



Queensland University of Technology
Brisbane Australia

This is the author's version of a work that was submitted/accepted for publication in the following source:

Alarco, Jose Antonio & Talbot, Peter Cade (2009) *Fuel additive*.
WO2009/089590A1.

This file was downloaded from: <http://eprints.qut.edu.au/64079/>

Notice: *Changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published source:*

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 July 2009 (23.07.2009)

PCT

(10) International Publication Number
WO 2009/089590 A1

- (51) **International Patent Classification:**
CIOL 1/10 (2006.01) *CIOL 1/12 (2006.01)*
CIOL 1/14 (2006.01) *CIOL 10/00 (2006.01)*
CIOL 10/18 (2006.01)
- (21) **International Application Number:**
PCT/AU2009/000050
- (22) **International Filing Date:** 16 January 2009 (16.01.2009)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
2008900211 16 January 2008 (16.01.2008) AU
- (71) **Applicant (for all designated States except US):**
VERY SMALL PARTICULE COMPANY LIMITED [AU/AU]; 31 Westgate Street, Wacol, Queensland 4076 (AU).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **ALARCO, Jose, Antonio** [AU/AU]; Unit 1, 44 Payne Street, Indooroopilly, QLD 4068 (AU). **TALBOT, Peter, Cade** [AU/AU]; 1 Welcome Street, Chapel Hill, QLD 4069 (AU).
- (74) **Agent:** CULLEN & COMPANY; Level 26, 239 George Street, Brisbane, QLD 4000 (AU).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, **BR**, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, **HR**, HU, **ID**, IL, IN, IS, **JP**, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report



WO 2009/089590 A1

(54) **Title:** FUEL ADDITIVE

(57) **Abstract:** A fuel additive comprising one or more complex oxides having a nominal composition as set out in formula (1): $A_x Bi_y M_z O_n$, wherein A is selected from one or more group III elements including the lanthanide elements or one or more divalent or monovalent cations; B is selected from one or more elements with atomic number 22 to 24, 40 to 42 and 72 to 75; M is selected from one or more elements with atomic number 25 to 30; x is defined as a number where $0 < x < 1$; y is defined as a number where $0 < y < 0.5$.

Fuel Additive

Field of the invention

The present invention relates to a fuel additive. In a more specific embodiment, the present invention relates to a fuel additive that is effective even with
5 high sulphur content in the fuel.

Background to the invention

Cerium oxide has been extensively used as a component in the catalyst of three-way converters for the elimination of toxic exhaust emissions in automobiles. The cerium oxide contained within the catalyst can act as a chemically active
10 component, working as an oxygen store by the release of oxygen in the presence of reductive gases, and removal of oxygen by interaction with oxidised species. Cerium oxide may store and release oxygen by the following processes:



Cerium oxide has also been used as an additive to be added to fuels. In such
15 uses, the cerium oxide provides a catalytic effect that has been found to reduce the emission of toxic exhaust gases. Addition of cerium oxide has also been found to improve the combustion of the fuel as it passes through an internal combustion engine. Due to improved combustion, far less pollutants are formed. For example, when cerium oxide is used as a fuel additive for diesel engines, an increase in
20 efficiency of approx 10% has been achieved and a reduction in emissions of NOx gases of up to 65% has also been measured [ref Oxonica Website].

In order to keep the cerium oxide particles suspended in the fuel, it is usually necessary to prepare a colloidal dispersion of the cerium oxide particles which requires the cerium oxide particles to be very fine, for example, sub-micron particles
25 having a maximum particle size of up to 300nm.

There have been several documents described in the patent literature that discuss the use of cerium oxide, or modified forms of cerium oxide, as fuel additives.

WO 03/040270 (the entire contents of which are herein incorporated by cross reference) describes a fuel additive which comprises a particle of cerium oxide which
30 has been doped with a divalent or trivalent metal or metalloid which is a rare earth

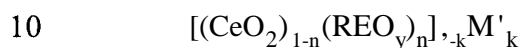
metal, a transition metal, including a noble metal, or a metal of groups HA, IHB, VB, or VIB of the periodic table, and a polar or non-polar organic solvent.

The doped cerium oxide particle described in this patent application may have the following formula:



where M is the metal or metalloid as described above, particularly Rh, Cu, Ag, Au, Pd, Pt, Sb, Se, Fe, Ga, Mg, Mn, Cr, Be, B, Co, V and Ca as well as Pr, Sm, and Gd and x has a value of up to 0.3. Copper is particularly preferred.

