

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 December 2006 (07.12.2006)

PCT

(10) International Publication Number
WO 2006/128316 A1

(51) International Patent Classification:
A61L 9/12 (2006.01)

(21) International Application Number:
PCT/CH2006/000287

(22) International Filing Date: 31 May 2006 (31.05.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
05291191.4 2 June 2005 (02.06.2005) EP

(71) Applicant (for all designated States except US): GIVAUDAN SA [CH/CH]; Chemin de la Parfumerie 5, CH-1214 Vernier (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BLONDEAU, Philippe [FR/FR]; 6, place du Colonel Fabien, F-75019 Paris (FR). BRESSON, Alice [FR/FR]; 32, boulevard Charles de Gaulle, F-95110 Sannois (FR).

(74) Agent: MCSTEA, John, Anthony; Ueberlandstrasse 138, CH-8600 Duebendorf (CH).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

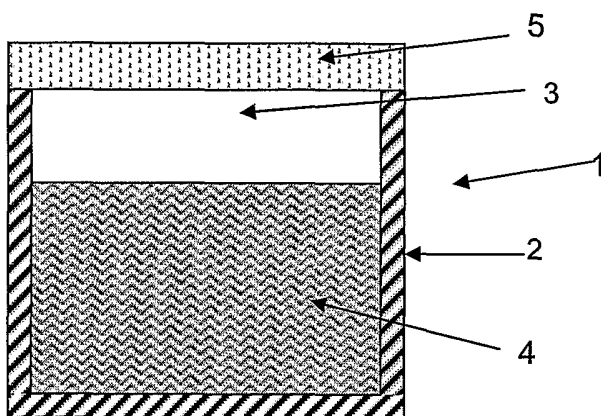
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, 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

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.

(54) Title: VOLATILE LIQUID DISPENSING APPARATUS



(57) Abstract: An apparatus (1) adapted to disseminate a volatile liquid (4), such as a fragrance, into an ambient atmosphere for a desired period of time, the apparatus comprising a reservoir (2) having a single opening (3) to the atmosphere, this opening being closed by a permeable membrane (5) not in contact with the liquid in the reservoir when the apparatus is in operation, the membrane having a thickness of from 0.1-5mm and being capable of absorbing a quantity of liquid that will evaporate over the desired period when the membrane is brought into direct contact with the liquid. The membrane may also act as an end-of-life indicator by changing colour as the liquid is disseminated. The apparatus is an easy-to-use, spill-proof device, with the ability to control the amount of liquid in an atmosphere and to prevent habituation to the liquid.

WO 2006/128316 A1

VOLATILE LIQUID DISPENSING APPARATUS

This invention relates to an apparatus for dispensing volatile substances, and more particularly to a membrane-based dispensing device for the delivery of volatile substances
5 from a liquid to an ambient environment by evaporation.

Membrane-based dispensing devices for the dispensing into an ambient environment of volatile liquids such as fragrances, bactericides, fungicides and disinfectants are well known in the art. One very common type of such dispensing devices consists essentially of
10 a reservoir containing the volatile liquid and a membrane covering the container and contacting the volatile liquid. Such dispensing devices employ diffusion phenomenon to provide the motive dispensing force. The liquid phase evaporates through the membrane to the ambient environment. Such a device may additionally comprise auxiliary dispensing means, such as heating elements and/or fans.

15

While such devices are undoubtedly successful and have been commercially successful, they have certain practical drawbacks. One is a phenomenon called "habituation", that is, with continuous emission, people simply get used to the odour and cease to notice it. Much of the fragrance is therefore wasted to a certain extent. This can be overcome, but means of
20 doing this have hitherto been both relatively complex and relatively expensive. For example, it is possible to provide programmable devices with automatically opening orifices and the like. Such expense and complexity is often not justified.

It has now been found that it is possible to provide a simple device that overcomes this
25 problem and allows the release of volatile liquid for a desired period, but without requiring complex means for achieving this. The invention therefore provides an apparatus adapted to disseminate a volatile liquid into an ambient atmosphere for a desired period of time, the apparatus comprising a reservoir having a single opening to the atmosphere, this opening being closed by a permeable membrane not in contact with the liquid in the reservoir when
30 the apparatus is in operation, the membrane having a thickness of from 0.1-5mm and being capable of absorbing a quantity of liquid that will evaporate over the desired period when the membrane is brought into direct contact with the liquid.

