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(71) Applicant (for all designated States except US): **ALBEMARLE CORPORATION** [US/US]; 451 Florida Street, Baton Rouge, LA 70801 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HEISZWOLF, Johan, Jurgen** [NL/NL]; Rosmolen 94, NL-1703 NC Heerhugowaard (NL). **VOGT, Eelco, Titus Carel** [NL/NL]; Postmastraat 16, NL-4105 DW Culemborg (NL). **VAN OENE, Johan** [NL/NL]; Flemingstraat 24, NL-2041 VH Zandvoort (NL). **LOUWEN, Ted, Michael** [NL/NL]; Prinseneiland 493, NL-1013 EC Amsterdam (NL).

(74) Agents: **KLIEBERT, Jeremy, J.** et al.; Albemarle Corporation, 451 Florida Street, Baton Rouge, LA 70801-1765 (US).

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[Continued on next page]

(54) Title: PROCESSES FOR SYNTHESIS OF LITHIUM MANGANESE SPINEL

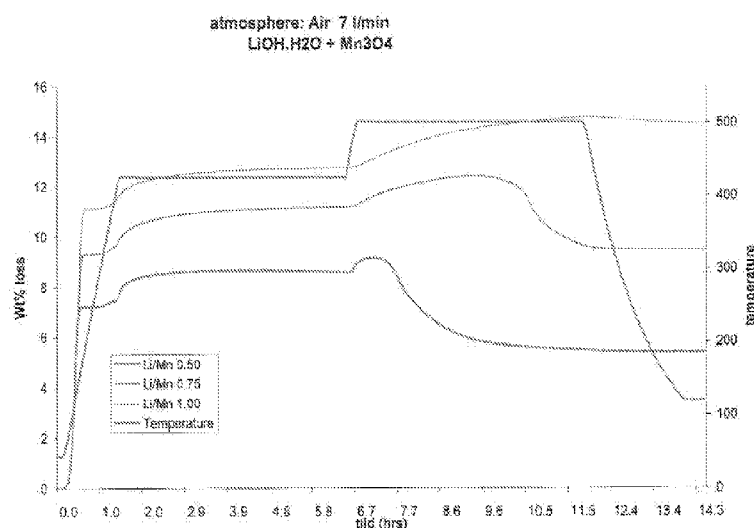


Figure 1 (prior art)

(57) Abstract: Processes are provided for producing lithium manganese spinels. Such processes comprise wet milling materials comprising lithium hydroxide and manganese oxide, spray drying the milled materials, and subjecting the spray dried materials to oxidative calcination.

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

PROCESSES FOR SYNTHESIS OF LITHIUM MANGANESE SPINEL

BACKGROUND

[0001] Due to its characteristics, such as a high electrical energy density, a high working voltage, a long cyclic life, etc., the lithium ion battery is widely used in notebook computers, mobile phones, and electric cars. The need for such batteries can be expected to grow substantially with the development of new electronic communication and transportation technologies.

[0002] Lithium manganese spinel (LiMn_2O_4) is commonly used as electrode material in lithium ion batteries since it can selectively adsorb and release lithium ions. Lithium manganese spinel (LiMn_2O_4) is also described in publications as a selective adsorbent for lithium from geothermal brines.

[0003] Open literature publications disclose LiMn_2O_4 production processes involving dry milling of lithium hydroxide with manganese oxides followed by stepwise oxidative calcination, sol gel synthesis using dissolved manganese and lithium compounds followed by drying, e.g., spray drying, and oxidative calcination. These published processes can be commercially disadvantageous in that the oxidative calcination step can take over 14 hours to complete, and because the dry milling leads to the formation of dust. In addition, the synthesis methods involving dissolved species are disadvantageous from a process perspective because of the larger number of unit operations and from an environmental perspective because of the higher energy consumption and larger waste steam generation.

[0004] There remains a need for new processes for synthesis of LiMn_2O_4 that are more suitable for use on a commercial scale.

