

⑪



Europäisches Patentamt

European Patent Office

Office européen des brevets

SECRET SERVICE

⑫ Publication number:

0 159 736

B1

⑬

EUROPEAN PATENT SPECIFICATION

⑭ Date of publication of patent specification: **02.11.89**

⑮ Int. Cl.⁴: **C 08 F 10/00, C 08 F 4/64**

⑯ Application number: **85200393.8**

⑰ Date of filing: **15.03.85**

6-4/90

⑱ Olefin polymerization catalyst composition.

⑲ Priority: **10.04.84 US 598616**

⑳ Date of publication of application:
30.10.85 Bulletin 85/44

㉑ Publication of the grant of the patent:
02.11.89 Bulletin 89/44

㉒ Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

㉓ References cited:
EP-A-0 018 738
EP-A-0 019 330
EP-A-0 135 973

㉔ Proprietor: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.**
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)

㉕ Inventor: **Job, Robert Charles**
12126 Westmere
Houston Texas 77077 (US)
Inventor: **Goodall, Brian Leslie**
14034 St. Mary's Lane
Houston Texas 77079 (US)

㉖ Representative: **Aalbers, Onno et al**
P.O. Box 302
NL-2501 CH The Hague (NL)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

Description

This invention relates to a process for preparing free-flowing solid olefin polymerization catalyst components comprising a magnesium halide/titanium halide/electron donor procatalyst and mineral oil.

5 Numerous proposals are known from the prior art to provide olefin polymerization catalysts by combining a solid component comprising at least magnesium, titanium and chlorine with an activating organoaluminium compound. These may be referred to as supported coordination catalysts or catalyst systems. The activity and stereospecific performance of such compositions is generally improved by incorporating an electron donor (Lewis base) in the solid component and by employing as a third catalyst
10 component an electron donor which may be complexed in whole or in part with the activating organoaluminium compound.

For convenience of reference, the solid titanium-containing constituent of such catalysts is referred to herein as "pro-catalyst", the organoaluminium compound, whether used separately or partially or totally complexed with an electron donor, as "cocatalyst", and the electron donor compound, whether used
15 separately or partially or totally complexed with the organo-aluminium compound, as "selectivity control agent" (SCA).

While the selection of cocatalyst and selectivity control agent affects the performance of those catalyst systems, the component which appears to be subject to most significant improvement with respect to activity and productivity of the system is the procatalyst.

20 Suitable methods of preparing such procatalysts have been disclosed in U.S. Patents 4,329,253; 4,393,182; 4,400,302; and 4,414,132. Procatalysts are highly active and stereospecific. Various studies have shown that such procatalysts may suffer from shelf-life problems when stored as a dry powder. Even though the catalysts are always stored under nitrogen, a catalyst which is aged as a dry powder invariably loses activity over time. The exact cause of the activity loss is not known. This shelf-life problem may be
25 overcome by storing and shipping the catalyst as a slurry in dry mineral oil, but this method has been found to suffer two disadvantages compared to dry-powder shipment:

i) slurry concentrations vary considerably causing inconsistencies in polymerization plant operation when switching catalyst drums;

30 ii) introducing the catalyst as a mineral oil slurry is not optimum for all processes. For example, in gas-phase operation a dry powder or a slurry in a volatile hydrocarbon might be preferable.

In U.S. Patent No. 4,290,915, the patentee prescribes driving the procatalyst such that the remaining procatalyst contains 1—25% by weight of the inert liquid hydrocarbon having a boiling point at less than 115°C (e.g. n-pentane, cyclohexane, benzene and the like). However, the patentee still finds that the procatalyst loses activity after storage for as little as two days. Further, there are problems in ascertaining
35 and controlling the level of the inert liquid hydrocarbon in the procatalyst.

It is an object of this invention to prepare procatalysts that do not show the activity loss problem associated with dry catalyst and which do not have the various disadvantages of the slurry method for storing and shipping procatalysts.

