

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 June 2002 (06.06.2002)

PCT

(10) International Publication Number
WO 02/44272 A1

- (51) International Patent Classification⁷: C08L 53/00, 23/10
- (74) Agent: VA TECH PATENTE GMBH & CO.; Stahlstrasse 21a, A-4031 Linz (AT).
- (21) International Application Number: PCT/EP01/13717
- (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, 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.
- (22) International Filing Date:
26 November 2001 (26.11.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
00126051.2 29 November 2000 (29.11.2000) EP
- (71) Applicant (*for all designated States except US*): BORE-ALIS GMBH [AT/AT]; Danubiastrasse 21-25, A-2323 Schwechat-Mannswörth (AT).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): HÄRKÖNEN, Mika [FI/NO]; Hegglia 18, N-3930 Porsgrunn (NO). WOLFSCHWENGER, Johannes [AT/AT]; Weichstetten 98, A-4491 Niederneukirchen (AT).
- (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, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (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.*



WO 02/44272 A1

(54) Title: POLYOLEFIN COMPOSITIONS WITH IMPROVED PROPERTIES

(57) Abstract: The invention relates to polyolefin compositions with good impact strength and transparency comprising a) 85-98 wt% based on the total weight of the composition of a heterophasic propylene/ α -olefin copolymer comprising a polymer or copolymer of propylene and an α -olefin with 0-15 mol% of the α -olefin as matrix polymer and a propylene/ α -olefin rubber copolymer comprising 20-80 mol% of the α -olefin and b) 15-2 wt% based on the total weight of the composition of an ethylene homopolymer or an ethylene/ α -olefin copolymer, the α -olefin in the ethylene copolymer having 4-10 carbon atoms, the ethylene homo- or copolymer having a density lower than 0,925 g/m³. processes for producing these compositions and their use. The compositions are particularly useful for food packaging, especially for deep freezing applications.

Polyolefin compositions with improved properties

The invention relates to polyolefin compositions with improved impact strength and improved optical properties. More particularly the invention relates to polyolefin compositions, especially polypropylene compositions with improved impact strength at temperatures below room temperature, especially at temperatures below 0°C, having improved optical properties, especially higher transparency and lower haze.

The compositions of the inventions are particularly useful for packaging applications, especially for food packaging for deep freezing application.

Background of the invention

Polypropylene homopolymers are widely used in packaging applications. Polypropylene homopolymers show balanced properties and are cheap, easily decomposable polymers, but they show poor transparency and low impact strength.

It has been suggested to improve the poor optical properties and the impact strength of polypropylene homopolymers by adding nucleating agents and/or clarifiers. Suitable nucleating agents are for example talcum, disorbitol, organic phosphates and the like.

Nevertheless the desired properties of propylene homopolymers cannot be improved to the extent desired, namely to show high impact strength at low temperatures.

Compositions with improved impact strength and improved optical properties are for example propylene/ α -olefin random copolymers, wherein the α -olefin is ethylene or an α -olefin with 4 - 10 carbon atoms. Although transparency is higher and impact strength is improved considerably at ambient temperature, impact strength at lower temperature, i.e. 0°C and below is still not satisfying. Propylene/ α -olefin random copolymers have a ductile to brittle transition temperature between -5°C and 5°C depending on the monomer content and therefore impact strength at lower temperatures is still very poor.

To improve the impact strength at lower temperatures heterophasic polymer compositions have been suggested. Heterophasic polymers are polymers having a matrix phase (phase 1) and a second phase. The matrix phase is usually a polypropylene homopolymer or polypropylene/ α -olefin copolymer phase and the second phase is usually a propylene/ α -olefin rubber polymer.

The polymers of the second phase have low glass transition temperatures, usually below -30°C . Therefore impact strength of such heterophasic systems is rather satisfying, even for deep freezing applications. A major drawback is the poor transparency due mostly due to big rubber particles in the heterophasic system.

Several attempts have been made to improve the transparency of heterophasic polymer systems.

