

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 February 2004 (12.02.2004)

PCT

(10) International Publication Number
WO 2004/013216 A1

(51) International Patent Classification⁷:

C08J 9/224

(21) International Application Number:

PCT/EP2003/007225

(22) International Filing Date:

3 July 2003 (03.07.2003)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

MI2002A001711 31 July 2002 (31.07.2002) IT

(71) Applicant (for all designated States except US):
POLIMERI EUROPA S.P.A. [IT/IT]; Via E. Fermi
4, I-72100 Brindisi (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): LANFREDI,
Roberto [IT/IT]; Via Parenza 20, I-46030 Virgilio-Mantova (IT). GHIDONI, Dario [IT/IT]; Via Gramsci, 15, I-46023 Gonzaga-Mantova (IT).

(74) Agents: DE GREGORI, Antonella et al.; Barzano' & Zanardo Milano S.p.A, Via Borgonuovo 10, I-20121 Milan (IT).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, 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, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 2004/013216 A1

(54) Title: BEADS OF EXPANDABLE VINYLAROMATIC POLYMERS AND PROCESS FOR THEIR PREPARATION

(57) Abstract: Beads of expandable vinylaromatic polymers which comprise: a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of at least one copolymerizable monomer; b) 1-10% by weight, calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix; c) 2 ppm-2% by weight, calculated with respect to the polymer (a), of an anti-lumping additive, distributed on the surface of the beads, comprising Oxides of metals of groups IB, IIB and VIIIB.

BEADS OF EXPANDABLE VINYLAROMATIC POLYMERS AND PROCESS FOR
THEIR PREPARATION

The present invention relates to beads of expandable
10 vinylaromatic polymers and a process for their preparation.

More specifically, the present invention relates to an
expandable polystyrene in the form of beads with a reduced
formation of lumps and the process for its preparation.

Vinylaromatic polymers, and among these, polystyrene
15 in particular, are known products which have been adopted
for a long time for preparing compact and/or expanded arti-
cles which can be used in various applicative sectors,
among which the most important are household appliances,
the transport and building industries, office machines,
20 etc. A particularly interesting sector is the field of
thermal insulation, where vinylaromatic polymers are essen-
tially used in expanded form.

These expanded products are obtained by swelling, in a
pre-expander, beads of expandable polymer previously im-
25 pregnated with an expanding agent and molding the swollen

particles inside a closed mould by means of the contemporaneous effect of pressure and temperature.

The swelling, or pre-expansion, of the particles is generally effected with vapour, or another gas, maintained 5 at a temperature slightly higher than the glass transition temperature (Tg) of the polymer. During this phase, the particles tend to stick to each other and to avoid this drawback, they are treated with additives generally known as anti-lumping additives.

10 The addition of metallic stearates, such as magnesium stearate, is known, for example. This additive is extremely effective in preventing the beads from sticking during the pre-expansion phase but results in poor adhesion in the moulding phase during the preparation of the end-products.

15 U.S. patent 3,520,833 describes the use of lecithin, added with the expanding agent during the impregnation of the particles, as anti-lumping additive. Unfortunately, lecithin gives the end-products an unacceptable odour making their use problematical.

20 U.S. patent 3,444,104 describes the use of calcium and silicon aluminates. The lumps, in this case, are eliminated and the adhesion remains acceptable. The density of the beads in expansion, however, is poor.

25 U.S. patent 3,462,293 describes the use of a polymeric latex, for example polyethylene or SAN copolymer, deposited

on the particles. The subsequent drying treatment of the latex with air, however, requires long times which make the preparation process quite unsuitable for industrial development.

5 Finally, European patent 449,065 describes the use of oxides such as silica, alumina and titanium oxide. Although these products have a good capacity against the formation of lumps, they have the disadvantage, as specified above, of reducing the adhesion of the expanded beads during the
10 moulding phase.

There are evident disadvantages associated with these systems for avoiding the formation of lumps as they either jeopardize the adhesion of the expanded beads, or the expansion of the beads themselves or they require processes,
15 for example drying, which are too elaborate for being conveniently used in the industrial field.