The present invention deals with a process for preparing free-flowing catalyst compositions for
40 alpha-monoolefin polymerization which process comprises:

a) halogenating a magnesium compound of the formula $MgR'R''$ wherein R' is an alkoxide or aryloxy group and R'' is an alkoxide or aryloxy group or halogen, with a halide of tetravalent titanium in the presence of a haloalkane and an electron donor, and separating the solid reaction product from the reaction mixture;

45 b) contacting the halogenated product with a tetravalent titanium halide and separating the resulting solid from the liquid medium;

c) contacting the resulting solid with an inert hydrocarbon liquid having a boiling point at less than 115°C to remove unreacted titanium compounds;

50 d) adding a certain amount of a hydrocarbon mineral oil to the mixture of light hydrocarbon liquid and solid component wherein said mineral oil is a viscous paraffinic/naphthenic hydrocarbon oil; and

e) removing by evaporation the hydrocarbon liquid having a boiling point at less than 115°C from the resulting mixture, wherein the amount of hydrocarbon mineral oil added in step d) is greater than five per cent by weight, based on the combined weight of the solid component plus mineral oil, but is less than the amount whereby the resulting solid component, is no longer free-flowing.

55 Expressed another way, the amount of hydrocarbon mineral oil which is added is greater than 5 per cent by weight (based on the combined weight of the mineral oil plus solid component) and is of a volume less than that corresponding to the pore volume of the solid component.

As is illustrated in the examples which follow, we have shown that:

60 i) the addition of 10 to 25 per cent by weight of mineral oil to certain procatalyst components still leaves the catalyst as a dry free-flowing powder;

ii) such modified catalysts have demonstrated improved activities in propylene polymerization;

65 iii) when stored as "dry powder" at ambient temperature over long periods (greater than 50 days), these catalysts maintain their activity much better than dry catalysts which have not been modified with mineral oil.

The procatalysts which are employed as solid catalyst components in this invention are produced by the method disclosed in EP 19330. The preferred starting materials, electron donor compounds, titanium halides, haloalkohydrocarbons, etc to be used in this invention are likewise as disclosed in EP 19330. Mg-dialkoxides and Mg-alkoxyhalides are the most preferred starting materials.

After the treatment with tetravalent titanium halide the catalyst component is isolated from the liquid reaction medium and then, the catalyst component is washed with an inert hydrocarbon liquid, having a boiling point at less than 115°C, to remove unreacted titanium halide. Preferred hydrocarbon liquids are aliphatic, alicyclic and aromatic hydrocarbons. Examples of such liquids include iso-pentane, n-hexane, iso-octane and toluene, with iso-pentane being most preferred. The amount of hydrocarbon liquid having a boiling point at less than 115°C employed is 50 to 300 ml/g of procatalyst in particular in 2 to 6 separate washes, preferably 120 to 170 ml/g.

A key aspect of the present invention is the addition of a certain amount of a hydrocarbon mineral oil. The hydrocarbon mineral oil employed herein is a viscous, principally paraffinic/naphthenic hydrocarbon oil having a viscosity of 7 to $433 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (50 to 2000 SSU) at 38°C. The mineral oil should also be essentially non-volatile at ambient conditions, i.e., preferably at least 80% by weight should have an initial boiling point of at least 300°C, corrected to atmospheric pressure. The mineral oil is best obtained from petroleum sources (i.e., it is a distillate product), and the extent of paraffinity naphthenicity and aromaticity will, of course, be dependent on the particular type of petroleum used as a source material. However, it should be principally non-aromatic in nature, i.e., contain less than 30% by weight of aromatics (by clay-gel analysis). Commercial mineral oils are well known and include Witco's Kaydol, Shell's Shellflex® 371, and Arco's Tufflo 6000 Series paraffinic/naphthenic oils.

The mineral oil is added to the mixture of light hydrocarbon liquid and solid catalyst during the wash steps. After the mineral oil is mixed with the light hydrocarbon liquid and solid catalyst, the light hydrocarbon liquid is removed, typically by evaporating the light hydrocarbon liquid. The evaporation or drying treatment is carried out preferably under relatively mild temperature conditions. For example, it is carried out at a temperature of not more than 80°C, preferably 0°C to 60°C, in an atmosphere of an inert gas at atmospheric pressure or reduced pressure.