The invention additionally provides a method of disseminating a volatile liquid into an ambient atmosphere for a desired time, comprising the application of the liquid to one side of a porous membrane permanently not exposed to the atmosphere, the membrane having a thickness of from 0.1-5mm and being capable of absorbing sufficient liquid for evaporation
5 from a side of the membrane exposed to the atmosphere over the desired time period.

Provided that the reservoir has the desired single opening, it may have any suitable shape and be made from any suitable material. Naturally it must be resistant to the volatile liquid contained therein, i.e., not be chemically degraded, softened or swollen by it. Glass,
10 ceramics, metals and selected plastics may be used, any such selection being within the skill of the art.

The membrane closing the opening must not have contact with the liquid in the reservoir when the apparatus is in operation, that is, the two must be physically separate. It therefore
15 follows that the opening must be located in a place on the reservoir where such contact does not occur. Generally, it means that the opening is located at or near the top of the reservoir, when the device is sitting on a horizontal surface, but it can also be in a side of the vessel, provided that the opening has no direct contact with the liquid in the reservoir when the apparatus is operating.

20

The membrane may be any membrane that meets the following requirements:

- it must permit liquid to pass through from that side of the membrane exposed to the interior of the reservoir to that exposed to the atmosphere;
- it must be of such a constitution that, when brought into contact with the liquid, it
25 can absorb sufficient liquid for evaporation into the atmosphere for the desired time.

The second of these conditions dictates that the membrane must be of a reasonable thickness – very thin membranes of the type currently used in the art will allow the passage of the liquid, but they will not be able to retain sufficient liquid for evaporation for a
30 significant time. The thickness of the membrane will depend on the natures of the liquid and the membrane, but typical thicknesses range from 0.1-5mm (compared to the typical 50 μ M of the art). It is possible to use thicker membranes, but these become more impractical and more expensive to manufacture. In particular embodiments, the thickness

lies between 0.5 and 5mm, 0.2 and 3mm, 0.6 and 2mm and 0.6 and 1.0mm. The provision of a membrane that holds the desired quantity of a given liquid is well within the skill of the art.

5 Any material that fulfils these requirements may be used in this invention. One particular membrane material is a polymeric material, in particular a microporous, filled polymeric material. In one particular embodiment, the material is polyolefin. Such materials are commercially available as battery separators. A typical such material consists essentially of a homogeneous mixture of 8 to 100 vol. % polyolefin having a molecular weight (weight-
10 average) of at least 300,000, a standard load melt index of substantially 0 and a reduced viscosity of not less than 4.0, 1 to 92 vol. % filler and 1 to 40 vol. % plasticizer.

Typical suitable materials are described in detail in U.S. Pat. No. 3,351,495. The polyolefin described therein is an ultra-high molecular weight polyolefin, in particular, ultra-high
15 molecular weight polyethylene. It has an average weight-average molecular weight of at least 300,000, preferably at least 1,000,000, and in particular about 4 to 7×10^6 . The standard load melt index of the polyolefin is substantially 0, i.e. it is less than 0.1, and more particularly less than 0.01. The reduced viscosity of the polyolefin is not less than 4.0, and in other embodiments more than 10, and in particular more than 15.

20

Although polyethylene is the most utilised material, polyolefin mixtures can also be used. In particular, also suitable are polypropylene, polybutene, polystyrene, ethylene/propylene copolymers, ethylene/hexylene copolymers, ethylene/butene copolymers, propylene/butene copolymers, ethylene/propylene/butene copolymers and copolymers of ethylene or
25 propylene with an ethylenically unsaturated monocarboxylic acid, that is to say acrylic acid, methacrylic acid or mixtures thereof.

Suitable fillers and plasticizers are known to the art. In this context, reference is again made to U.S. Pat. No. 3,351,495. A particular filler is finely-divided silica (silicic acid). The
30 average particle size (diameter) of the filler is the range from 0.01 to about 20 μm , the surface area of the filler being in the range from 30 to 950 m^2/g , and particularly at least 100 m^2/g .

The material to be used according to the invention may comprise a plasticizer, particularly a water-insoluble oil, in particular process oil.

Particularly desirable ranges of amounts for the homogeneous mixture are 15 to 60, preferably 30 to 45, vol.% polyolefin, and 35 to 80, particularly 50 to 65, vol. % filler, and 1 to 10 vol. % plasticizer.

