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(21) International Application Number: PCT/AU00/00393 (22) International Filing Date: 28 April 2000 (28.04.00) (30) Priority Data: PQ 0015 28 April 1999 (28.04.99) AU (71) Applicant (for all designated States except US): CAST CENTRE PTY LTD [AU/AU]; Cooper Road, St Lucia, QLD 4067 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): RICKETTS, Nigel, Jeffrie [AU/AU]; 7 Burke Place, Forest Lake, QLD 4078 (AU). FROST, Malcolm, Timothy [AU/AU]; 104 Creekside Street, Kenmore Hills, Queensland 4069 (AU). CASHION, Simon, Paul [AU/AU]; 41 Baty Street, St Lucia, QLD 4067 (AU). KORN, Craig, John [AU/AU]; 10 Aquamarine Street, Springfield, QLD 4300 (AU). BAKER, Phillip, Wilmott [AU/AU]; 23 Carrington Road, Indooroopilly, QLD 4068 (AU). (74) Agent: GRIFFITH HACK; GPO Box 3125, Brisbane, Queensland 4001 (AU).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: COVER GASES (57) Abstract A cover gas composition for protecting molten magnesium/magnesium alloy includes a fluorine containing inhibiting agent and a carrier gas. Each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) of less than 5000.		

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COVER GASESFIELD OF THE INVENTION

5 The present invention relates to compositions useful as cover gases for protecting molten magnesium/magnesium alloys. The present invention also relates to a method for protecting molten magnesium/magnesium alloys and to a method for extinguishing magnesium/magnesium alloy fires.

10 BACKGROUND ART

Magnesium is a highly reactive and thermodynamically unstable element. Molten magnesium is readily and violently oxidised in ambient air, burning with a flame temperature of approximately 2820°C. Three approaches have been used to
15 inhibit the severe oxidation process. Salt cover fluxes may be sprinkled over the molten metal; oxygen may be excluded from contacting the molten metal by blanketing the molten metal with an inert gas such as helium, nitrogen or argon; or a protective cover gas composition may be used to blanket
20 the molten metal. Protective cover gas compositions typically comprise air and/or carbon dioxide and a small amount of an inhibiting agent which reacts/interacts with the molten metal to form a film/layer on the molten metal surface which protects it from oxidation. To this day, the
25 mechanism by which inhibiting agents protect molten reactive metals is not well understood.

US patent no. 1,972,317 relates to methods for inhibiting the oxidation of readily oxidisable metals, including magnesium and its alloys. The patent notes that
30 at the time of its filing in 1932, numerous solutions had been proposed to the oxidation problem including displacing the atmosphere in contact with the metal with a gas such as nitrogen, carbon dioxide or sulphur dioxide. US 1,972,317 teaches inhibition of oxidation by maintaining in the
35 atmosphere in contact with molten metal an inhibiting gas containing fluorine, either in elemental or combined form. Reference is made to many fluorine containing compounds with

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the solids ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate or the gases evolved therefrom upon heating being said to be preferred. Notwithstanding the issue of US 1,972,317 in 1934, it was
5 not until about the mid-1970's that a fluorine containing compound found commercial acceptance as an inhibiting agent in a cover gas.

Prior to about the mid-1970's, sulphur dioxide (SO_2) was widely used as an inhibiting agent in a magnesium cover
10 gas composition but was replaced by sulphurhexafluoride (SF_6) which has become the industry standard. Typically, SF_6 based cover gas compositions contain 0.2-1% by volume SF_6 and a carrier gas such as air, carbon dioxide, argon or nitrogen. SF_6 has the advantages that it is a colourless,
15 odourless, non-toxic gas which can be used for protecting molten magnesium/magnesium alloy and in the production of bright and shiny ingots with relatively low dross formation. However, SF_6 suffers from several disadvantages. Its sulphur based decomposition products at high temperature are
20 very toxic. It is expensive, has limited sources of supply, and is one of the worst known greenhouse gases having a Global Warming Potential (GWP) at a time horizon of 100 years of 23,900 relative to 1 for carbon dioxide.