As shown in the examples which follow, the incorporation of mineral oil results in an activity improvement for the catalyst. We assume that the activity improvement is related to enhanced heat removal (during polymerization), from the catalyst active centres, due to the mineral oil trapped in the catalyst pores. These pores (capillary-type) are normally nitrogen-filled voids since viscous mineral oil will not enter the pores when dry catalyst is suspended in oil. Our technique of diluting the required amount of mineral oil in light hydrocarbon liquid diluent (and then evaporating the diluent) greatly reduces the viscosity allowing permeation of the catalyst by mineral oil (as witnessed by the dry, free-flowing nature of the resulting catalyst).

The amount of hydrocarbon mineral oil which is employed herein is a critical aspect of the present invention. Typically, the amount of hydrocarbon mineral oil employed herein is between 5% by weight and 25% by weight, based on the combined weight of solid procatalyst component and mineral oil, preferably between 10%w and 25%w. The upper (higher) limit for mineral oil addition is most critical, and should be less than the amount whereby the solid component, upon drying is no longer free-flowing. Expressed another way, sufficient mineral oil is added to fill the pores of the solid catalyst, but no more. This amount may be determined experimentally or via measuring the pore volume of the solid catalyst. Pore volume is measured by BET methods. The pore volume of the solid procatalysts employed herein is typically from 0.1 to 1.0 ml/g.

The mineral oil-modified catalysts (which are free-flowing, resembling dry powder) may be stored for relatively long periods of time prior to use.

To prepare the final polymerization catalyst composition, procatalyst, cocatalyst and selectivity control agent, if used separately, may be simply combined, as has been set out in EP 19330. The very same applies to the use of the present catalyst systems in olefin polymerization, particularly propylene polymerization.

In the following examples the selectivity to isotactic polypropylene is determined by measuring the amount of xylene soluble polymer (XS), in accordance with regulations of the U.S. Food and Drug Administration. The XS test is carried out as follows:

The sample is completely dissolved in xylene, which contains oxydation inhibitor, in a stirred flask by heating under reflux at 120°C. The flask is then immersed in a water bath at 25°C without stirring for one hour during which the insoluble portion precipitates. The precipitate is filtered off and the solubles present in the filtrate are determined by evaporating a 20 ml aliquot of the filtrate, drying the residue under vacuum, and weighing the residue. The xylene-solubles consist of amorphous material with some low molecular weight crystalline material. (FDA regulations 121.2501 and 121.2510, 1971).

Catalyst productivity at standard conditions exhibits an inverse relationship with stereoselectivity. This relationship is characteristic for any given procatalyst. It is generally possible to control these variables, within limits, by changing the proportion of selectivity control agent (SCA). Increasing the amount of SCA increases selectivity to isotactic or stereo-regular polymer but reduces activity, and hence productivity, in a standard one hour test. The relationship in propylene polymerization is such that a decrease of 1% of XS, e.g., from 5 to 4, corresponds approximately to a decrease in activity of 5 kg/g/hr.

Examples

In these examples, the procatalysts were composites of tetravalent titanium, magnesium, chloride, ethoxy groups and ethyl benzoate. They were prepared by reacting magnesium ethoxide, titanium tetrachloride and ethyl benzoate (EB) in the presence of a halohydrocarbon at elevated temperatures to produce a solid containing Mg, Cl, Ti, —OEt groups and EB, contacting this solid with TiCl_4 at elevated temperatures in two or three additional contacting steps, and completely washing off unbound TiCl_4 by six washes with isopentane.

Four identical procatalyst preparations were executed. Catalyst 1 was simply finished, dried and stored as a dry powder in a sealed bottle in a nitrogen-filled dry-box. The other catalysts were prepared and stored in exactly the same manner except that immediately prior to evaporating the isopentane originating from the last catalyst wash a certain volume of mineral oil was added (10%w, 20%w and 30%w, respectively based on combined weight of catalyst plus mineral oil). On drying the catalyst (i.e., evaporating the isopentane under nitrogen at 40°C) the mineral oil is forced into the pores of the solid. The pore volume of the catalysts is obviously >20%w and <30%w since the 10%w and 20%w catalysts were dry free-flowing powders whereas the 30%w catalyst was slightly tacky (presumably due to excess mineral oil) although it still flowed. A portion of each of these catalysts was made up into a mineral oil slurry ("fresh catalysts") while the remainder was stored in an inert atmosphere (glove box) at ambient temperature. At monthly intervals (1—3) months portions of each of the catalyst powder remainders were made up into mineral oil slurries; in this way the shelf-life stability of each powder could be determined by running liquid propylene polymerizations with each of the slurries.