EP-B 0 373 660 discloses heterophasic polymer systems with improved impact strength and improved transparency an elastomeric propylene/ethylene as matrix phase and a phase 2 being propylene/ α -olefin rubber, wherein the intrinsic viscosity ratio between phase 1 and phase 2 has to be a defined value, namely 0.2. Therefore the heterophasic system of the disclosure of EP B 0 373 660 is restricted to very special combinations of phase 1 and 2 polymers.

EP-A 0 814 127 discloses embrittlement resistant polyolefin compositions and flexible articles thereof based on propylene homopolymers or propylene/ α -olefin copolymers and elastomeric copolymers of ethylene with propylene or butene-1. The elastomeric copolymers enhance the flexibility without affecting the clarity of the polymer composition, which is not at least satisfying for packaging applications, although these compositions are claimed to be used for the production of medical articles and food packaging material.

EP B 0 593 221 discloses polypropylene resin compositions comprising polypropylenes of defined MFR and ethylene/ α -olefin copolymers with good balance between impact strength and rigidity and high moldability useful for

automotive parts. These compositions do not have good optical properties, especially low transparency and high haze.

Object of the invention

It is an object of the invention to provide polypropylene compositions for packaging applications with improved impact strength at ambient and low temperatures having improved optical properties, especially good transparency and low haze.

A further object of the invention is a process for producing polypropylene compositions for packaging applications with improved impact strength at low temperatures and good optical properties.

It is still a further object of the invention to provide articles made of these polypropylene compositions useful for packaging applications, especially for food packaging for deep freezing applications.

Brief description of the invention

The object of the invention has been solved by providing heterophasic polymer systems which are modified by a modifier which shows improved impact strength as well as improved optical properties.

The invention therefore relates to polyolefin compositions with good impact strength and transparency comprising

- a) 85 – 98 wt% based on the total weight of the composition of a heterophasic propylene/ α -olefin copolymer comprising a polymer or copolymer of propylene and an α -olefin with 0-15 mol% of the α -olefin as matrix polymer and a propylene/ α -olefin rubber copolymer comprising 20 –80 mol% of the α -olefin
- b) 15 – 2 wt% based on the total weight of the composition of an ethylene homopolymer or an ethylene/ α -olefin copolymer, the α -olefin in the ethylene copolymer having 4 – 10 carbon atoms, the ethylene homo-or copolymer having a density lower than 0,925 g/m³.

Detailed description of the invention

Component a) is preferably a heterophasic propylene/ α -olefin copolymer comprising a polymer or a copolymer of propylene with 0 - 15 mol% of an α -olefin as matrix polymer (phase 1 polymer) and a propylene/ α -olefin rubber copolymer comprising 20 – 80 mol% of the α -olefin.

Preferably the molecular weight of the propylene/ α -olefin rubber is equal or lower than the molecular weight of the propylene homopolymer resp. the polypropylene/ α -olefin copolymer.

The heterophasic polymer of component a) may be produced by multistage process polymerisation of polypropylene or polypropylene and α -olefin such as bulk polymerisation, gas phase polymerisation, slurry polymerisation, solution polymerisation or combinations thereof using conventional catalysts. Those processes are well known to one skilled in the art.

A preferred process is a combination of a bulk slurry loop reactor(s) and gas phase reactor(s). The matrix polymer can be made either in loop reactors or in a combination of loop and gas phase reactor.

The polymer produced in this way is transferred into another reactor and the propylene/ α -olefin rubber is polymerised. Preferably this polymerisation step is done in a gas phase polymerisation.

A suitable catalyst for the polymerisation of the heterophasic copolymer is any stereospecific catalyst for propylene polymerisation which is capable of polymerising and copolymerising propylene and comonomers at a temperature of 40 to 110°C and at a pressure from 10 to 100 bar. Ziegler Natta catalysts as well as metallocene catalysts are suitable catalysts.

One skilled in the art is aware of the various possibilities to produce such heterophasic systems and will simply find out a suitable procedure to produce suitable heterophasic polymer systems which are used in the present invention.

The matrix polymers of the heterophasic polymers of component a) may have a ratio of matrix polymer (polymer of phase 1) to polymer of phase 2 of about 97 : 3 to 80 : 20, preferably 95 : 5 to 90 : 10.

