPSA), temperature swing adsorption, and/or absorption. The regeneration of the ionic liquids can be achieved by vacuum, heating, purging with the product gas stream and/or extraction using another gas stream with high selectivity for acid gases. The removal of acid gases from the feed gas stream can be carried out in a single bed or multiple beds operated in cyclical modes.

A typical PSA cycle consists of the following sequence of steps: pressurization, adsorption with product withdrawal, blowdown, desorption at lower pressure, pressure equalization, and rinse.

The present invention is described with reference to the figure which represents a two bed system for removing acid gases from a gas stream. The feed gas which can be natural gas from a wellhead or that which is obtained from a coal-bed enters through line 1 to line 2. Valves 2A and 2B are controlled so that the feed gas stream containing the acid gas impurity is directed along line 2 to line 3. Valve 2B remains closed while the feed gas stream travels through line 3 to first

bed A. The first bed A will contain any of the variant means for removing the acid gases from the feed gas stream such as the ionic liquid coated on a monolith substrate, the ionic liquid coated onto or impregnated in porous membrane materials, the ionic liquid coated on or encapsulated in beads and/or pellets, or the ionic liquid impregnated into the layered or laminated sheet materials. The acid gases will remain in the acid gas separation means which is employed in first bed A while the feed gas stream will continue through line 4 and open valve 5A through line 5 where the purified feed gas stream is recovered as product gas.

A portion of the feed gas stream that has been purified will flow through line 5 and open valve 5B to enter second bed B. In this explanation of the operation of the two bed system, bed A is the production bed and bed B is the desorption or countercurrent bed. The order of which bed is the production bed will alternate so that while one bed is producing purified feed gas, the other bed is being purged of the acid gases that were adsorbed or absorbed when it was acting as the production bed. The purified feed gas stream entering second (bed B) will help desorb the acid gases that were adsorbed or absorbed when bed B was acting as the production bed. The purified gas stream which now contains the previously adsorbed or absorbed acid gases will travel through line 7 where it will enter line 8 and open valve 8B and ultimately be vented through line 9, or it can be directed through line 8 and open valve 8A to line 3 where it will enter the first bed A for purification purposes.

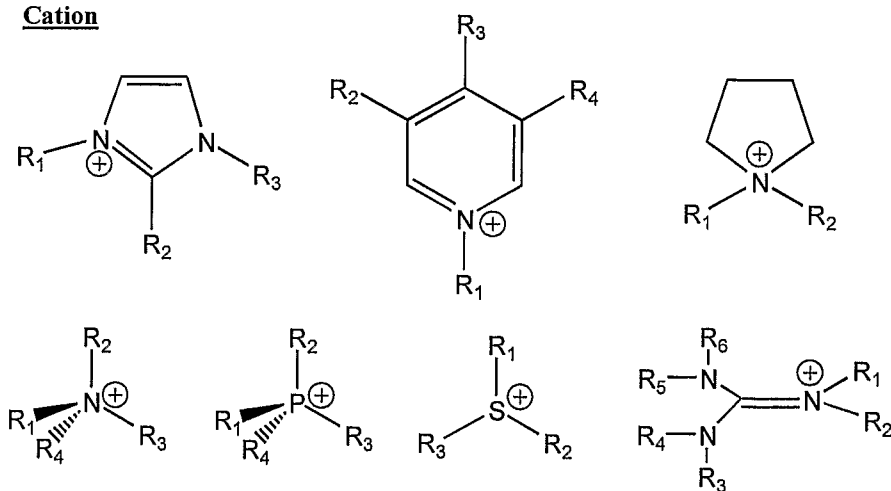
Alternatively the gas stream containing the purged acid gases can travel through line 7 to line 2 and open valve 2B where it will further travel through line 2 to open valve 2A and join the feed gas stream entering through line 1 for purification.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appending claims in this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

Having thus described the invention, what we claim is:

1. A method for separating acid gases from a feed gas stream containing acid gases comprising contacting said feed gas stream with a monolith substrate that has been coated with an ionic liquid or mixtures of ionic liquids.
2. The method as claimed in claim 1 wherein said feed gas stream is natural gas.
3. The method as claimed in claim 2 wherein said acid gases are selected from the group consisting of hydrogen sulfide, carbon dioxide, nitrogen oxides and sulfur oxides.
4. The method as claimed in claim 1 wherein said ionic liquids are selected from the group consisting of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, sulphonium and/or guanidinium-based ionic liquids having the following structures:

Cation



wherein R_{1-6} = hydrocarbon chains

Anion



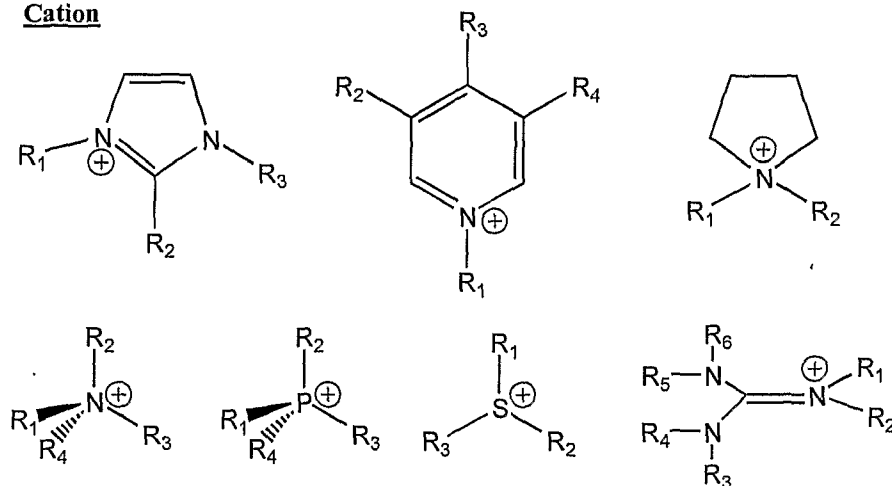
wherein R_1 , R_2 , R_3 , and R_4 are H groups and straight or branched alkyl and alkenyl

groups having 1 to 12 carbons.

5. The method as claimed in claim 1 wherein said ionic liquids are substituted with thiourea, amino or hydroxyl groups.
6. The method as claimed in claim 1 wherein said ionic liquids are regenerated by vacuum, heating, purging with the product gas stream and/or extraction using another gas stream with high selectivity for acid gases.
7. The method as claimed in claim 1 wherein said monolith substrate is in the shape of a honeycomb, foam or reticulate.
8. The method as claimed in claim 1 wherein said contacting occurs in a gas reactor column.
9. The method as claimed in claim 6 wherein the removal of acid gases from the feed gas stream can be carried out in a single bed or multiple beds operated in cyclical modes.
10. A method for separating acid gases from a feed gas stream containing acid gases comprising contacting said feed gas stream with a porous membrane that has been coated or impregnated with an ionic liquid or mixtures of ionic liquids.
11. The method as claimed in claim 10 wherein said feed gas stream is natural gas.
12. The method as claimed in claim 10 wherein said acid gases are selected from the group consisting of hydrogen sulfide, carbon dioxide, nitrogen oxides and sulfur oxides.

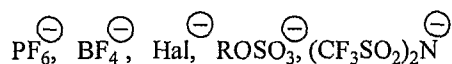
13. The method as claimed in claim 10 wherein said ionic liquids are selected from the group consisting of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, sulphonium and/or guanidinium-based ionic liquids having the following structures:

Cation



wherein R_{1-6} = hydrocarbon chains

Anion



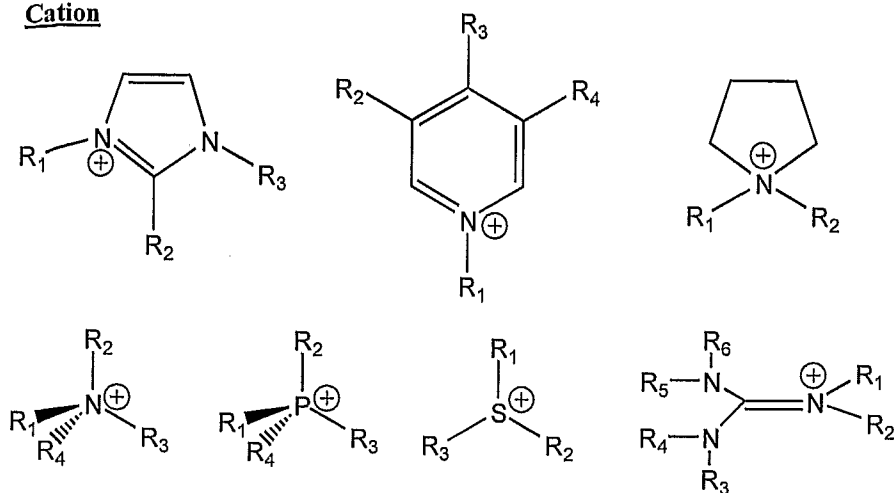
wherein R_1 , R_2 , R_3 , and R_4 are H groups and straight or branched alkyl and alkenyl groups having 1 to 12 carbons.

14. The method as claimed in claim 13 wherein said ionic liquids are substituted with thiourea, amino or hydroxyl groups.

15. The method as claimed in claim 10 wherein said ionic liquids are regenerated by vacuum, heating, purging with the product gas stream and/or extraction using another gas stream with high selectivity for acid gases.