TABLE 1
Procatalyst compositions

| Catalyst | Ti %w | OEt %w | EB %w | Mg %w | Cl %w | i-C ₅ %w | Mineral oil %w* |
|----------|----------|-----------|----------|----------|----------|------------------------|-----------------------|
| 1 | 3.49 | 0.82 | 11.6 | 18.6 | 65.0 | 0.4 | 0 |
| 2 | 3.16 | 0.76 | 10.3 | 16.2 | 55.9 | 2.1 | 10 |
| 3 | 2.92 | 0.70 | 9.3 | 14.8 | 51.6 | 0.4 | 20 |
| 4 | 2.60 | 0.65 | 8.7 | 13.4 | 46.3 | 0.0 | 30 |

* Mineral oil content calculated on the basis of the amount of mineral oil added.

Propylene polymerization was conducted as follows: 1400 g of liquid propylene and 132 mmol of hydrogen in a one gallon (about 4 litre) autoclave equipped with an agitator, was heated to 60°C under sufficient pressure to maintain it in liquid phase. A predetermined amount of p-ethyl ethoxy benzoate and 2.5 ml (0.7 mmol) of triethyl aluminium as a 5% solution in C_7 — C_8 paraffin diluent were then successively added to the propylene. To the agitated mixture there was added a sufficient amount of the slurry of mineral oil-modified procatalyst in mineral oil slurry (or of unmodified procatalyst in the control experiments) to provide about 0.01 m atoms of titanium. The mixture was agitated and maintained at 67°C for one hour. The pressure was then released and the powdered polypropylene recovered.

The polymerization results are listed in Table 2.

Comparing the polypropylene yield data it can be seen that the dry powder procatalyst No. 1 lost more than 25% of its original activity after aging for 2 months. On the other hand all of the "mineral oil-modified" procatalysts still possessed the expected performance of a fresh catalyst after the same period.

TABLE 2

| | Catalyst | Oil, %w | Aged | XS, %w | Yield at 4.5% XS kg/g cat. |
|----|----------|------------|--------------|-----------|-------------------------------|
| 5 | 1 | 0 | Fresh | 4.3 | 23.8 |
| | | | One month | 4.1 | 19.0 |
| 10 | | | Two months | 4.8 | 15.0 |
| | | | Three months | 4.9 | 17.7 |
| | 2 | 10 | Fresh | 4.5 | 34.7 |
| 15 | | | One month | 4.5 | 21.6 |
| | | | Two months | 5.1 | 23.2 |
| 20 | | | Three months | 4.2 | 22.5 |
| | 3 | 20 | Fresh | 4.9 | 29.5 |
| 25 | | | One month | 4.3 | 25.8 |
| | | | Two months | 3.9 | 22.7 |
| | | | Three months | 4.4 | 29.1 |
| 30 | 4 | 30 | Fresh | 5.1 | 25.2 |
| | | | One month | 3.9 | 30.7 |
| | | | Two months | 4.4 | 29.1 |
| 35 | | | Three months | 3.7 | 30.0 |

40 Claims

1. A process for preparing high-activity, free-flowing olefin polymerization solid catalyst components comprising:

45 a) halogenating a magnesium compound of the formula $MgR'R''$ wherein R' is an alkoxide or aryloxy group and R'' is an alkoxide or aryloxy group or halogen, with a halide of tetravalent titanium in the presence of a halohydrocarbon and an electron donor, separating the solid reaction product from the reaction mixture;

b) contacting the halogenated product with a tetravalent titanium halide and separating the resulting solid from the liquid medium;

50 c) contacting the resulting solid with 50 to 300 ml/g of procatalyst of an inert, hydrocarbon liquid having a boiling point at less than 115°C to remove unreacted titanium compounds;

d) adding a certain amount of a hydrocarbon mineral oil to the mixture of hydrocarbon liquid having a boiling point at less than 115°C and solid product, said mineral oil being a viscous, paraffinic/naphthenic hydrocarbon oil with a viscosity of 7 to $443 \times 10^{-6} m^2 s^{-1}$ at 38°C; and

55 e) removing by evaporation the low boiling hydrocarbon liquid from the resulting mixture, wherein the amount of hydrocarbon mineral oil added in step d) is greater than five per cent by weight, based on the combined weight of the solid component plus mineral oil, but is less than the amount whereby the resulting solid product is no longer free-flowing.