The heterophasic polymer shows a melt flow rate of about 0.1 to 200g/10 min, preferably 0,2 to 50g/10 min, more preferable 0.3 to 20 g/10 min according to ISO 1133. The ethylene content of the matrix polymer may be up to 7 mol% and the overall ethylene content of the heterophasic polymer of component a) may be up to 30 mol%, preferably up to 15 mol %.

The polymer of component a) preferably has a flexural modulus of higher than 500 MPa (DIN 53457).

Component b) is an ethylene homopolymer or an ethylene/ α -olefin copolymer the α -olefin having 4 – 10 carbon atoms.

For example component b) may be a low density ethylene homopolymer or a copolymer of ethylene with for example vinylacetate or butylacrylate or the like. The amount of component b) is 2 – 15 wt% based on the total weight of the composition, preferably 3 – 10 wt%, most preferably 4 – 7 wt%.

Preferably the density of the low density ethylene homo- or copolymer (component b)) is lower than 0.925g/cm³ according to ISO 1183. More preferably the density of the low density ethylene homo- or copolymer is lower than 0.920g/cm³. Most preferably the density is 0.890 – 0,920 g/cm³.

Preferably the ethylene-homo- or copolymer (component b)) should have a substantially higher melt flow rate (MFR) (temperature: 190 °C; load: 2.16 kg) than the heterophasic polymer of component a) under melting and blending conditions. Preferably the melt flow rate of component b) is at least two times, more preferably at least five times higher than the melt flow rate of component a). MFR's of component b) are determined at a temperature of 190 °C and a load of 2.16 kg. MFR's of component a) are determined at a temperature of 230 °C and a load of 2.16 kg.

Those ethylene homo- or copolymers may be produced in a high pressure tubular process or in a high pressure autoclave process.

Alternatively, a linear low density type ethylene copolymer may be produced in a low pressure process typically with a Ziegler type catalyst. Further the polymers of component b) may be produced using a metallocene catalyst. The polymers of component b) produced by using metallocene catalysts are typically elastic copolymers of ethylene and butene or octane having a density of preferably 0.890 - 0,915g/cm³.

The compositions of the present invention may further comprise conventional additives, such as antioxidants, stabilisers, acid scavengers, clarifying agents, coloring agents, anti-UV agents, nucleating agents, antistatic agents, slip/mould release agents, fillers, like nanofillers, etc. Typically these additives may be present at less than 2 wt% each, more preferably less than 0.5 wt% relative to the total weight of the composition.

Examples of such conventional additives include Irganox 1010 and Irgafos 168 (commercially available stabilizers from Ciba Speciality Chemicals), calcium stearate and synthetic hydrotalcite (e.g. DHT-4A from Kyowa Chemical Industry) and 1,2:3,4-di(ethylbenzylidene)sorbitol - EBDS (e.g. NC-4 from Mitsui Toatsu and 1,3:2,4 bis(3,4-dimethylbenzylidene)sorbitol -DMBDS (e.g. Millad 3988 from Milliken Chemicals).

The polypropylene composition of the present invention is preferably clarified. Clarified polypropylenes can be produced for example by adding clarifying or nucleating agents, for examples sorbitol derivatives such as EBDS, MDBS (1,3:2,7-di(methylbenzylidene)sorbitol and DMDBS, phosphate salts, such as for example sodium 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate, polyvinylcyclohexane etc. Typically such clarifying or nucleating agents may result in haze levels after injection moulding of lower than 60%, preferably lower than 40% in 2 mm injection moulding sheets.

The polyolefin compositions of the present invention are produced by mixing the heterophasic polymer of component a) with component b) optionally adding conventional additives and/or stabilisers and/or fillers.

Preferably, mixing is done by melt blending in an extruder or another melt blending unit, preferably in a twin screw extruder usually followed by pelletisation. The components may be melt blended as such, or melt blending can be done in the presence of a peroxide component for increasing the melt flow rate of the composition. Then the peroxide, preferably an organic peroxide, which is suitable for degradation of polypropylene (visbreaking) is fed to the blending unit together with components a) and b) or the peroxide may be fed separately into the melt blending unit.

The compositions of the present invention show improved impact strength, especially at temperatures below 0°C and improved optical properties, especially high transparency and low haze.