THE INVENTION

[0005] This invention meets the above-described needs by providing processes that comprise wet milling materials comprising lithium hydroxide and manganese oxide; spray drying the milled materials; and subjecting the spray dried materials to oxidative calcination, to produce lithium manganese spinel.

Figures

[0006] The invention will be better understood by reference to the Figures in which:

[0007] Figure 1 (Prior Art) illustrates weight loss as function of time for the calcination of material made via the dry mill method of Example 1.

[0008] Figure 2 illustrates weight loss as function of time for a wet milled and then stove dried (120 degrees C) sample made via the wet mill method of Example 2.

[0009] Figure 3 illustrates weight loss as function of time for the spray dried sample made via the wet mill spray method of Example 5.

[0010] The processes of this invention comprise wet milling of lithium hydroxide and manganese oxide raw materials followed by spray drying and rapid oxidative calcination. In a typical embodiment, Mn_3O_4 is slurried in water, and a solution of lithium hydroxide in water is added. The resulting slurry is mixed until substantially homogeneous, and subsequently wet-milled in a pearl mill. Optionally, the milled slurry can be wet-milled again to control the particle size. After milling, the resulting slurry is spray-dried to yield a solid mixture. In order to increase the strength and stability of the spray dried particle, a small amount of binder may be added to the slurry prior to spray drying. The resulting powder is calcined at about 400 degrees C to about 450 degrees C for about 1 hour to yield the $LiMn_2O_4$ spinel.

[0011] Processes of this invention allow flexibility in setting the Li/Mn ratio of the product spinel. A variety of binders (for example, waterglas, colloidal silica, precipitated silica, and peptized alumina) at a variety of loadings from about 1 wt% to about 30 wt% assist in production of mechanically stable micro spheres. The mild calcination step also assists in production of mechanically stable micro spheres. Mechanical stability can be tested in aqueous media using ultra sound energy input testing, which is a known test for determining strength of particles. Alternatively, air jet attrition tests, commonly used to test the strength of fluidized catalytic cracking microspheres, can be applied (ASTM-5757)

[0012] $LiMn_2O_4$ prepared according to this invention can be used, for example, in battery electrode material(s) for lithium-ion batteries, or as an adsorbent for the removal of lithium from aqueous solutions such as brine, sea water, and the like. The preparation method is not believed to be limited to lithium manganese spinel. Admixtures with other transition elements that increase performance (like Co) can likely be applied also (making Li-MnCo spinel), and presumably other lithium compounds that are conventionally prepared using currently known processes can be prepared using processes of this invention as well (e.g. $LiFePO_4$).

EXAMPLES

[0013] The following examples are illustrative of the principles of this invention. It is understood that this invention is not limited to any one specific embodiment exemplified herein, whether in the examples or the remainder of this patent application.

EXAMPLE 1. (Prior Art)

[0014] Powdered commercial grade manganese oxide (Mn_3O_4) in a quantity of 100 grams was mixed with 41.3 gram of commercial grade lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) and was milled in a ball mill for five hours. The mixture was subsequently heated in an electric furnace under atmospheric conditions using a temperature ramp of 5 degrees / minute followed by a 5 hour calcination period at 698 K. The sample temperature was subsequently increased to 773 K at 5 degrees C/min and the temperature was maintained for 5 hours. Finally, after 12 hours, the sample was gradually cooled back to ambient temperature. Figure (1) shows the mass of the sample as a function of time. After an initial weight loss due to release of moisture and crystal water, the sample weight increased during the oxidative calcination formation of lithium manganese spinel via a reaction between the lithium and manganese compounds and oxygen from the air. The reaction is nearly complete after 10 hours of calcination.