The Applicant has now found a simple system for eliminating the formation of agglomerates of swollen vinylaromatic polymer beads without jeopardizing the subsequent adhesion and/or expandability.
20

An object of the present invention therefore relates to beads of expandable vinylaromatic polymers which comprise:

a) a matrix obtained by polymerizing 50-100% by weight of
25 one or more vinylaromatic monomers and 0-50% by weight of

at least one copolymerizable monomer;

b) 1-10% by weight, calculated with respect to the polymer

(a), of an expanding agent englobed in the polymeric ma-
trix;

5 c) 2 ppm-2% by weight, calculated with respect to the poly-
mer (a), of an anti-lumping additive, distributed on the

surface of the beads, selected from oxides of metals of
groups IB and VIIIB or from mixtures consisting of oxides
of metals of groups IB, IIB and VIIIB and esters of C₈-C₂₅

10 fatty acids with the same metals.

A further object of the present invention relates to a
process for the preparation of expandable vinylaromatic
polymer beads which comprises:

- polymerizing 50-100% by weight of one or more vinylaro-
15 matic monomers and 0-50% by weight of at least one co-
polymerizable monomer;

- englobing an expanding agent in the polymeric matrix;
· and

- distributing on the surface of the beads obtained 2 ppm-
20 2% by weight, calculated with respect to the polymer, of
an anti-lumping additive selected from oxides of metals
of groups IB and VIIIB or from mixtures consisting of
oxides of metals of groups IB, IIB and VIIIB and esters
of C₈-C₂₅ fatty acids with the same metals.

25 According to the present invention, the vinylaromatic

polymers can be obtained with a polymerization process in aqueous suspension or continuous mass. In particular, the polymerization in suspension of the vinylaromatic monomer is carried out under conditions and in the presence of additives well known in the art. In addition to the suspending agent, selected from insoluble inorganic salts, for example calcium or magnesium such as tricalcium phosphate or magnesium phosphate, or from organic suspending agents such as polyvinylpyrrolidone, the polymerization is carried out in the presence of an initiating system or an expanding system.

The initiating system generally comprises two peroxides, one with a halving time of an hour at 85-95°C and the other with a halving time of an hour at 110-120°C. Examples of these initiators are benzoylperoxide and terbutylperbenzoate.

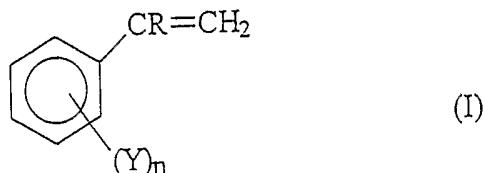
Any expanding agent capable of being englobed in the polymeric matrix can be used in a combination with the vinylaromatic polymers object of the present invention. In general, liquid substances are used, with a boiling point ranging from 10 to 100°C, preferably from 20 to 80°C. Typical examples are aliphatic hydrocarbons, freon, carbon dioxide, water, etc.

The expanding agent can be added to the polymer during the polymerization phase in suspension, or, alternatively,

by impregnation of the beads produced at the end of the polymerization or by injection into the molten polymer according to the continuous mass preparation process. At the end of the addition, a polymer is obtained in the form of 5 beads, which can be transformed to produce expanded articles with a density ranging from 5 to 50 g/l, preferably from 8 to 25 g/l, with an excellent thermal insulation capacity. In order to favour the retention of the expanding agent in the polymeric matrix, additives capable of forming 10 bonds both of the weak type (for example hydrogen bridges) or strong type (for example acid-base adducts), can be used with the expanding agent. Examples of these additives are methyl alcohol, isopropyl alcohol, dioctylphthalate, dimethylcarbonate, compounds containing an amine group, etc. 15 These additives are generally added during the polymerization and/or englobed in the polymer together with the expanding agent.

The expanding agents are preferably added during the polymerization phase and are selected from aliphatic or 20 cycloaliphatic hydrocarbons containing from 3 to 6 carbon atoms, such as n-pentane, iso-pentane, cyclopentane or their mixtures; halogenated derivatives of aliphatic hydrocarbons containing from 1 to 3 carbon atoms such as, for example, dichlorodifluoromethane, 1,2,2-trifluoroethane, 25 1,1,2-trifluoroethane; carbon dioxide and water.