2. A process of claim 1, wherein said magnesium compound is a magnesium dialkoxide or a magnesium alkoxyhalide.

60 3. A process of claim 1, wherein said inert light hydrocarbon liquid is selected from the group consisting of iso-pentane, n-hexane, iso-octane and toluene.

4. A process as claimed in claims 1 to 3, wherein the amount of mineral oil employed herein is between 5 and 25%w, based on the combined weight of said solid product and said mineral oil.

65 5. A process of claim 4, wherein the amount of mineral oil is between 10 and 25%w.

Patentansprüche

1. Verfahren zur Herstellung von hochaktiven, freifließenden, festen Olefinpolymerisationskatalysator-komponenten, umfassend:
 - 5 a) Halogenieren einer Magnesiumverbindung der Formel $MgR'R''$, worin R' eine Alkoxid- oder Aryloxidgruppe bedeutet, und R'' eine Alkoxid- oder Aryloxidgruppe oder Halogen darstellt, mit einem Halogenid von vierwertigem Titan in Gegenwart eines Halogenkohlenwasserstoffes und eines Elektronendonors, und Abtrennen des festen Reaktionsproduktes aus dem Reaktionsgemisch;
 - b) In-Berührung-Bringen des halogenierten Produktes mit einem vierwertigen Titanhalogenid und
 - 10 Abtrennen des gebildeten Feststoffes aus dem flüssigen Medium;
 - c) In-Berührung-Bringen des erhaltenen Feststoffes mit 50 bis 300 ml/g Prokatalysator einer inerten Kohlenwasserstoffflüssigkeit mit einem Siedepunkt von unter 115°C zur Beseitigung nicht umgesetzter Titanverbindungen;
 - d) Zusetzen einer bestimmten Menge eines Kohlenwasserstoffmineralöls zu dem Gemisch aus der
 - 15 Kohlenwasserstoffflüssigkeit mit einem Siedepunkt von unter 115°C und dem festen Produkt, welches Mineralöl ein viskoses, paraffinisch/naphthenisches Kohlenwasserstofföl mit einer Viskosität von 7 bis $443 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ bei 38°C ist;
 - e) Abtrennen der niedrigsiedenden Kohlenwasserstoffflüssigkeit aus dem erhaltenen Gemisch durch Verdampfen, wobei die in Stufe d) zugesetzte Menge an Kohlenwasserstoffmineralöl größer ist als 5
 - 20 Gew.-%, bezogen auf das Gesamtgewicht aus der festen Komponente und dem Mineralöl, aber geringer ist als jene Menge, durch welche das gebildete feste Produkt nicht mehr freifließend ist.
2. Ein Verfahren des Anspruchs 1, worin die genannte Magnesiumverbindung ein Mg-Dialkoxid oder ein Mg-Alkoxyhalogenid ist.
3. Ein Verfahren des Anspruchs 1, worin die genannte inerte Kohlenwasserstoffflüssigkeit selektiert ist
- 25 from die Gruppe bestehend aus Isopentan, n-Hexan, Isooktan und Toluol.
4. Verfahren nach Ansprüchen 1—3, worin die Menge des hier verwendeten Mineralöls zwischen 5 und 25 Gew.-% bezogen auf das Gesamtgewicht aus dem festen Produkt und dem Mineralöl, beträgt.
5. Verfahren nach Anspruch 4, worin die Menge an Mineralöl zwischen 10 und 25 Gew.-% beträgt.