EXAMPLE 2

[0015] Powdered commercial grade manganese oxide (Mn_3O_4) in a quantity of 100 grams was mixed with 41.3 gram of commercial grade lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) and was added to 520 ml of deionized water. The mixture was agitated with a high shear impeller to obtain a homogeneous suspension. The resulting slurry was milled in a dynamill bead mill using a low flow rate. The resulting slurry was dried in an oven for 12 hours at 120 degrees C. The material was subsequently heated in an electric furnace under atmospheric conditions using a temperature ramp of 5 degrees / minute followed by a 5 hour calcination period at 698 K. The sample temperature was subsequently increased to 773 K at 5 degrees C/min and its temperature was maintained for 5 hours. Finally, after 12 hours, the sample was gradually cooled back to ambient temperature. Figure 2 shows the mass of a sample as a function of time. After an initial weight loss due to release of moisture and crystal water, the sample weight increased during the oxidative calcination formation of lithium manganese spinel via a

reaction between the lithium and manganese compounds and oxygen from the air. The reaction was nearly complete after 9 hours of calcination very similar to Example 1.

EXAMPLE 3

[0016] Lithium nitrate (LiNO_3) and manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) were dissolved into deionized water. The resulting clear solution was spray dried in a bench top spray dryer using an air inlet temperature of 200 degrees C and an outlet temperature of 120 degrees C. The resulting powder material was subsequently heated in an electric furnace under atmospheric conditions using a temperature ramp of 5 degrees / minute followed by a 5 hour calcination period at 698 K. The sample temperature was subsequently increased to 773 K at 5 degrees C/min and its temperature was maintained for 5 hours. Finally, after 12 hours, the sample was gradually cooled back to ambient temperature. Then, decomposition of nitrate was observed which was accompanied with the release of toxic NO_x vapors. Finally, the oxidative calcination formation of lithium manganese spinel occurred via a reaction between the lithium and manganese compounds and oxygen from the air. The reaction is nearly complete after calcination.

EXAMPLE 4

[0017] Lithium acetate (LiAc) and manganese acetate ($\text{Mn}(\text{Ac})_2 \cdot x \text{H}_2\text{O}$) were dissolved into deionized water. The resulting clear solution was spray dried in a bench top spray dryer using an air inlet temperature of 200 degrees C and an outlet temperature of 120 degrees C. The resulting powder material was subsequently heated in an electric furnace under atmospheric conditions using a temperature ramp of 5 degrees / minute followed by a 5 hour calcination period at 698 K. The sample temperature was subsequently increased to 773 K at 5 degrees C/min and its temperature was maintained for 5 hours. Finally, after 12 hours, the sample was gradually cooled back to ambient temperature. Then, decomposition of acetate was observed which was accompanied with the release of toxic VOC vapors. Finally, the oxidative calcination formation of lithium manganese spinel occurred via a reaction between the lithium and manganese compounds and oxygen from the air. The reaction was nearly complete after calcination.

EXAMPLE 5

[0018] Powdered commercial grade manganese oxide (Mn_3O_4) in a quantity of 100 grams was mixed with 41.3 gram of commercial grade lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) and was added to 520 ml of deionized water. The mixture was agitated with a high shear impeller to obtain a homogeneous suspension. The resulting slurry was milled in a Dyno-mill bead mill using a low flow rate. The resulting slurry was spray dried in a bench top spray dryer using an air inlet temperature of 200 degrees C and an outlet temperature of 120 degrees C. The resulting powder material was subsequently heated in an electric furnace under atmospheric conditions using a temperature ramp of 5 degrees / minute followed by a 5 hour calcination period at 698 K. The sample temperature is subsequently increased to 773 K at 5 degrees C/min and its temperature was maintained for 5 hours. Finally, after 12 hours, the sample was gradually cooled back to ambient temperature. Figure 3 shows the mass of the sample as a function of time. After an initial weight loss due to release of moisture and crystal water, the sample weight increased during the oxidative calcination formation of lithium manganese spinel via a reaction between the lithium and manganese compounds and oxygen from the air. The reaction was complete after only 3 hours of calcination which includes the sample heat up time. Surprisingly, the conditions during the spray drying step, in which the material encounters mild temperatures in an oxygen containing environment, greatly accelerated the formation of spinel during the oxidative calcination step. In addition, no decomposition products were formed during the oxidative calcination step.