The term "vinylaromatic monomer", as used in the present description and claims, essentially refers to a product which corresponds to the following general formula:



wherein n is zero or an integer ranging from 1 to 5, R is a hydrogen atom or a methyl and Y is a halogen, such as chlorine or bromine, or an alkyl or alkoxy radical having from 10 1 to 4 carbon atoms.

Examples of vinylaromatic monomers having the general formula defined above are: styrene, α -methylstyrene, methylstyrene, ethylstyrene, butylstyrene, dimethylstyrene, 15 mono-, di-, tri-, tetra- and penta-chlorostyrene, bromostyrene, methoxy-styrene, acetoxy-styrene, etc. Styrene and α -methylstyrene are the preferred vinylaromatic monomers.

The vinylaromatic monomers having general formula (I) can be used alone or in a mixture of up to 50% by weight 20 with other copolymerizable monomers. Examples of these monomers are (meth)acrylic acid, C₁-C₄ alkyl esters of (meth)acrylic acid, such as methyl acrylate, methyl-methacrylate, ethyl acrylate, ethylmethacrylate, isopropyl acrylate, butyl acrylate, amides and nitriles of 25 (meth)acrylic acid such as acrylamide, methacrylamide,

acrylonitrile, methacrylonitrile, butadiene, ethylene, di-vinylbenzene, maleic anhydride, etc. Preferred copolymerizable monomers are acrylonitrile and methylmethacrylate.

The vinylaromatic polymer or copolymer which is obtained has a molecular weight M_w ranging from 50,000 to 250,000, preferably from 70,000 to 200,000. In general, greater details on a process for the preparation of expandable vinylaromatic polymers in aqueous solution or, more generally, on polymerization in suspension, can be found in 10 Journal of Macromolecular Science, Review in Macromolecular Chemistry and Physics c31 (263) 215-299 (1991) or in international patent application WO 98/51734.

Conventional additives, generally used with commercial materials, such as pigments, stabilizers, flame-retardant 15 agents, antistatic agents, detaching agents, shock-resistant agents, etc., can be added to the expandable vinylaromatic polymers obtained with the process, object of the present invention. In particular, it is preferable to add mineral fillers of athermanous materials during the polymerization, such as graphite or refracting agents such as 20 titanium dioxide, in a quantity ranging from 0.05 to 25% by weight, calculated with respect to the resulting polymer.

At the end of the polymerization, substantially spherical polymer beads are obtained, with an average diameter ranging from 0.2 to 2 mm, inside which the expanding 25

agent is homogeneously dispersed.

To improve the stability of the suspension, it is possible to increase the viscosity of the reagent solution by dissolving the vinylaromatic polymer therein, in a concentration ranging from 1 to 30% by weight, preferably from 5 to 20%, calculated with respect to the monomer alone. The solution can be obtained either by dissolving a preformed polymer (for example fresh polymer or the waste products of previous polymerizations and/or expansions) in the reagent mixture or by pre-polymerizing the monomer, or mixture of monomers, in mass, in order to obtain the above concentrations, and then continuing the polymerization in aqueous suspension in the presence of the remaining additives.

At the end of the polymerization, the beads are discharged from the polymerization reactor, washed and dried.

The beads produced are subjected to pre-treatment generally applied to traditional materials and which essentially consists in:

1. coating the beads with a liquid antistatic agent such as amines, tertiary alkylamines, ethylene oxide-propylene oxide copolymers, etc. The purpose of this agent is to facilitate both the adhesion of the coating and also the screening of the beads prepared in suspension;
2. applying the coating to the above beads, said coating essentially consisting of a mixture of mono-, di- and

tri-esters of glycerin (or other alcohols) with fatty acids; and

3. distributing on the surface of the beads, the anti-lumping additive preferably selected from powders of oxides of iron (Fe_2O_3), copper (CuO) and zinc (ZnO), optionally mixed with the corresponding ester of fatty acids such as stearic acid, palmitic acid, myristic acid, etc. The anti-lumping additive is generally used in the form of powders with an average particle-size ranging from 0.1 to 50 μm .