30 Revendications

1. Un procédé de préparation de constituants solides, sous la forme d'une poudre qui roule, de catalyseurs d'une haute activité pour la polymérisation d'oléfines, comprenant:
 - 35 a) l'halogénéation d'un composé du magnésium de la formule $MgR'R''$ où R' est un groupe alcoolate ou aryloxyde et R'' est un groupe alcoolate ou aryloxyde ou un halogène, avec un halogénure de titane tétravalent en présence d'un halo-hydrocarbure et d'un donneur d'électrons et la séparation du produit de réaction solide du mélange de réaction;
 - b) la mise en contact du produit halogéné avec un halogénure de titane tétravalent et la séparation du produit solide résultant du milieu liquide;
 - 40 c) la mise en contact du produit solide résultant avec 50 à 300 ml/g de procatalyseur d'un liquide hydrocarboné inerte ayant un point d'ébullition au-dessous de 115°C pour élimination des composés du titane n'ayant pas réagi;
 - d) l'addition d'une certaine quantité d'une huile minérale d'hydrocarbures au mélange de liquide hydrocarboné ayant un point d'ébullition au-dessous de 115°C et de produit solide, cette huile minérale
 - 45 étant une huile d'hydrocarbures paraffinique/naphthénique visqueuse ayant une viscosité de 7 à $443 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ à 38°C; et
 - e) l'élimination par évaporation du liquide hydrocarboné à bas point d'ébullition du mélange résultant, la quantité d'huile minérale d'hydrocarbures ajoutée dans l'étape d) étant supérieure à 5% en poids, par rapport au poids combiné du constituant solide et de l'huile minérale, mais inférieure à une quantité telle
 - 50 que le produit solide résultant ne soit plus une poudre qui roule.
2. Un procédé de la revendication 1, dans lequel ledit composé du magnésium est une dialcoolate de Mg ou une alkoxyhalogénure de Mg.
3. Un procédé de la revendication 1, dans lequel ladite liquide hydrocarboné inerte est sélectionnée de la groupe, comprenant l'isopentane, n-hexane, l'isooctane et le toluène.
- 55 4. Un procédé selon les revendications 1—3, dans lequel la quantité d'huile minérale utilisée est comprise entre 5 et 25% en poids, par rapport au poids combiné du produit solide et de l'huile minérale.
5. Un procédé selon la revendication 4, dans lequel la quantité d'huile minérale est comprise entre 10 et 25% en poids.

REGISTER ENTRY FOR EP0159736

European Application No EP85200393.8 filing date 15.03.1985

Priority claimed:

10.04.1984 in United States of America - doc: 598616

Designated States BE CH DE FR GB IT LI NL SE AT

Title OLEFIN POLYMERIZATION CATALYST COMPOSITION

Applicant/Proprietor

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., Carel van Bylandtlaan 30,
NL-2596 HR Den Haag, Netherlands [ADP No. 50701200001]

Inventors

ROBERT CHARLES JOB, 12126 Westmere, Houston Texas 77077, United States of
America [ADP No. 53614202001]BRIAN LESLIE GOODALL, 14034 St. Mary's Lane, Houston Texas 77079, United
States of America [ADP No. 53614210001]

Classified to

C3P C3W

C08F

Address for Service

D A H BENNETT, Shell Centre, London, SE1 7NA, United Kingdom
[ADP No. 00961037001]

EPO Representative

ONNO AALBERS, P.O. Box 302, NL-2501 CH The Hague, Netherlands
[ADP No. 50774652001]

Publication No EP0159736 dated 30.10.1985

Publication in English

Examination requested 15.03.1985

Patent Granted with effect from 02.11.1989 (Section 25(1)) with title OLEFIN
POLYMERIZATION CATALYST COMPOSITION.

05.02.1987 EPO: Search report published on 04.02.1987

Entry Type 25.11 Staff ID.

Auth ID. EPT

03.11.1989 D A H BENNETT, Shell Centre, London, SE1 7NA, United Kingdom

[ADP No. 00961037001]

registered as address for service

Entry Type 8.11 Staff ID. JN1 Auth ID. F51

**** END OF REGISTER ENTRY ****

OA80-01
FG

OPTICS - PATENTS

19/03/90 15:29:19
PAGE: 1

RENEWAL DETAILS

PUBLICATION NUMBER EP0159736

PROPRIETOR(S)

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., Carel van
Bylandtlaan 30, NL-2596 HR, Netherlands

DATE GRANTED 02.11.1989

DATE NEXT RENEWAL DUE 15.03.1991

DATE NOT IN FORCE

DATE OF LAST RENEWAL 31.01.1990

YEAR OF LAST RENEWAL 06

STATUS PATENT IN FORCE