In addition to the constituents mentioned, the material to be used according to the invention can comprise art-recognised additives, such as antioxidants (usually 0.1 to 1%), lubricants (usually 0.1 to 1%), antistatics, pigments, dyestuffs, conductive carbon black, stabilizers, light stabilizers and the like.

A particular membrane is a high density polyolefin/finely-divided silica membrane.

In a further embodiment of the invention, the apparatus according to the invention comprises an end-of-life indicator. Such an embodiment is very useful, as it can inform when the device needs replacing, or when a charge of liquid on the membrane is exhausted. In this invention, this is achieved by a change in colour of the membrane, that is, a membrane charged with liquid is a different colour from a dry membrane. This can be achieved by any convenient means. For example, it may be achieved by the incorporation in the membrane of a material that interacts with the liquid to produce a colour change. The interacting material must naturally be chosen such that the colour change is reversible.

In one embodiment of the invention, the ability to change colour depending on the presence or absence of liquid is an inherent property of the membrane, so that it need not be modified to achieve this. This is a property of the preferred polyolefin/silica battery separator-type membranes hereinabove described, and another reason for their particular utility in the working of this invention. Thus, the invention further provides an apparatus as hereinabove described, in which the need for replenishment of the membrane is indicated by a change in colour of the membrane.

In operation, the liquid is brought into contact with the membrane for a time sufficient to charge it with liquid, and the two are then separated. This can be done, for example, by

simply inverting the apparatus and then turning it back again. For example, the membrane may be located near a flat top of the apparatus, such that the apparatus can stand upside-down. Alternatively, the apparatus may be mounted in a cradle or on pivots.

- 5 The invention is further described with reference to the accompanying drawing, which depicts a preferred embodiment.

Figure 1 is a schematic vertical cross-section through a preferred embodiment.

- 10 Figure 2 is a chart, showing the liquid release characteristics of the embodiment over a period of time.

The apparatus, generally indicated as 1 consists of a reservoir 2 that has the shape of a vessel with an opening 3 at one end. The reservoir contains a volatile liquid 4, in this case, a
15 fragrance. The open end of the reservoir is closed with a membrane 5. The membrane is a polyethylene/silica membrane of 1mm thickness (the actual membrane used is Membrane DS2 drying sweat system ex Daramic, Inc. The membrane 5 has a flat top, which allows the apparatus to be inverted and to sit stably on a horizontal surface.

- 20 In operation, the apparatus is inverted and kept in that position for 15 seconds. This allows the membrane to charge with liquid. This is evidenced by a change in colour of the membrane from opaque white to the colour of the liquid phase – the membrane also becomes slightly translucent. The apparatus is set the right way up and volatile liquid commences to emanate from the membrane. The end of life of the particular charge may be
25 observed by observing the colour of the membrane. When it returns to its original colour, it can again be inverted to recharge.

Figure 2 shows graphically the results of measurements taken over a time period of just over a day, using a fragrance. The strength figures depicted on the ordinate are assessments
30 of the strength of the fragrance taken at intervals by an experienced panel, as used in the fragrance industry. The strengths are 5 = very strong, 4 = strong, 3 = average, 2 = weak, 1 = very weak, 0 = odourless

The membrane is charged, as hereinabove described and allowed to discharge over a period of 7 hours, prior to recharging and reinverting. It can be seen in this particular embodiment that the emission of liquid falls to a low level over the seven hours, but the 15 seconds' charging returns the apparatus to the same level of performance as did the initial charging.

5 This result is repeated in the two subsequent chargings depicted on the graph.

The result is that the user does not become habituated to the fragrance, but perceives it as fresh and new. In addition, the user does not need to continue to utilise the fragrance in such a manner, but can leave the membrane fully discharged for as long as desired, and
10 then return the apparatus to full operating condition by simply inverting to charge the membrane.

The skilled person will perceive many possible variations of this invention, which lie within the scope of the invention.