[0019] A process according to this invention has been demonstrated experimentally on small scale (bench top Büchi spray dryer) with 50 grams of material and on pilot scale (Pilot scale Niro spray dryer) with 6 kg of material and is expected to scale-up to commercial scale without mayor issues. Commercial scale would be a few tons (>1000 kg) of material prepared in a commercial spray dryer.

[0020] This invention is advantageous as compared to currently known methods in that use of wet milling instead of dry milling provides better control of the oxidation state of the materials, easier and higher throughput in processing equipment, and minimization of environmental impact by reducing dust make.

[0021] In processes of this invention, the manganese oxide is not dissolved but it is merely milled to a fine particle size. This allows for use of cheaper raw materials and

smaller processed volumes as compared to currently known processes for LiMn_2O_4 production. Further in comparison to these known processes, this invention provides increased throughput in the spray dryer and reduced emissions in the calcination step. Quite surprisingly, in processes of this invention, the time required in the oxidative calcination step is significantly reduced to just about one hour compared to over 14 hours in the currently known processes.

[0022] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to being combined with or coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting combination or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical reaction or in forming a combination to be used in conducting a desired reaction. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, combined, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. Whatever transformations, if any, which occur in situ as a reaction is conducted is what the claim is intended to cover. Thus the fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, combining, blending or mixing operations, if conducted in accordance with this disclosure and with the application of common sense and the ordinary skill of a chemist, is thus wholly immaterial for an accurate understanding and appreciation of the true meaning and substance of this disclosure and the claims thereof. As will be familiar to those skilled in the art, the terms "combined", "combining", and the like as used herein mean that the components that are "combined" or that one is "combining" are put into a container with each other.

Likewise a "combination" of components means the components having been put together in a container.

[0023] While the present invention has been described in terms of one or more preferred embodiments, it is to be understood that other modifications may be made without departing from the scope of the invention, which is set forth in the claims below.

CLAIMS

What is claimed is:

1. A process comprising:
 - wet milling materials comprising lithium hydroxide and manganese oxide;
 - spray drying the milled materials; and
 - subjecting the spray dried materials to oxidative calcination, to produce lithium manganese spinel.

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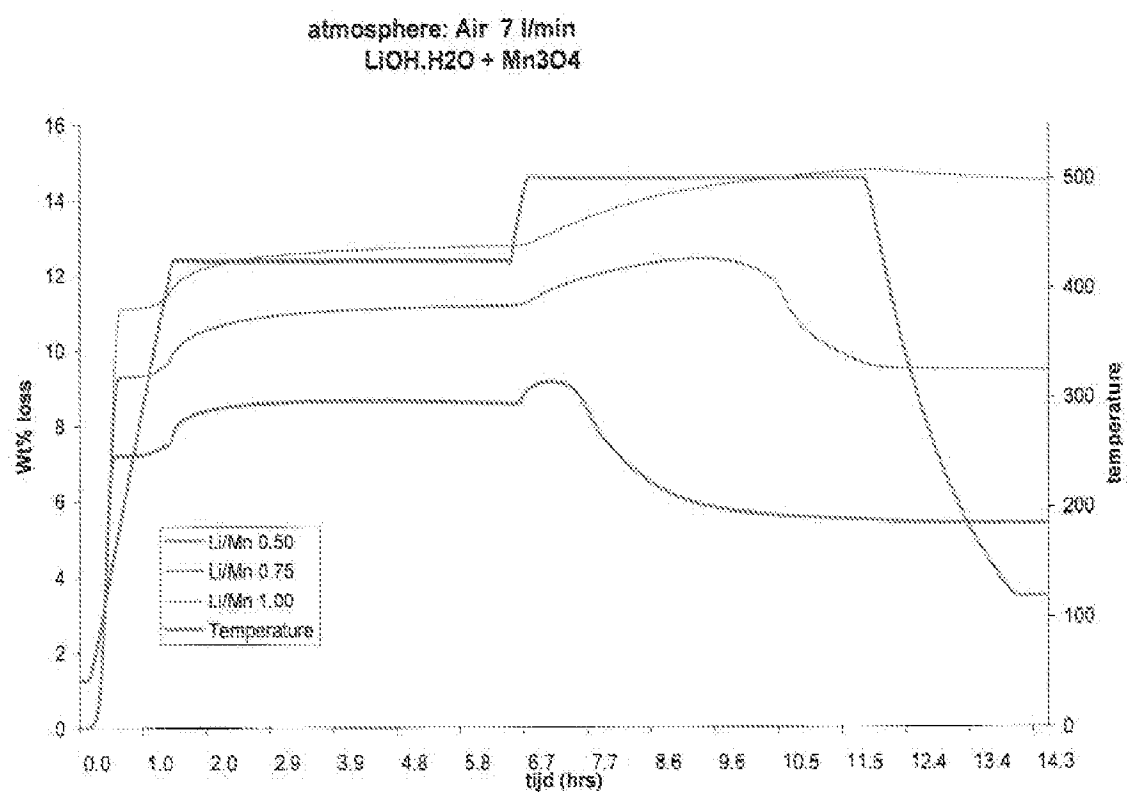