It is also noted that once magnesium has ignited, the
25 resulting fire cannot be extinguished even with high concentrations of SF_6 . SO_2 is even worse in this respect as it can accelerate a magnesium fire. The only known cover gas for extinguishing a magnesium fire is boron trifluoride (BF_3) which is very expensive and very toxic.

30 Alternative cover gas compositions are desirable.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a
cover gas composition for protecting molten
magnesium/magnesium alloy, the composition including a
35 fluorine containing inhibiting agent and a carrier gas, wherein each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for

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carbon dioxide at a time horizon of 100 years) of less than 5000.

Preferably, the inhibiting agent has minimal ozone depletion potential, more preferably the inhibiting agent
5 has no ozone depletion potential.

Preferably, the inhibiting agent is non-toxic. In this regard, compounds having a Threshold Limit Value - Time Weighted Average (TLV-TWA) (the time weighted average concentration for a normal 8 hour workday and a 40 hour
10 workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect) as issued by the American Conference of Governmental Industrial Hygienists of less than 100ppm are considered to be toxic. By way of example, BF_3 , silicon tetrafluoride (SiF_4),
15 nitrogen trifluoride (NF_3) and sulfuryl fluoride (SO_2F_2) disclosed in US 1972317 are toxic.

The composition may include a mixture of inhibiting agents (each having a GWP less than 5000) and preferably comprises a minor amount of inhibiting agent and a major
20 amount of a carrier gas. Preferably, the composition consists of less than 1% by volume inhibiting agent and the balance carrier gas. More preferably, the composition contains less than 0.5% by volume (most preferably less than 0.1% by volume) inhibiting agent.

25 Preferably, each component of the composition has a GWP of less than 3000, more preferably, less than 1500.

Suitable carrier gases include air, carbon dioxide, argon, nitrogen and mixtures thereof.

The inhibiting agent may be selected from the group
30 consisting of hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) and mixtures thereof. Preferably, the inhibiting agent has a boiling point of less than 100°C , more preferably less than 80°C . Where the inhibiting agent is gaseous at ambient temperature, it may be diffused in the
35 carrier gas at the desired concentration. Where the inhibiting agent is liquid at ambient temperature, it may be entrained in the carrier gas to a desired concentration by

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passing a flow of carrier gas over the inhibiting agent. Suitable hydrofluorocarbons and hydrofluoroethers are listed in Table 1 below which includes their boiling points (BP) and their GWP's (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) which have been sourced from IPCC 1996.

TABLE 1

Chemical Name	Industry Name	Formula	GWP	BP
difluoromethane	HFC-32	CH ₂ F ₂	580	-52°C
pentafluoroethane	HFC-125	C ₂ HF ₅	3,200	-49°C
1,1,1,2-tetrafluoroethane	HFC-134a, R134a	C ₂ H ₂ F ₄	1,300	-26°C
difluoroethane	HFC-152a, R152a	C ₂ H ₄ F ₂	140	-27°C
heptafluoropropane	HFC-227ea	C ₃ HF ₇	2,900	-17°C
methoxy-nonafluorobutane	HFE-7100	C ₄ F ₉ OCH ₃	480	61°C
ethoxy-nonafluorobutane	HFE-7200	C ₄ F ₉ OC ₂ H ₅	90	78°C
dihydrodecafluoropentane	HFC-43-10-mee	C ₅ H ₂ F ₁₀	1,300	54°C

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A preferred cover gas composition consists of 1,1,1,2-tetrafluoroethane and dry air. Experimental work has demonstrated that such a cover gas composition provides protection at least the equal of SF₆ based compositions and
5 can be utilised at lower concentrations of inhibiting agent. SF₆ has a GWP in excess of 18 times that of 1,1,1,2-tetrafluoroethane and is presently more than 2½ times the cost of 1,1,1,2-tetrafluoroethane.