Alternatively, the doped cerium oxide particle may have following formula:



where M' is said metal or metalloid other than a rare earth, RE is a rare earth, y is one or 1.5 and each of n and k has a value up to 0.5, preferably up to 0.3.

Copper is the preferred metal or metalloid.

15 WO 2004/065529 (the entire contents of which are herein incorporated by cross reference) has a similar disclosure, but it relates to a method of improving the efficiency of a fuel for an internal combustion engine which comprises adding to the fuel prior to the introduction of the fuel to a vehicle or other apparatus comprising an internal combustion engine, cerium oxide and/or doped cerium oxide and, optionally, one or more fuel additives.

20 The doped cerium oxides that may be used in the invention described in this patent application will have the formula $Ce_{1-x}M_xO_2$, where M is the metal or metalloid as described above, particularly Rh, Cu, Ag, Au, Pd, Pt, Sb, Se, Fe, Ti, Ga, Mg, Mn, Cr, Be, B, Co, V and Ca as well as Pr, Sm, and Gd.

25 The fuel additive may be provided in the form of a product to be mixed with the fuel at the point of dispensing the fuel (for example, at a service station). In these embodiments, the fuel additive may be poured directly into the fuel tank of a motor vehicle prior to or just after filling up the fuel tank of the motor vehicle. Alternatively, the fuel additive may be mixed with the fuel in the fuel storage tanks at the service station. However, it is even more desirable to have the fuel additive mixed
30 with the fuel at the point of production of the fuel, which is typically at an oil refinery.

In our copending international patent application number PCT/AU 2007/000488, the entire contents of which are herein incorporated by cross reference, we describe a material that is useful as an exhaust emissions catalyst.

The present applicant does not concede that the prior art discussed here in forms part of the common general knowledge in Australia or elsewhere.

Throughout this specification, the word "comprising" and its grammatical equivalents shall be taken to have an inclusive meaning unless the context of use clearly indicates otherwise.

Brief description of the invention

The present inventors have now discovered that the catalytic material described in our copending international patent application number PCT/AU 2007/000488 is also especially useful as a fuel additive.

In a first aspect, the present invention provides a fuel additive comprising one or more complex oxides having a nominal composition as set out in formula (1):



wherein

A is selected from one or more group III elements including the lanthanide elements or one or more divalent or monovalent cations;

B is selected from one or more elements with atomic number 22 to 24, 40 to 42 and 72 to 75;

M is selected from one or more elements with atomic number 25 to 30;

x is defined as a number where $0 < x \leq 1$;

y is defined as a number where $0 < y < 0.5$.

In one embodiment, the one or more complex oxides have a general composition as set out in formula (2):



wherein

A is one or more group III elements including the lanthanide elements;

A' is one or more divalent or monovalent cations;

w is defined as a number where $0 \leq w \leq 1$;

$0.5 < x+w \leq 1$ and

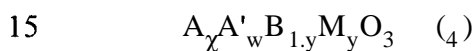
B, M, P, x and y are as set out in formula (1).

5 In a preferred embodiment A is selected from La, Ce, Sm and Nd, A' is selected from Sr, Ba, and Ca, B is selected from Ti, V, W and Mo, and M is selected from Cu and Ni.

In a more preferred embodiment A is La and/or Ce, A' is Sr, B is Ti, and M is Cu and/or Ni. In this embodiment, the complex oxide has the general formula as set
10 out in formula (3):



In a further preferred embodiment at least one of the complex oxide phases is a perovskite with a general formula (4):



and more preferably of formula (5):



where the terms in (4) and (5) are as defined in (1) and (2) above.

The perovskite component of the formula may suitably exhibit substantially
20 homogenous and phase-pure composition.

The complex oxide material may have an initial surface area greater than approximately $15 \text{m}^2/\text{g}$, preferably greater than approximately $20 \text{m}^2/\text{g}$, more preferably greater than approximately $30 \text{m}^2/\text{g}$, and a surface area after aging for 2 hours at 1000°C in air greater than approximately $5 \text{m}^2/\text{g}$, preferably greater than
25 approximately $10 \text{m}^2/\text{g}$, more preferably greater than approximately $15 \text{m}^2/\text{g}$.