10 Some illustrative but non-limiting examples are provided for a better understanding of the present invention and for its embodiment.

COMPARATIVE EXAMPLE 1

15 100 parts of styrene monomer, 0.30 parts of benzoyl peroxide, 0.15 parts of terbutylperbenzoate, 100 parts of demineralized water, 0.2 parts of tricalcium phosphate and 20 ppm of sodium dodecylbenzenesulfonate, were charged into a 2 litre reactor equipped with a stirrer.

20 The mixture was then heated to 90°C for 4 hours and to 125°C for a further 6 hours.

The expanding agent (7 parts of n-pentane) was added during the rise from 90 to 125°C.

25 At the end of the polymerization, the beads were centrifuged, washed with water and dried with air at room tem-

perature.

0.02% of diethanol alkyl amine was added to the beads of expandable polymer thus produced, which were then sieved, separating the fraction with a diameter ranging 5 from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of magnesium stearate were then added to the fraction.

The product is pre-expanded the following day with vapour at a temperature of 100°C at a density of 20 g/l, 10 evaluating the quantity of clots, which proved to be practically zero.

The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars. The adhesion of the beads 15 proved to be 5%.

COMPARATIVE EXAMPLE 2

The beads polymerized according to Comparative example 1 were lubricated with 0.02% of diethanol alkyl amine and sieved, separating the fraction with a diameter ranging 20 from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of zinc stearate were then added to the fraction.

The product is pre-expanded the following day with vapour at a temperature of 100°C at a density of 20 g/l, 25 evaluating the quantity of lumps, which proved to be equal

to 3%.

The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars. The adhesion of the beads 5 proved to be 40%.

COMPARATIVE EXAMPLE 3

The beads polymerized according to Comparative example 1 were lubricated with 0.02% of diethanol alkyl amine and sieved, separating the fraction with a diameter ranging 10 from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of silica Sipernat D 17 (diameter of 10 μm) of Degussa, were then added to the fraction.

The product is pre-expanded the following day with va- 15 pour at a temperature of 100°C at a density of 20 g/l, evaluating the quantity of lumps, which proved to be ab- sent.

The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars. The adhesion of the beads 20 proved to be 5%.

COMPARATIVE EXAMPLE 4

The beads polymerized according to Comparative example 1 were lubricated with 0.02% of diethanol alkyl amine and 25 sieved, separating the fraction with a diameter ranging

from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of alumina, with a diameter <10 µm, commercialized by Aldrich, were then added to the fraction.

5 The product is pre-expanded the following day with vapour at a temperature of 100°C at a density of 20 g/l, evaluating the quantity of lumps, which proved to be absent.

10 The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars. The adhesion of the beads proved to be 5%.

EXAMPLE 1

15 Comparative example 2 is repeated, reducing the zinc stearate to 0.05% and adding 0.05% of zinc oxide. There were no lumps and the adhesion was excellent, equal to 70%.

EXAMPLE 2

20 Comparative example 1 is repeated, substituting the magnesium stearate with 5 ppm of ferric oxide in powder form, produced by Aldrich, with an average particle diameter of about 1 µm. There were no lumps and the adhesion was excellent, equal to 80%.

EXAMPLE 3

25 Comparative example 1 is repeated, substituting the magnesium stearate with 5 ppm of copper oxide (CuO) in powder

der form, produced by Aldrich, with an average particle diameter < 5 μm . There were no lumps and the adhesion was excellent, equal to 70%.

5

10

15

20

25

CLAIMS

1. Beads of expandable vinylaromatic polymers which comprise:

5 a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of at least one copolymerizable monomer;

b) 1-10% by weight, calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix;

10 c) 2 ppm-2% by weight, calculated with respect to the polymer (a), of an anti-lumping additive, distributed on the surface of the beads, selected from oxides of metals of groups IB and VIIIB or from mixtures consisting of oxides of metals of groups IB, IIB and VIIIB and esters of C₈-C₂₅ fatty acids with the same metals.

15 2. The beads of expandable vinylaromatic polymers according to claim 1, having an average molecular weight Mw ranging from 50,000 to 250,000.