In a second aspect, the present invention provides a
10 method of protecting molten magnesium/magnesium alloy, the method including blanketing the molten magnesium/magnesium alloy with a cover gas composition according to the first aspect of the present invention.

The method according to the second aspect of the
15 present invention is applicable to protecting molten magnesium/magnesium alloy in a foundry vessel such as a furnace and during casting.

In a third aspect, the present invention provides use of an inhibiting agent as defined with respect to the first
20 aspect of the present invention for preventing or minimising oxidation of molten magnesium/magnesium alloy. By way of example, an inhibiting agent of the present invention may be used to prevent or minimise oxidation of molten magnesium/magnesium alloy during sand casting. Where the
25 inhibiting agent is gaseous at ambient temperature, the sand mould may be purged with inhibiting agent prior to pouring of the molten metal. Where the inhibiting agent is liquid at ambient temperature, the sand mould may be sprayed with inhibiting agent from a squeeze bottle or the like prior to
30 pouring of the molten metal. Other suitable methods of using inhibiting agents of the present invention to prevent or minimise oxidation of molten magnesium/magnesium alloy will be readily apparent to those of skill in the art of foundry practice.

35 In a fourth aspect, the present invention provides a method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of

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an inhibiting agent as defined with respect to the first aspect of the present invention. The fire may be so exposed by, for example, subjecting it to a flow of the inhibiting agent or immersing it in a reservoir containing the inhibiting agent.

EXAMPLES

The ensuing non-comparative Examples are illustrative of preferred embodiments of the present invention and are not to be construed as limiting the scope of the present invention in any way.

Example 1

A crucible furnace containing 100 grams of molten pure magnesium at 680°C was blanketed with a gaseous composition consisting of 0.02% by volume 1,1,1,2-tetrafluoroethane and the balance dry air. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

Comparative Example 1

Comparative Example 1 was identical to Example 1 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF₆. Good molten magnesium protection was not observed, and the magnesium sample burned rapidly. Adequate protection of the molten magnesium sample was only achieved when the gaseous composition consisted of 0.05% by volume SF₆ and the balance dry air. At this concentration of SF₆, deliberate rupturing of the surface film resulted in localised burning of the molten magnesium sample.

Example 1 and Comparative Example 1 demonstrate that the inventive cover gas composition provides good protection of molten magnesium at a lower concentration than an SF₆ based composition.

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Example 2

A series of single ingots of both pure magnesium and magnesium-aluminium alloy AZ91 were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with a cover gas composition, and the molten metal was allowed to solidify. In the case of AZ91 alloy the cover gas composition consisted of 0.04% by volume 1,1,1,2-tetrafluoroethane and the balance dry air. The cover gas composition for the pure magnesium casting consisted of 0.1% by volume 1,1,1,2-tetrafluoroethane and the balance dry air.

Single ingots of both pure magnesium and AZ91 alloy were produced free of burning, with bright shiny surface finishes, with very low levels of dross, and with no reaction with boron nitride mould coatings.

Comparative Example 2

Comparative Example 2 was identical to Example 2 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF₆ which was used at the same concentrations, ie. 0.04% by volume in dry air for AZ91 alloy and 0.1% by volume in dry air for pure magnesium.

The ingots produced in Example 2 had lower levels of dross and had a more attractive surface finish than those produced in Comparative Example 2.

Example 3

A small flow of 1,1,1,2-tetrafluoroethane was continuously metered into a container that is used to collect molten magnesium dross. During transport of the dross from the furnace to the container, the dross contacted the air and ignited. Upon placing the dross into the container, the burning quickly stopped.

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Comparative Example 3

Comparative Example 3 was identical to Example 3 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF_6 . In this case, the dross continued to burn after being
5 placed into the container.