The complex oxide material may generally exhibit an average grain size of approximately 2 nm to approximately 150 nm, preferably approximately 2 to 100 nm and has pores ranging in size from approximately 7 nm to approximately 250 nm, more preferably approximately 10 nm to approximately 150 nm. However, the

average grain and pore size of the complex oxide materials may vary, depending on the specific complex oxide selected.

More preferably, the complex oxide material may exhibit a substantially disperse pore size range.

5 The complex oxide material of the invention may be formed by mixing precursors of the elements described above in the general formula (1) followed by appropriate heat treatment to form the target phases. The precursors may be of any suitable form such as salts, oxides or metals of the elements used. The precursor mixture may be in the form of a mixture of solids, a solution or a combination of
10 solids and solutions. The solutions may be formed by dissolving salts in a solvent such as water, acid, alkali or alcohols. The salts may be but are not limited to nitrates, carbonates, oxides, acetates, oxalates, and chlorides. Organometallic form of elements such as alkoxides may also be used.

Solid dispersions may also be used as suitable precursor materials.

15 Various methods of mixing precursors to produce the complex oxide may include but are not limited to techniques such as, mixing and grinding, co-precipitation, thermal evaporation and spray pyrolysis, polymer and surfactant complex mixing and sol gel. Where necessary, the final phase composition is achieved by thermal processing following mixing. The heating step may be carried out using
20 any suitable heating apparatus and may include but are not limited to, hot plates or other heated substrates such as used in spray pyrolysis, ovens stationary table furnaces, rotary furnaces, induction furnaces, fluid bed furnace, bath furnace, flash furnace, vacuum furnace, rotary dryers, spray dryers, spin-flash dryers.

25 In a preferred embodiment a homogeneous complex oxide is formed by the method outlined in US Patent 6,752,679, "Production of Fine-Grained Particles", the entire contents of which are herein incorporated by cross reference.

30 In a further preferred embodiment a homogeneous complex oxide is formed, has nano-sized grains in the size range indicated and nano-scale pores in the size range indicated by using the method outlined in US Patent 6,752,679 and US Patent application 60/538867, the entire contents of which are herein incorporated by cross reference.

In a more preferred embodiment a homogeneous complex oxide is formed, has nano-sized grains in the size range indicated and nano-scale pores in the size range indicated and uses an aqueous colloidal dispersion of nano-scale particles as one of the precursor elements by using the method outlined in US Patent 6,752,679 and US Patent application 60/538867 and US patent application 60/582905, the entire contents of which are herein incorporated by cross reference.

In some embodiments, the complex oxide is provided in the form of dispersed particles. The dispersed particles may have a particle size of up to 300nm. The dispersed particles may be formed by forming the complex oxide material in accordance with the methods as described in US Patent 6,752,679 or US Patent application 60/538867 or US patent application 60/582905 and subsequently grinding the complex oxide material to form dispersed particles. It has been surprisingly found that the agglomerated particles that are formed by the methods described in our US Patent 6,752,679 and US Patent application 60/538867 and US patent application 60/582905 are only loosely agglomerated and can be easily ground or milled to form dispersed particles.

In some embodiments of the present invention, A is Ce, B is Ti, y is zero, z is zero and n is 4. This results in a complex oxide having the formula $CeTiO_4$.

The fuel additive in accordance with the present invention may further comprise one or more solvents. The one or more solvents may comprise an organic solvent. The one or more solvents may comprise a non-polar organic solvent or a polar organic solvent. The person skilled in the art will readily understand that a number of solvents may be used in the fuel additive in accordance with the present invention. The solvents are soluble in the fuel and act as a carrier or delivery agent for the particles of metal oxide.

A number of other components may also be added to the fuel additive. These other components may include:

Detergents,

dehazers

anti-foaming agents

ignition improvers

anti-rust agents or corrosion inhibitors

deodorants

antioxidants

metal deactivatorss

5 lubricating agents

dyes.

The skilled person will readily understand the nature and sources of supply of the above additives. The skilled person will also understand how much of each additive may be added to the fuel additive.