Claims:

1. An apparatus (1) adapted to disseminate a volatile liquid (3) into an ambient atmosphere for a desired period of time, the apparatus comprising a reservoir (2) having a single opening to the atmosphere, this opening being closed by a permeable membrane (4) not in contact with the liquid in the reservoir when the apparatus is in operation, the membrane having a thickness of from 0.1-5mm and being capable of absorbing a quantity of liquid that will evaporate over the desired period when the membrane is brought into direct contact with the liquid.
2. An apparatus according to claim 1, in which the membrane thickness is from 0.5-5mm, preferably from 0.2-3mm, more preferably from 0.6-2mm and most preferably from 0.6-1.0mm.
3. An apparatus according to claim 1, in which the material of the membrane is selected from the group consisting of polyethylene, polypropylene, polybutene, polystyrene, ethylene/propylene copolymers, ethylene/hexylene copolymers, ethylene/butene copolymers, propylene/butene copolymers, ethylene/propylene/butene copolymers and copolymers of ethylene or propylene with an ethylenically unsaturated monocarboxylic acid; which material is preferably filled.
4. An apparatus according to claim 3, in which the membrane is microporous filled polyolefin.
5. An apparatus according to claim 4, in which the material of the membrane consists essentially of a homogeneous mixture of 8 to 100 vol. % polyolefin having a molecular weight (weight-average) of at least 300,000, a standard load melt index of less than 0.1 and a reduced viscosity of not less than 4.0, 1 to 92 vol. % filler and 1 to 40 vol. % plasticizer.

6. An apparatus according to claim 5, in which the polyolefin is an ultra-high molecular weight polyolefin, preferably an ultra-high molecular weight polyethylene.
- 5 7. An apparatus according to claim 5, in which the polyolefin has a molecular weight of at least 1,000,000, preferably from $4 - 7 \times 10^6$.
8. An apparatus according to claim 5, in which the standard load melt index is less than 0.01, and is preferably effectively 0.
- 10 9. An apparatus according to claim 5, in which the reduced viscosity of the polyolefin is more than 10, preferably more than 15.
10. An apparatus according to claim 3, in which the filler is finely divided silica (silicic acid) having an average particle size (diameter) in the range from 0.01 to about 20 . μ .m, the surface area of the filler being in the range from 30 to 950 m^2/g , and preferably at least 100 m^2/g .
- 15 11. An apparatus according to claim 4, in which the membrane comprises from 15 to 60, preferably 30 to 45, vol.% polyolefin, and 35 to 80, preferably 50 to 65, vol. % filler, and 1 to 10 vol. % plasticizer.
- 20 12. An apparatus according to claim 1, in which the membrane comprises an end-of-life indicator by means of colour change.
- 25 13. An apparatus according to claim 12, in which the material is a polyolefin/silica mixture and the end-of-life colour indication is an inherent property of the material.
- 14 A method of disseminating a volatile liquid into an ambient atmosphere for a
30 desired time, comprising the application of the liquid to one side of a porous membrane permanently not exposed to the atmosphere, the membrane having a thickness of from 0.1-5mm and being capable of absorbing sufficient liquid for

evaporation from a side of the membrane exposed to the atmosphere over the desired time period.

1/1

Fig.1

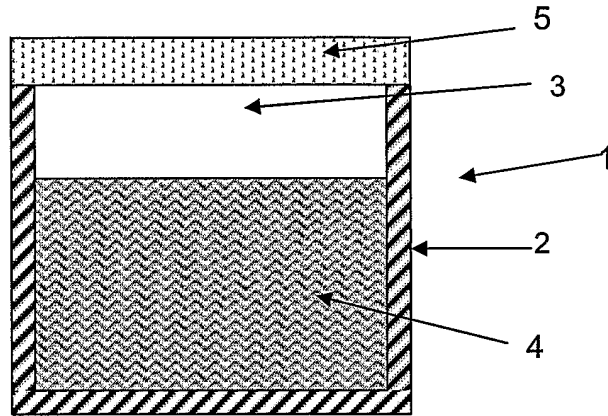
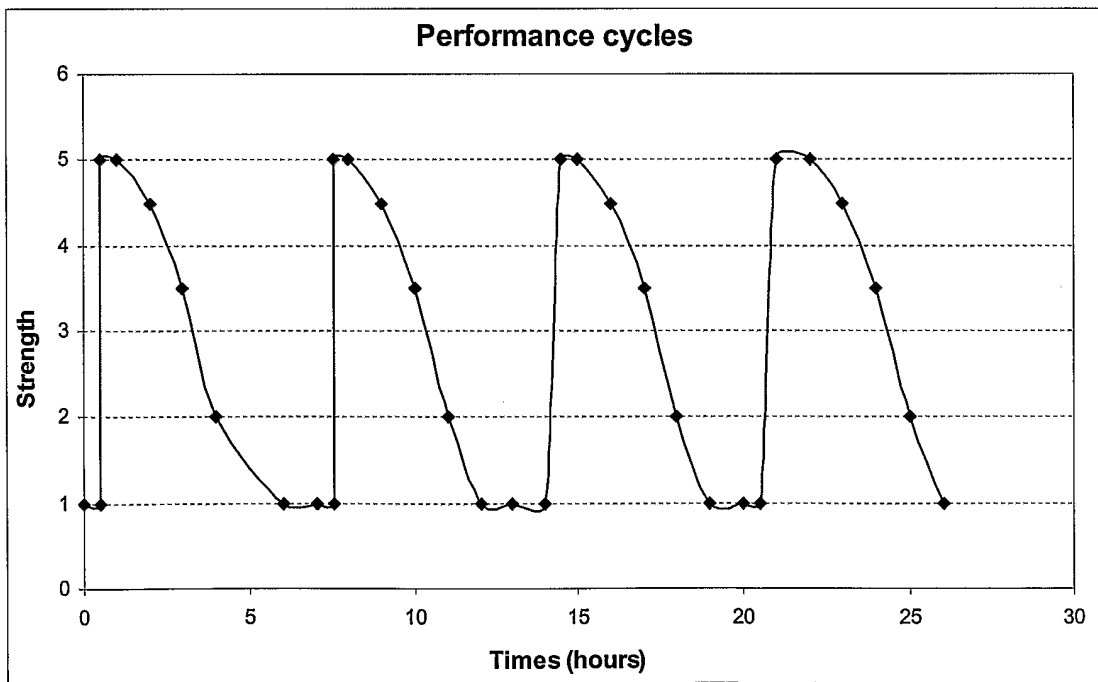