Example 3 and Comparative Example 3 demonstrate that an inhibiting agent of the present invention is able to suppress the burning of magnesium metal/dross. This enables minimisation of magnesium fume in a working environment and
10 prevention of oxidation of the magnesium metal content in the dross. This would enable dross processing operations to recover valuable magnesium metal content.

Example 4

15 Ingots of pure magnesium were cast in 8kg ingot moulds on an industrial-sized ingot casting machine having a controllable atmosphere chamber. The casting machine was operated at a casting rate of 3 tonnes of cast metal per hour with 330 litres per minute dry air and 3.3 litres per
20 minute 1,1,1,2-tetrafluoroethane introduced into the chamber. Ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

25 Comparative Example 4

Comparative Example 4 was identical to Example 4 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF_6 , which was used at the same flow rate and at the same concentration in dry air. Ingots produced in Comparative
30 Example 4 exhibited similar properties to those produced in Example 4.

Example 4 and Comparative Example 4 demonstrate that the inventive gas can successfully replace SF_6 for industrial scale continuous production of magnesium ingot.

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Example 5

A series of single ingots of pure magnesium were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the
5 chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with cover gas composition, and the molten metal was allowed to solidify. The cover gas composition was produced by passing
10 0.5 litres per minute of dry air over 50ml of the HFE liquid methoxy-nonafluorobutane. The resulting gas phase mixture flowed to the single ingot casting apparatus. Single ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

15

Example 6

A series of single ingots of pure magnesium were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the
20 chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with a cover gas composition, and the molten metal was allowed to solidify. The cover gas composition was produced by passing
25 0.5 litres per minute of dry air over 50ml of the HFC liquid dihydrodecafluoropentane. The resulting gas phase mixture flowed to the single ingot casting apparatus. Single ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

30

Example 7

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.6 litres per minute of
35 dry air over 50ml of the HFE liquid methoxy-nonafluorobutane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed,

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with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

5 **Example 8**

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.9 litres per minute of dry air over 50ml of the HFE liquid ethoxy-nonafluorobutane.
10 The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

15

Example 9

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.9 litres per minute of dry air over 50ml of the HFC liquid dihydrodecafluoropentane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not
20 induce burning of the molten magnesium sample.
25

Example 10

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a gaseous composition consisting of 0.4% by volume difluoroethane and the balance dry air. Good
30 molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

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Comparative Example 10

Comparative Example 10 was identical to Example 10 with the exception that difluoroethane was replaced by SF_6 , which was used at the same concentration. Good molten magnesium protection was observed.

Example 10 and Comparative Example 10 demonstrate that an inhibiting agent of the present invention provides equivalent protection of molten magnesium metal compared to SF_6 .

Example 11

Magnesium squeeze-castings were produced by hand-pouring molten magnesium into the shot sleeve of a vertical injection squeeze casting machine. Prior to pouring the molten magnesium into the shot sleeve, a small volume of pure 1,1,1,2-tetrafluoroethane was introduced into the shot sleeve. This protected the molten magnesium in the shot sleeve and prevented the molten magnesium from burning during the filling of the mould.

Example 12

Various magnesium components were produced using the investment casting technique. Prior to filling the investment casting shell with molten magnesium, the shell was purged with pure 1,1,1,2-tetrafluoroethane. This prevented the magnesium from burning while solidifying inside the shell. Upon cooling, the shell mould was removed. The magnesium casting exhibited a good surface finish.

Example 13

Various magnesium components were produced using the sand casting technique. Prior to filling the sand mould with molten magnesium, the sand mould was purged with pure

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1,1,1,2-tetrafluoroethane. This prevented the magnesium from burning while solidifying inside the sand mould. Upon cooling, the sand mould was removed. The magnesium casting exhibited a good surface finish.

5

Example 14

A melt furnace having a diameter of 1.6 metres and containing 4 tonnes of molten pure magnesium was blanketed with 60 litres per minute dry air and 0.6 litres per minute
10 1,1,1,2-tetrafluoroethane. Good molten magnesium protection was observed, with the formation of a thin protective surface film.