10 The present inventors have found that complex metal oxides, as described with reference to the first aspect of the present invention, are particularly suitable for use as fuel additives in accordance with the present invention. In particular, the fuel additives of the present invention show enhanced resistance to deactivation or poisoning by sulphur. The present inventors believe that, due to the enhanced
15 resistance to deactivation or poisoning by sulphur, the fuel additive in accordance with the present invention is particularly suitable for adding to fuels, such as diesel fuel, at the manufacturing facility of the fuels (which will typically be an oil refinery) or at bulk storage facilities for the fuel. Previous efforts to incorporate cerium oxide-based fuel additives into fuels at an oil refinery or bulk storage facilities have resulted
20 in inadequate performance of the fuel additive, which the present inventors have postulated is due to deactivation or poisoning by sulphur. In this regard, it will be understood that even modern high quality diesel fuels contain up to 50 ppm sulphur.

In a second aspect, the present invention provides a method for making a fuel additive comprising the steps of forming a complex metal oxide of formula (1) as
25 described above, the complex metal oxide being formed in the form of the agglomerated particles having nano sized grains, breaking the agglomerates of particles to form dispersed particles of complex metal oxide having a particle size of less than 300nm and adding said particles to a fuel.

In some embodiments, the method may further comprise the step of mixing the
30 particles with one or more solvents. The solvent(s) are soluble in the fuel and act as a

carrier or delivery agent for the particles of metal oxide. Other additives, as described above, may also be added to the fuel additive.

In a third aspect, the present invention provides a fuel additive comprising a solvent and one or more complex oxides having a nominal composition as set out in formula (1) above. The solvent(s) are soluble in the fuel and act as a carrier or delivery agent for the particles of metal oxide. The fuel additive may be in the form of a suspension or a dispersion of particles of the complex oxide in the solvent.

In a further aspect, the present invention also provides a fuel comprising a hydrocarbon-based fuel and a fuel additive as described herein. The hydrocarbon-based fuel may be diesel fuel.

As will be understood by the person skilled in the art, in all of the chemical formulae given in this specification, n will be a value that essentially balances the oxygen with the metallic species in the formulae.

EXAMPLES

15 Material Preparation

Example 1

A complex metal oxide of the nominal formula $\text{La}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ plus 10 w% CeO_2 was produced as follows.

A solution containing all the required elements except Ti was made by mixing 45mls of water, 10g of nitric acid, 46.29g of lanthanum nitrate hexahydrate, 5.66g of strontium nitrate and 7.57g of cerium nitrate hexahydrate.

10.67g of Titanium-based nano-particles were added to the solution and stirred at a temperature of 50°C until the particles were dispersed and a clear solution was formed.

The solution was then added to 16g of carbon black and mixed with a high-speed stirrer. The resulting mixture was added to 70g of anionic surfactant and again mixed with a high-speed stirrer.

The final mixture was heat treated slowly to 650°C and then treated at 800°C for 2hrs

and a further 2hrs at 1000°C. XRD analysis showed that the perovskite phase $\text{LaSr}_{0.5}\text{Ti}_2\text{O}_6$ and $(\text{Ce},\text{La})_2\text{Ti}_2\text{O}_7$ were the main types of phases present in Example 1.

Example 2

A complex metal oxide of nominal formula $\text{La}_{0.5}\text{Sr}_{0.25}\text{Ti}_{0.96}\text{Ni}_{0.04}\text{O}_n$ plus 10 w% CeO_2 was produced using a similar method to Example 1. XRD analysis showed that the perovskite phase $\text{LaSr}_{0.5}\text{Ti}_2\text{O}_6$ and $(\text{Ce}_5\text{La})_2\text{Ti}_2\text{O}_7$ were the main types of phases present.

Example 3

A complex metal oxide of nominal formula $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.96}\text{Ni}_{0.04}\text{O}_n$ plus 10 w% CeO_2 was produced using a similar method to Example 1. XRD analysis showed that the perovskite phase $\text{LaSr}_{0.5}\text{Ti}_2\text{O}_6$ and $(\text{Ce},\text{La})_2\text{Ti}_2\text{O}_7$ were the main types of phases present.

Example 4

A complex metal oxide of nominal formula $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.93}\text{Ni}_{0.04}\text{Cu}_{0.03}\text{O}_n$ plus 10 w% CeO_2 was produced using a similar method to Example 1. XRD analysis showed that the perovskite phase $\text{LaSr}_{0.5}\text{Ti}_2\text{O}_6$ and $(\text{Ce},\text{La})_2\text{Ti}_2\text{O}_7$ were the main types of phases present.