Fig.2



INTERNATIONAL SEARCH REPORT

International application No
PCT/CH2006/000287

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61L9/12

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)
A61L A01M

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*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/086490 A (INOVAIR LIMITED; MAAT, HUIB) 23 October 2003 (2003-10-23) page 2, line 18 - page 4, line 12 page 5, lines 19-25; figure 2 -----	1-14
X	US 4 889 286 A (SPECTOR ET AL) 26 December 1989 (1989-12-26) column 1, line 64 - column 2, line 30 column 2, line 50 - column 4, line 31; figures -----	1-14
X	US 5 716 000 A (FOX ET AL) 10 February 1998 (1998-02-10) column 2, lines 20-58 column 3, line 63 - column 4, line 14 column 4, line 40 - column 5, line 30; figures 1,2 -----	1-4, 14
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier 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

31 August 2006

Date of mailing of the international search report

08/09/2006

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

Maremonti, M

INTERNATIONAL SEARCH REPORT

International application No

PCT/CH2006/000287

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 459 766 A (FIRMENICH SA) 16 January 1981 (1981-01-16) page 4, line 14 - page 5, line 37 -----	1-4, 12-14
X	DE 198 12 022 A1 (CLIMAROTEC GESELLSCHAFT FUER RAUMKLIMATISCHE SPEZIALANLAGEN) 30 September 1999 (1999-09-30) column 2, line 26 - column 3, line 44 column 4, line 14 - column 5, line 29 column 6, lines 38-52; figures -----	1,2,14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/CH2006/000287

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
WO 03086490	A	23-10-2003	AU 2003232307 A1 EP 1499365 A1 US 2005199742 A1	27-10-2003 26-01-2005 15-09-2005
<hr/>				
US 4889286	A	26-12-1989	NONE	
<hr/>				
US 5716000	A	10-02-1998	AU 670451 B2 AU 4727093 A BR 9307089 A CA 2145188 A1 DE 69302693 D1 DE 69302693 T2 EP 0662845 A1 ES 2086957 T3 FI 951331 A WO 9406480 A1 HK 1007964 A1 JP 8505066 T MX 9305808 A1 NZ 254954 A ZA 9305920 A	18-07-1996 12-04-1994 30-03-1999 31-03-1994 20-06-1996 26-09-1996 19-07-1995 01-07-1996 21-03-1995 31-03-1994 30-04-1999 04-06-1996 31-03-1994 27-02-1996 13-10-1995
<hr/>				
FR 2459766	A	16-01-1981	CH 647413 A5 CH 639282 A5 WO 8100051 A1 GB 2066665 A IT 1209230 B JP 56500953 T NL 8020178 A	31-01-1985 15-11-1983 22-01-1981 15-07-1981 16-07-1989 16-07-1981 29-04-1981
<hr/>				
DE 19812022	A1	30-09-1999	NONE	
<hr/>				