Comparative Example 14

15 Comparative Example 14 was identical to Example 14 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF₆ at differing flow rates. The flow rate of dry air was maintained at 60 litres per minute. Good molten magnesium protection was only achieved at an SF₆ flow rate of 2 litres
20 per minute.

Example 14 and Comparative Example 14 demonstrate that the inventive cover gas composition provides good industrial scale protection of molten magnesium at a lower
25 concentration than an SF₆ based composition.

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CLAIMS

1. A cover gas composition for protecting molten magnesium/magnesium alloy, the composition including a
5 fluorine containing inhibiting agent and a carrier gas, wherein each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) of less than 5000.
10
2. A composition as claimed in claim 1 wherein the inhibiting agent has no ozone depletion potential.
3. A composition as claimed in claim 1 or claim 2 wherein
15 the carrier gas is selected from the group consisting of air, carbon dioxide, argon, nitrogen and mixtures thereof.
4. A composition as claimed in any one of the preceding
20 claims wherein each component of the composition has a GWP of less than 3000.
5. A composition as claimed in any one of the preceding
25 claims wherein the inhibiting agent is selected from the group consisting of hydrofluorocarbons, hydrofluoroethers and mixtures thereof.
6. A composition as claimed in any one of the preceding
30 claims wherein the inhibiting agent has a boiling point of less than 100°C.
7. A composition as claimed in any one of the preceding
35 claims wherein the inhibiting agent is selected from the group consisting of difluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane, difluoroethane, heptafluoropropane, methoxy-nonafluorobutane, ethoxy-nonafluorobutane,

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dihydrodecafluoropentane and mixtures thereof.

8. A composition as claimed in any one of the preceding claims wherein each component of the composition has a GWP of less than 1500.
9. A composition as claimed in any one of the preceding claims wherein the inhibiting agent is 1,1,1,2-tetrafluoroethane and the carrier gas is dry air.
10. A composition as claimed in any one of the preceding claims containing less than 1% by volume inhibiting agent.
11. A composition as claimed in claim 10 containing less than 0.5% by volume inhibiting agent.
12. A composition as claimed in claim 11 containing less than 0.1% by volume inhibiting agent.
13. A cover gas composition substantially as herein described in any non-comparative Example.
14. A method of protecting molten magnesium/magnesium alloy, the method including blanketing the magnesium/magnesium alloy with a cover gas composition as claimed in any one of the preceding claims.
15. Use of an inhibiting agent as defined in any one of claims 1-12 for preventing or minimising oxidation of molten magnesium/magnesium alloy.
16. A method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of an inhibiting agent as defined in any one of claims 1-12.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : B22D 21/04, 21/02; A62D1/02; C22B 26/22, 4/02; C22C 1/02, 23/00		
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: B22D 21/04, 21/02; A62D1/02; C22B 26/22, 4/02; C22C 1/02, 23/00		
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) DWPI - Key words: fluoro:		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/22129 A (Minnesota Mining and Manufacturing Company) 25 July 1996 (see page 7, line 21 to last line; page 12, lines 21 to 23; page 14 lines 2 to 7)	1-8,10-12
X	US 5115868 A (Dougherty, Jr. et al.) 26 May 1992 (see col 2, line 65 to col 3, line 33; col 4, lines 31 to 38; Example 1, Example 5)	1-13
X	WO 91/02564 A (Great Lakes Chemical Corporation) 7 March 1991 (see page 4, lines 1 to 20; page 7, lines 19 to 25)	1-8, 10-12
A	US 5855647 A (Li et al.) 5 January 1999 (see the entire document)	1-16
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Date of the actual completion of the international search 8 June 2000		Date of mailing of the international search report 16 JUN 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer B. PREMARATNE

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00393

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	Derwent Abstract Accession No. 96-319293/32, class M25, JP, A, 08143985 (Tokai Rika Denki KK) 4 June 1996 (see the whole abstract)	1-16

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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