Figure 1 (prior art)

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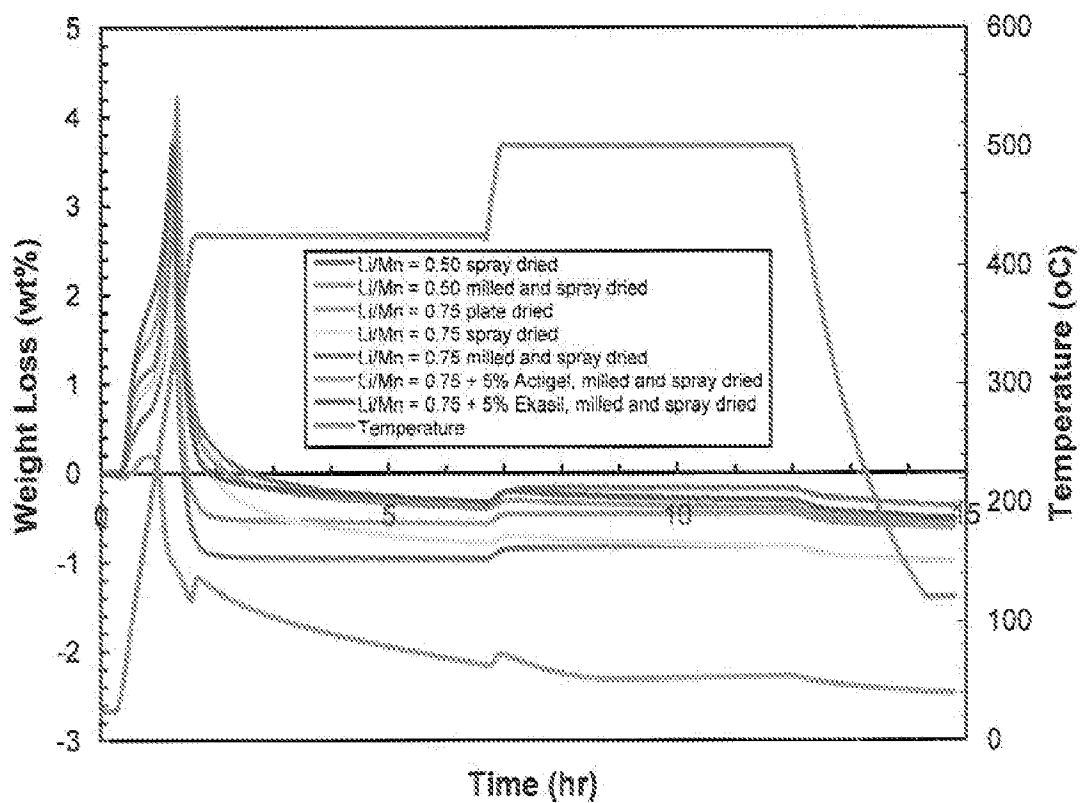