Example 5

A complex metal oxide of nominal formula $\text{LaTi}_{0.95}\text{Ni}_{0.04}\text{O}_n$ plus 10 w% CeO_2 was produced using a similar method to Example 1. XRD analysis showed that the perovskite phase $\text{LaSr}_{0.5}\text{Ti}_2\text{O}_6$ and $(\text{Ce}_5\text{La})_2\text{Ti}_2\text{O}_7$ were the main types of phases present.

Example 6

A complex metal oxide of nominal formula $\text{CeTi}_{0.96}\text{Ni}_{0.04}\text{O}_n$ was produced using a similar method to Example 1. XRD analysis showed that the $(\text{Ce}_5\text{La})_2\text{Ti}_2\text{O}_7$ phase was the main type of phase present.

Claims.

1. A fuel additive comprising one or more complex oxides having a nominal composition as set out in formula (1):



5 wherein

A is selected from one or more group III elements including the lanthanide elements or one or more divalent or monovalent cations;

B is selected from one or more elements with atomic number 22 to 24, 40 to 42 and 72 to 75;

10 M is selected from one or more elements with atomic number 25 to 30;

x is defined as a number where $0 < x < 1$;

y is defined as a number where $0 < y < 0.5$.

15 2. A fuel additive as claimed in claim 1 wherein the one or more complex oxides have a nominal composition as set out in formula (2):



wherein

A is one or more group III elements including the lanthanide elements;

A' is one or more divalent or monovalent cations;

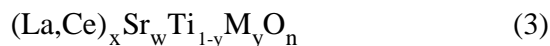
20 w is defined as a number where $0 \leq w \leq 1$;

$0.5 < x + w \leq 1$ and

B, M, P, x and y are as set out in formula (1).

25 3. A fuel additive as claimed in claim 2 wherein A is selected from La, Ce, Sm and Nd, A' is selected from Sr, Ba, and Ca, B is selected from Ti, V, W and Mo, and M is selected from Cu and Ni.

4. A fuel additive as claimed in claim 3 wherein A is La and/or Ce, A' is Sr, B is Ti, and M is Cu and/or Ni and the complex oxide has the general formula as set out in formula (3):



5

5. A fuel additive as claimed in 2 wherein at least one complex oxide phase is a perovskite with a general formula (4):



10

6. A fuel additive as claimed in 6 wherein at least one complex oxide phase is a perovskite with a general formula (5):



15

7. A fuel additive as claimed in any one of the preceding claims wherein the complex oxide material has an initial surface area greater than approximately 15m²/g, and a surface area after aging for 2 hours at 1000⁰C in air greater than approximately 5m²/g.

20

8. A fuel additive as claimed in claim 7 wherein the complex oxide material has an initial surface area greater than approximately 30m²/g, and a surface area after aging for 2 hours at 1000⁰C in air greater than approximately 15m²/g.

9. A fuel additive as claimed in any one of the preceding claims wherein the complex oxide material exhibits an average grain size of approximately 2 run to approximately 150 nm and has pores ranging in size from approximately 7 nm to approximately 250 nm.

25

10. A fuel additive as claimed in any one of the preceding claims wherein A is Ce, B is Ti, y is zero, z is zero and n is 4 and the complex oxide has the formula CeTiO₄.

11. A fuel additive as claimed in any one of the preceding claims further comprising one or more solvents that are soluble in the fuel and act as a carrier or delivery agent for the particles of metal oxide.

5 12. A fuel additive as claimed in any one of the preceding claims further comprising other components or additives selected from the group comprising detergents, dehazers, anti-foaming agents, ignition improvers, anti-rust agents or corrosion inhibitors, deodorants, antioxidants, metal deactivators, lubricating agents, dyes or mixtures of two or more thereof.

10 13. A method for making a fuel additive as claimed in claim 1 comprising the steps of forming a complex metal oxide of formula (1), the complex metal oxide being formed in the form of the agglomerated particles having nano sized grains, breaking the agglomerates of particles to form dispersed particles of complex metal oxide having a particle size of less than 300nm and adding said particles to a fuel.

15 14. A method as claimed in claim 13 further comprising the step of mixing the particles with one or more solvents that are soluble in the fuel and act as a carrier or delivery agent for the particles of metal oxide.

