PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) **International Patent Classification** ^{6} :
C08G 63/185, 63/189, B29C 49/08, B65D 1/02

A1

(11) **International Publication Number:** **WO 99/05197**

(43) **International Publication Date:** 4 February 1999 (04.02.99)

(21) **International Application Number:** PCT/US98/15467

(22) **International Filing Date:** 24 July 1998 (24.07.98)

(30) **Priority Data:**

60/053,717	25 July 1997 (25.07.97)	US
09/106,294	29 June 1998 (29.06.98)	US

(71) **Applicant:** EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).

(72) **Inventor:** SPRAYBERRY, Harold, Blake; 252 Ascot Drive, Kingsport, TN 37663 (US).

(74) **Agent:** HARDING, Karen, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).

(81) **Designated States:** BR, CA, CN, JP, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) **Title:** LARGE POLYESTER CONTAINERS AND METHOD FOR MAKING SAME

(57) **Abstract**

The present application relates to a large molded polyester container weighing greater than about 200, and preferably between about 200 and about 800 grams. Specifically, the present application relates to polyester containers having a volume of several gallons. In one embodiment the container is a bottle formed from a diacid component comprising up to about 96.5 mol % therephthalic acid or naphtalene dicarboxylic acid and a glycol component, wherein said polyester possesses an IV of about 0.75 to about 0.85.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

LARGE POLYESTER CONTAINERS AND METHOD FOR MAKING SAME

Cross References to Related Applications

This application claims the benefit of United States Provisional Application Serial No. 60\053,717 filed July 25, 1997.

Field of the Invention

The present invention relates to polyester compositions suitable for making large (1-10 gallon) stretch blow molded containers. A process for making large containers is also disclosed.

Background of the Invention

Standard PET bottle polymer typically has an intrinsic viscosity, or IV in the range of 0.76 to 0.84 dl/g. Copolymer modification (acid or glycol) has been used to decrease the crystallization rate and widen the injection molding processing window. Standard PET bottle polymers with copolymer modification typically have between 0% and 6% IPA modification, or 0% and 3% CHDM modification in order to reduce the crystallization rate and allow the production of clear preforms weighing up to 100 grams.

Processing equipment and technology have been developed to produce stretch blow molded bottles weighing up to 800 grams specifically for the bulk delivered bottled water market. The use of stretch blow molding technology provides advantages in production output and bottle thread finish quality. However, this equipment has been limited to the use of amorphous resins, such as polycarbonate, in order to maintain the desired clarity in the preforms and bottles.

The use of a crystallizable polyester, such as PET, in a stretch blow molded application can give important advantages when compared to the use of an amorphous polymer. Specifically, the crystallizable polyester can be oriented, or mechanically stretched to give dramatically improved mechanical properties and crack resistance at reduced bottle weight. Using standard PET bottle polymer formulations in these large containers, however, results in the either the formation of crystalline haze in the thicker areas of the bottle, or a very narrow processing window during the production of the preforms and bottles.

Description of the Invention

The present invention relates to large stretch blow molded polyester containers, generally weighing between about 200 and about 800 grams. The containers of the present invention are generally capable of holding several gallons, specifically from about one to about 10 gallons, and preferably from greater than about two gallons to about 10 gallons. Specifically containers of the present invention are formed from polyesters formed from a diacid component comprising up to about 96.5 mol % terephthalic acid or naphthalene dicarboxylic acid and a glycol component, wherein said polyester possesses an IV of about 0.75 to about 0.85. The disclosed polyesters have improved crystallization and stretching characteristics.

The compositions of the present invention generally possess an IV of about 0.75 to about 0.85 and copolymer modification of about about 3.5 mol % up to about 20 mol %. More specifically, the compositions of the present invention comprise copolymer modifications of about 4 mol % to about 10 mol % CHDM; about 6 mol % to about 17 mol % IPA and mixtures thereof (higher than that of standard PET bottle polymer). The net effect was a PET bottle polymer with significantly reduced crystallization rate, increased stretch ratios, and otherwise acceptable processing performance. It should be understood that the desired crystallization and stretching characteristics can be obtained using any combination of IV and modification, such as higher IV and lower copolymer modification or lower IV and higher copolymer modification.