The polypropylene composition of this invention can be further converted to an end product by using normal conversion techniques, such as injection moulding, compression moulding, blow moulding (extrusion or injection stretch blow moulding), extrusion (film, sheet, pipe, tuber, profile extrusion), film blowing, thermoforming and the like. Preferably end products are packaging containers made by injection moulding, blow moulding or thermoforming, or packaging films made by film extrusion.

The products are particularly suitable for food packaging applications, especially for deep freezing applications.

It is a still further object of the invention to provide new articles with good impact strength and good optical properties, especially good transparency and low haze.

This object is achieved by using a polyolefin composition comprising

- a) 85 – 98 wt% based on the total weight of the composition of a heterophasic propylene/ α -olefin copolymer comprising a polymer or copolymer of

propylene and an α -olefin with 0-15 mol% of the α -olefin as matrix polymer and a propylene/ α -olefin rubber copolymer comprising 20 –80 mol% of the α -olefin and

- b) 15 – 2 wt% based on the total weight of the composition of an ethylene homopolymer or an ethylene/ α -olefin copolymer, the α -olefin in the ethylene copolymer having 4 – 10 carbon atoms, the ethylene homo-or copolymer having a density lower than 0,925 g/m³,

for the production of articles with good impact strength good transparency.

Examples:

Heterophasic polymers:

The heterophasic polymers were produced in a two step process. In the first stage a random propylene/ethylene copolymer was polymerised (polymerisation in liquid propylene) and in the second stage a propylene/ethylene rubber was polymerised. The ratio between the propylene/ethylene random copolymer and the propylene/ethylene rubber was 92:8.

For visbreaking from the basic melt flow rate to a melt flow rate of about 10 – 15 g/10min Di-tertiary-butylperoxide was used.

The compositions and the additives were compounded in a twin screw extruder at a temperature of 250°C. The strands were quenched in cold water and pelletized.

The characteristics of the heterophasic polymers are given in table 1.

Table 1

	MFR2	XCS	C2	MFR2	XCS	C2	i..V.	C3/XCS
	matrix	matrix	matrix	total	total	total	XCS	
polymer	[g/10']	[wt%]	[mol%]	[g/10']	[wt%]	[mol%]	[ml/g]	[wt%]
polymer 1	1.09	7.2	5.6	1.22	12.2	8.5	1.38	66.0
polymer 2	1.13	6.7	6.3	1.27	12.0	9.8	1.65	65.0
polymer 3	1.13	6.7	6.3	1.19	12.1	9.2	1.59	66.0
polymer 4	1.05	6.6	6.0	1.12	13.3	8.4	1.70	68.5

MFR2 matrix: melt flow rate acc. ISO 1133 of phase (1)

XCS matrix: xylene cold soluble fraction of phase (1)

C2 matrix: ethylene content (randomly incorporated) of phase (1)

MFR2 total: melt flow rate acc. ISO 1133 of the heterophasic system
(phase 1+2)

XCS total: xylene cold soluble fraction of the heterophasic system (phase 1+2)

- C2 total: total ethylene content of the heterophasic system (phase 1+2)
i.V./XCS: intrinsic viscosity of xylene cold soluble fraction (indication of the molecular weight of the propylene/ethylene rubber – phase 2)
C3/XCS: propylene content of xylene cold soluble fraction

The polymers were mixed with conventional additives (0.05% Irgafos 168, 0.05% Irganox 1010, 0.1 Ca-stearate, 0.06% Glycerol monostearate, 0.18 % Millad 3988) in an intensive mixer (Henschel mixer) for 20 seconds.

Examples 1 – 4:

Polymers 1 – 4 of table 1 (component a) were mixed with 5% Exact 2M048, a commercial metallocene catalyst based polyethylene grade of MFR(190°C, 2.16 kg) 10 g/10min, density 902 g/cm³; DexPlastomers (component b)) was added.

For visbreaking from the basic melt flow rate to a melt flow rate of about 10 – 15 g/10min Di-tertiary-butylperoxide was used.

The compositions and the additives were compounded in a twin screw extruder at a temperature of 250°C. The strands were quenched in cold water and pelletized. Injection molded test bars were produced and the notched impact strength according to ISO 179 was measured.