15 15. A method for making a fuel comprising refining oil at a refinery to form a fuel and adding a fuel additive as claimed in any one of claims 1 to 12 to the fuel at the refinery or at a bulk storage facility for the fuel.

20 16. A method as claimed in claim 15 wherein the fuel is diesel fuel.

17. A fuel additive as claimed in claim 11 or claim 12 when appended to claim 11 wherein the fuel additive is on the form of a suspension or dispersion of particles of the complex oxide in the solvent.

25 18. A fuel comprising a hydrocarbon-based fuel and a fuel additive as claimed in any one of claims 1 to 12 or 17.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2009/000050

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

CIOL 1/10 (2006.01)
CIOL 1/12 (2006.01)

CIOL 1/14 (2006.01)
CIOL 10/00 (2006.01)

CIOL 10/18 (2006.01)

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)

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

Electronic database consulted during the international search (name of data base and, where practicable, search terms used)
 EPODOC and WPI-IPC CIOL/-, Fuel or oil, additive, oxide and for compound IPC COI/-, lanthanide+, oxide, ceri+
 Google patents search: fuel, additive, cerium, lanthanide, oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | US 7169196 B2 (WAKEFIELD) 30 January 2007 Please see abstract, column 1 lines 64-65, column 2 lines 1-21, column 3 lines 39-43, claims 1-6, 8-10, 13, 16, 17-19 | 1-12 |
| Y | | 11-18 |
| X | WO 2007/1 15380 A1 (VERY SMALL PARTICLE COMPANY PTY LTD) 18 October 2007 Please see page 3 lines 25-27, page 4 lines 1-26, page 5 lines 1-26, page 6 lines 1-28, page 7 lines 1-8, examples 1-4, claims 1-12 | 1-10 |
| Y | | 11-18 |
| X | Derwent Abstract Accession No. 74485W/45, Class E36, H06, J04 DT 2518537 A (DUPONT DENEMOURS CO) 30 October 1975 Please see whole Abstract | 1, 2, 5 |
| Y | US 7195653 B2 (HAZARIKA et al.) 27 March 2007 Please see abstract, column 3 lines 20-60, claims 1, 2, 4 | 13-18 |



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 | "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 | |
| "E" earlier application or patent but published on or after the international filing date | "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 | |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "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 | |
| "O" document referring to an oral disclosure, use, exhibition or other means | "&" document member of the same patent family | |
| "P" document published prior to the international filing date but later than the priority date claimed | | |

Date of the actual completion of the international search
 12 February 2009

Date of mailing of the international search report

26 FEB 2009

Name and mailing address of the ISA/AU
 AUSTRALIAN PATENT OFFICE
 PO BOX 200, WODEN ACT 2606, AUSTRALIA
 E-mail address: pct@ipaustralia.gov.au
 Facsimile No. +61 2 6283 7999

Authorized officer
Heramb M Bai
 AUSTRALIAN PATENT OFFICE
 (ISO 9001 Quality Certified Service)
 Telephone No : +61 2 6283 7966

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2009/000050

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|--|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US 2006/0254130 A1 (SCATTERGOOD) 16 November 2006 Please see claims 1-25 | 1-10 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2009/000050

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report | | Patent Family Member | | | | | |
|---|------------|----------------------|------------|----|------------|----|-------------|
| WO | 2007115380 | AU | 2007236562 | EP | 2010317 | | |
| US | 7169196 | CA | 2467957 | CN | 1612925 | EP | 1442102 |
| | | MX | PA04004253 | NZ | 533239 | US | 2005066571 |
| | | WO | 03040270 | | | | |
| DT | 2518537 | NONE | | | | | |
| US | 7195653 | AU | 67700/01 | AU | 2005203020 | BR | 0112274 |
| | | CA | 2413744 | CN | 1449434 | CN | 1821365 |
| | | EP | 1299508 | EP | 1484386 | EP | 1953209 |
| | | JP | 2007154203 | MX | PA02012584 | US | 2003154646 |
| | | US | 2008028673 | WO | 0200812 | | |
| us | 2006254130 | AU | 2004205788 | BR | PI0406921 | CA | 2514146 |
| | | CN | 1764711 | EP | 1587898 | KR | 20060006890 |
| | | MX | PA05007820 | NZ | 541393 | RU | 2005123391 |
| | | WO | 2004065529 | ZA | 200505933 | | |
| Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. | | | | | | | |
| END OF ANNEX | | | | | | | |