16. The method as claimed in claim 10 wherein said porous membrane is in symmetric or asymmetric form.

17. The method as claimed in claim 10 wherein said porous membrane is coated as one layer or filled with said ionic liquids.
18. The method as claimed in claim 10 wherein said contacting occurs in a gas reactor column.
19. The method as claimed in claim 15 wherein the removal of acid gases from the feed gas stream can be carried out in a single bed or multiple beds operated in cyclical modes.
20. A method for separating acid gases from a feed gas stream containing acid gases comprising contacting said feed gas stream with porous beads and/or pellets that have been coated or filled with an ionic liquid or mixtures of ionic liquids, or are impregnated within layered or laminated sheet materials.
21. The method as claimed in claim 20 wherein said feed gas stream is natural gas.
22. The method as claimed in claim 20 wherein said acid gases are selected from the group consisting of hydrogen sulfide, carbon dioxide, nitrogen oxides and sulfur oxides.
23. The method as claimed in claim 20 wherein said ionic liquid(s) is/are selected from the group consisting of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, sulphonium and/or guanidinium-based ionic liquids having the following structures:

Cation

wherein R_{1-6} = hydrocarbon chains

Anion

wherein R_1 , R_2 , R_3 , and R_4 are H groups and straight or branched alkyl and alkenyl groups having 1 to 12 carbons.

24. The method as claimed in claim 23 wherein said ionic liquids are substituted with thiourea, amino or hydroxyl groups.
25. The method as claimed in claim 20 wherein said ionic liquids are regenerated by vacuum, heating, purging with the product gas stream and/or extraction using another gas stream with high selectivity for acid gases.
26. The method as claimed in claim 20 wherein said beads and/or pellets coated or filled with an ionic liquid or mixtures of ionic liquids are loaded in a fixed, moving or fluidized beds, or packed in layered or laminated sheet materials.
27. The method as claimed in claim 26 wherein said layered or laminated sheet materials are coated with said ionic liquids.

28. The method as claimed in claim 20 wherein said contacting occurs in a gas reactor column.

29. The method as claimed in claim 25 wherein the removal of acid gases from the feed gas stream can be carried out in a single bed or multiple beds operated in cyclical modes.

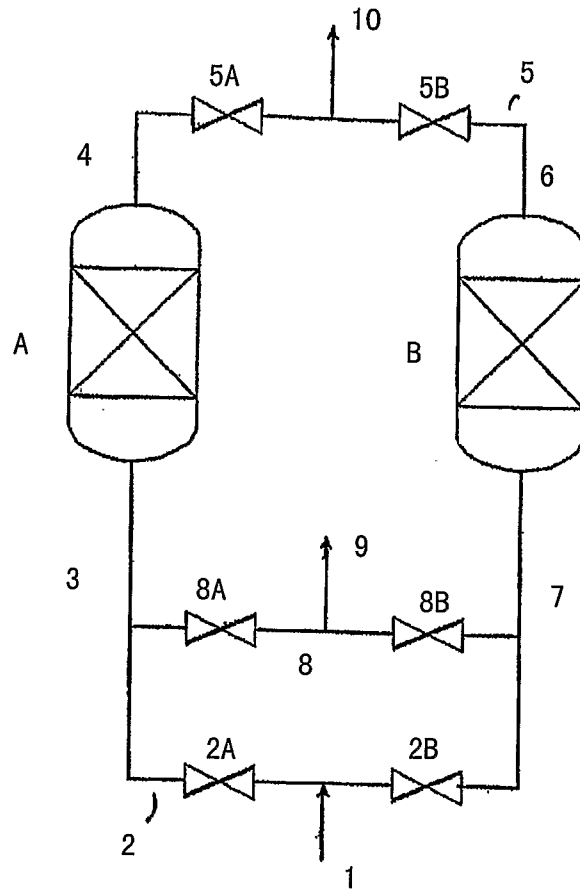


Fig 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2007/000686

A. CLASSIFICATION OF SUBJECT MATTER

B01D53/14(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)

IPC B01D

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)

WPI, PAJ, EPODOC, CNPAT,CNKI (ionic liquid, gas, CO₂, carbon dioxide, remov+, separat+)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Separation Science and Technology, 40: 2005, Ruth E. Baltus et al, Examination of the Potential of ionic Liquids for Gas Separations, p525-541	1-29
X	US6958085B1 (US NAT AERO & SPACE ADMI) 25 Oct. 2005 (25.10.2005) Claims 1-26	1-29
X	US20050129598A1 (CHEVRON TEXACO CORPORATION) 16 Jun. 2005 (16.06.2005) Claims 1-15	1-29
X	CN1709553A (PROCESS ENG INST CHINESE ACAD SC) 21 Dec. 2005 (21.12.2005) Claims 1-8	1-29

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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“E” earlier application or patent but published on or after the international filing date

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“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 May 2007 (21.05.2007)

Date of mailing of the international search report

07 Jun. 2007 (07.06.2007)

Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
US20050129598A1	16.06.2005	US2006251558 A1	09.11.2006
US6958085B1	25.10.2005	None	
CN1709553A	21.12.2005	None	