20 3. The beads of expandable vinylaromatic polymers according to claim 1 or 2, wherein the beads are substantially spherical with an average diameter ranging from 0.2 to 2 mm.

25 4. The beads of expandable vinylaromatic polymers according to any of the previous claim, wherein the beads comprise fillers of athermanous materials in quantity ranging

from 0.05 to 25% by weight.

5. A process for the preparation of beads of expandable vinylaromatic polymers which comprises:

- polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of at least one copolymerizable monomer;

- englobing an expanding agent in the polymeric matrix; and

- distributing on the surface of the beads obtained 2 ppm-10 2% by weight, calculated with respect to the polymer, of an anti-lumping additive selected from oxides of metals of groups IB and VIIIB or from mixtures consisting of oxides of metals of groups IB, IIB and VIIIB and esters of C₈-C₂₅ fatty acids with the same metals.

15 6. The process according to claim 5, wherein the polymerization is carried out in aqueous suspension or in continuous mass.

7. The process according to claim 5 or 6, wherein the polymerization is carried out in suspension in the presence 20 of a suspending agent, an initiating system and an expanding system.

8. The process according to claim 7, wherein the expanding system consists of liquid substances with a boiling point ranging from 10 to 100°C.

25 9. The process according to any of the previous claims

from 5 to 8, which comprises:

1. coating the beads with a liquid antistatic agent such as amines, tertiary alkylamines, ethylene oxide-propylene oxide copolymers;

5 2. applying the coating to the above beads, said coating essentially consisting of a mixture of mono-, di- and tri-esters of glycerin (or other alcohols) with fatty acids; and

3. distributing on the surface of the beads, the anti-lumping additive preferably selected from powders of oxides of iron (Fe_2O_3), copper (CuO) and zinc (ZnO), optionally mixed with the corresponding ester of fatty acids.

10. The process according to any of the claims from 5 to 15 9, wherein the anti-lumping additive is used in the form of powders with an average particle-size ranging from 0.1 to 50 μm .

20

25

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/07225A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/224

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 7 C08J

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 124 365 A (RAPPOLD KURT ET AL) 23 June 1992 (1992-06-23) column 2, lines 51-58 claims -----	1-10
A	DATABASE WPI Section Ch, Week 198449 Derwent Publications Ltd., London, GB; Class A31, AN 1984-304985 XP002224215 & JP 59 191744 A (TOYO KAGAKU KK) 30 October 1984 (1984-10-30) abstract -----	1-10
A	GB 1 409 285 A (SHELL INT RESEARCH) 8 October 1975 (1975-10-08) page 2, columns 20-40 claims -----	1-10
	-/-	

 Further documents are listed in the continuation of box C. Patent family members are listed in 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 document but published on or after the international filing date
- "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)
- "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

Date of mailing of the international search report

18 December 2003

02/01/2004

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Oudot, R

INTERNATIONAL SEARCH REPORTInternational Application No
PCT/EP 03/07225**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92/11298 A (ECOSTAR INT LP) 9 July 1992 (1992-07-09) claims -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/07225

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5124365	A	23-06-1992		DE 4009897 A1 AT 130334 T AU 7388891 A CA 2039287 A1 DE 59106879 D1 EP 0449065 A2 ES 2078983 T3 JP 4224835 A	02-10-1991 15-12-1995 03-10-1991 29-09-1991 21-12-1995 02-10-1991 01-01-1996 14-08-1992
JP 59191744	A	30-10-1984		NONE	
GB 1409285	A	08-10-1975		AU 475223 B2 AU 6329973 A BE 808164 A2 DE 2360901 A1 FR 2209790 A1 IT 1001198 B NL 7316694 A , B, SE 398239 B ZA 7309287 A	12-08-1976 12-06-1975 04-06-1974 12-06-1974 05-07-1974 20-04-1976 11-06-1974 12-12-1977 30-10-1974
WO 9211298	A	09-07-1992		CA 2098911 A1 EP 0563291 A1 JP 3184886 B2 JP 6504079 T WO 9211298 A1	22-06-1992 06-10-1993 09-07-2001 12-05-1994 09-07-1992