For determining optical properties, especially transparency and haze injection molded plaques (60*60*2mm) were produced. The optical properties were measured according to ASTM D-1003-92.

Comparative examples 1- 4:

Heterophasic polymers of table 1 were used as comparative compounds.

Impact strength and optical properties were determined as described.

The results are given in table 2.

Table 2

			MFR	NIS/+23°C	IS/-20°C	haze
example	polymer	modifier	[g/10']	179 1eA/+23°C	179 1eU/- 20°C	[%]
				[kJ/m ²]	[kJ/m ²]	
example 1	polymer 1	5% Exact 2M048	12.7	11.6	77.5	28.0
example 2	polymer 2	5% Exact 2M048	12.4	13.2	131.7	39.4
example 3	polymer 3	5% Exact 2M048	12.5	11.8	125.9	38.5
example 4	polymer 4	5% Exact 2M048	12.0	11.1	130.3	43.5
comp. Example 1	polymer 1		13.8	9.4	62.9	36.0
comp. Example 2	polymer 2		13.6	10.5	88.9	54.0
comp. Example 3	polymer 3		13.4	9.3	75.8	53.6
comp. Example 4	polymer 4		13.0	8.8	70.4	60.6

Examples 5 – 6:

Selected heterophasic polymers of table 1 (component a) were mixed with 5% Borealis CA9150 (commercial available LDPE grade of MFR(190°C, 2.16 kg) 15 g/10min, density 915 g/cm³, (component b)).

Comparative example 5 and 6 were prepared without adding component b).

The compositions were treated as described above, impact strength and optical properties were determined as described above.

The results are given in table 3.

Table 3

			MFR	NIS/+23°C	IS/-20°C	Haze
example	polymer	modifier	[g/10']	179 1eA/+23°C	179 1eU/- 20°C	[%]
				[kJ/m ²]	[kJ/m ²]	
example 5	polymer 2	5% Borealis CA 9150	13.5	10.5	108.3	40.8
example 6	polymer 4	5% Borealis CA 9150	12.5	10.0	115.8	44.2

Claims:

- 1) Polyolefin compositions with good impact strength and transparency comprising
 - a) 85 – 98 wt% based on the total weight of the composition of a heterophasic propylene/ α -olefin copolymer comprising a polymer or copolymer of propylene and an α -olefin with 0-15 mol% of the α -olefin as matrix polymer and a propylene/ α -olefin rubber copolymer comprising 20 – 80 mol% of the α -olefin and
 - b) 15 – 2 wt% based on the total weight of the composition of an ethylene homopolymer or an ethylene/ α -olefin copolymer, the α -olefin in the ethylene copolymer having 4 – 10 carbon atoms, the ethylene homo-or copolymer having a density lower than 0,925 g/m³.
- 2) Polyolefin compositions according to claim 1, comprising
 - a) 90 – 97 wt% of a heterophasic propylene/ α -olefin copolymer and
 - b) 10 – 3 wt% of an ethylene homopolymer or an ethylene/ α -olefin copolymer.
- 3) Polyolefin compositions according to one of claims 1 to 2, wherein the matrix polymer of the heterophasic polypropylene/ α -olefin copolymer is a propylene/ethylene copolymer and the phase 2 polymer is a propylene/ethylene rubber.
- 4) Polyolefin compositions according to one of the claims 1 to 3 wherein the ratio of the matrix polymer to phase 2 polymer is about 97:3 to 80:20.
- 5) Polyolefin compositions according to one of the claims 1 to 4 wherein component b) is selected from the group of low density ethylene homopolymers and metallocene based ethylene/ α -olefin copolymers.
- 6) Polyolefin compositions according to one of the claims 1 to 5, wherein the ethylene content of the polyolefin composition is up to 15 mol%.