Figure 2

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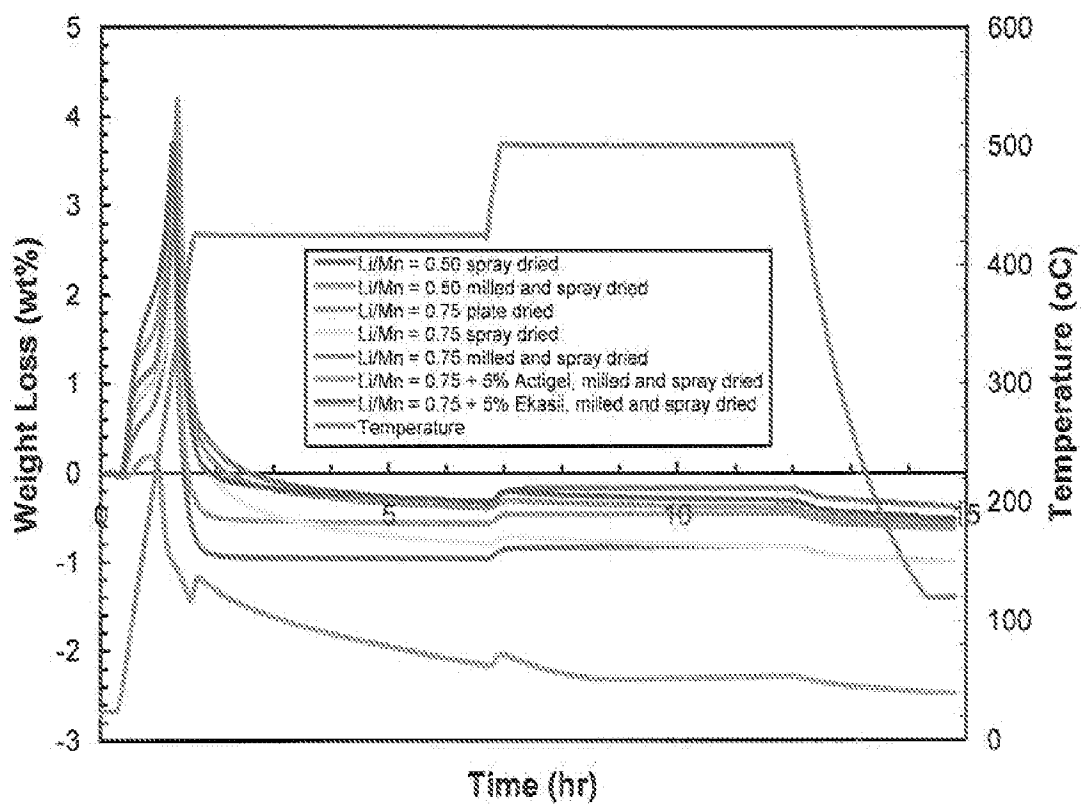


Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/035225

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/04 H01M10/0525 H01M4/485 H01M4/505
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)
H01M

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)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005 347134 A (SUMITOMO METAL MINING CO) 15 December 2005 (2005-12-15) paragraphs [0001], [0023], [0024], [0025], [0027], [0031], [0035], [0036], [0038] -----	1
X	JP 2004 107095 A (MITSUBISHI CHEM CORP) 8 April 2004 (2004-04-08) paragraphs [0022], [0052], [0053] -----	1
X	JP 2002 145619 A (MITSUBISHI CHEM CORP) 22 May 2002 (2002-05-22) paragraphs [0049], [0050], [0051], [0052], [0063] -----	1

☐

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

"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

9 July 2012

Date of mailing of the international search report

17/07/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Langouët, Sylvain

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/035225

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2005347134	A	15-12-2005	NONE	

JP 2004107095	A	08-04-2004	NONE	

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