- 7) Polyolefin compositions according to one of the claims 1 to 6, wherein the melt flow rate of the polymer composition is 0.1 – 200 g/min, preferably 0.2 – 50 g/10 min, most preferably 0.5-20 g/min.
- 8) Polyolefin compositions according to one of the claims 1 to 7, wherein the melt flow rate (190 °C, 2.16 kg) of component b) is higher, preferably at least two times and more preferably at least 5 times higher than the melt flow rate (230 °C, 2.16 kg) of component a) under melting and blending conditions.
- 9) Polyolefin compositions according to one of the claims 1 to 8 further comprising conventional additives and/or stabiliser and/or fillers.
- 10) Process for producing polyolefin compositions according to one of the claims 1 to 9, wherein the heterophasic polymer of component a) is produced in a multi stage process and mixed with the ethylene homopolymer or the ethylene/ α -olefin copolymer.
- 11) Process according to claim 10, wherein components a) and b) are mixed by melt blending in the presence or in the absence of peroxides.
- 12) Use of the polymer compositions of one of the claims 1 to 9 for producing products for packaging applications by injection moulding, compression moulding, blow moulding, extrusion (film-, sheet-, pipe-, tube-, profile extrusion), film blowing, and thermoforming.
- 13) Use of a polyolefin composition comprising
 - a) 85 – 98 wt% based on the total weight of the composition of a heterophasic propylene/ α -olefin copolymer comprising a polymer or copolymer of propylene and an α -olefin with 0-15 mol% of the α -olefin as matrix polymer and a propylene/ α -olefin rubber copolymer comprising 20 –80 mol% of the α -olefin and

b) 15 – 2 wt% based on the total weight of the composition of an ethylene homopolymer or an ethylene/ α -olefin copolymer, the α -olefin in the ethylene copolymer having 4 – 10 carbon atoms, the ethylene homo-or copolymer having a density lower than 0,925 g/m³,
for the production of articles with good impact strength good transparency.

INTERNATIONAL SEARCH REPORT

Int'l Patent Application No

PCT/EP 01/13717

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L53/00 C08L23/10

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 C08L

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	EP 0 593 221 A (MITSUBISHI PETROCHEMICAL CO) 20 April 1994 (1994-04-20) cited in the application example 19 ---	1-13
X	EP 0 714 923 A (SHOWA DENKO KK) 5 June 1996 (1996-06-05) page 4, line 13; example 14 ---	1-13
X	EP 0 844 281 A (JAPAN POLYCHEM CORP) 27 May 1998 (1998-05-27) page 7, line 29; example 3 ---	1-13
X	US 5 331 047 A (GIACOBBE JAMES) 19 July 1994 (1994-07-19) page 3, line 31; example 4 -----	1-3, 5, 7-13

 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

4 March 2002

Date of mailing of the international search report

14/03/2002

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

Schmidt, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/13717

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0593221	A	20-04-1994	DE 69320135 D1	10-09-1998
			DE 69320135 T2	10-12-1998
			EP 0593221 A2	20-04-1994
			JP 3234070 B2	04-12-2001
			JP 6192500 A	12-07-1994
			US 5391618 A	21-02-1995
			US 5391618 A	21-02-1995
EP 0714923	A	05-06-1996	AU 705455 B2	20-05-1999
			AU 3790395 A	30-05-1996
			CA 2162946 A1	22-05-1996
			CN 1128767 A	14-08-1996
			DE 69517771 D1	10-08-2000
			DE 69517771 T2	23-11-2000
			EP 0714923 A1	05-06-1996
			JP 3002119 B2	24-01-2000
			JP 8198922 A	06-08-1996
			US 5703172 A	30-12-1997
			US 5804665 A	08-09-1998
			JP 3034452 B2	17-04-2000
			JP 8198923 A	06-08-1996
			EP 0844281	A
EP 0844281 A1	27-05-1998			
US 6015857 A	18-01-2000			
US 5331047	A	19-07-1994	AT 156169 T	15-08-1997
			AU 667764 B2	04-04-1996
			AU 5520694 A	25-08-1994
			CA 2115534 A1	18-08-1994
			CN 1097432 A ,B	18-01-1995
			DE 69404495 D1	04-09-1997
			DE 69404495 T2	29-01-1998
			EP 0611801 A1	24-08-1994
			FI 940752 A	18-08-1994
			JP 7026084 A	27-01-1995
			MX 9401189 A1	31-08-1994
			NO 940552 A	18-08-1994
			RU 2124535 C1	10-01-1999
			US 5453318 A	26-09-1995