Polyesters with optimized crystallization and stretching characteristics have been shown to possess the processing characteristics necessary to make 5 gallon, stretch blow molded PET bottles with excellent physical properties and acceptable bottle appearance (clarity). The decreased crystallization rate results in the ability to injection mold clear thick-walled preforms at the desired processing conditions. The higher stretch ratios result in enough orientation to give the bottles excellent physical properties , even at the lower blow molding temperatures necessary for avoiding the formation of crystalline haze during the blow molding process for large, greater than about 200, preferably greater than about 600 gram containers.

Any polyester composition which is suitable for making a bottle may be utilized so long as the appropriate amount of copolymer modification is present. Examples of suitable polyesters include poly(ethylene terephthalate), poly(ethylene naphthalenedicarboxylate) comprising about 4 mol % to about 10 mol % CHDM, or about 6 mol % to about 17 mol % IPA, and mixtures thereof. The polyester compositions suitable for the present invention may also containing up to about 50 mol % of modifying dibasic acids and/or glycols other than CHDM and IPA, and more preferably up to about 20% and most preferably up to about 10 mol %. Modifying dibasic acids may contain from about 2 to about 40 carbon atoms, and preferably include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acids to be included with terephthalic acid are: phthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. Examples of dicarboxylic acids to be included with naphthalenedicarboxylic acid are: terephthalic acid, phthalic acid, naphthalene-2,-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. Polyesters may be prepared from two or more of the above dicarboxylic acids.

The glycol component of the present invention comprises about 4 mol % to about 10 mol % CHDM and from about 10 to about 94 mol % ethylene glycol. The glycol component may be further modified with additional modifying glycol components which include, but are not limited to cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include diethylene glycol, triethylene glycol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane. Polyesters may be prepared from two or more of the above diols.

The resin may also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art.

Highly useful naphthalenedicarboxylic acids include the 2,6-, 1,4-, 1,5-, or 2,7-isomers but the 1,2-. 1.3-, 1,6-, 1,7-, 1,8-, 2,3-, 2,4-, 2,5-, and/or 2,8-isomers may also be used.

The dibasic acids may be used in acid form or as their esters such as the dimethyl esters for example.

The polyesters of this invention are readily prepared using polycondensation reaction conditions well known in the art. Typical polyesterification catalysts which may be used include titanium alkoxides, dibutyl tin dilaurate, and antimony oxide or antimony triacetate, used separately or in combination, optionally with zinc, manganese, or magnesium acetates or benzoates and/or other such catalyst materials as are well known to those skilled in the art. Phosphorus and cobalt compounds may also optionally be present. Although we prefer to use continuous polycondensation reactors, batch reactors operated in series may also be used.

Other components such as nucleating agents, branching agents, colorants, pigments, fillers, antioxidants, ultraviolet light and heat stabilizers, impact modifiers, reheat improving aids, crystallization aids, acetaldehyde reducing additives and the like may be used if desired and to the extent they do not impair the objectives of the present invention.

Bottles of the present invention are produced using a stretch blow molding process. Stretch blow molding is accomplished in two distinct steps; first, the polyester is melted in an extruder and injected into a mold forming a preform or parison; second, the preform is then blown into the final bottle shape. The actual blowing of the preform must occur at a temperature slightly above the glass transition temperature of the polyester. In a "single stage" SBM process the preform is transferred from the injection mold directly to a blow molding station; during the transfer time, the preform cools to the proper blow molding temperature. In a "two stage" SBM process the preform is ejected from the injection mold and then held at ambient temperatures for a time long enough to achieve a consistent temperature within the lot of preforms; and then, in a separate process, is reheated to the proper blow molding temperature before being blown into the bottle shape. The specific type of process used is determined by the volume of production, or the production rate desired for a specific application; and the machine design and capabilities.

It is well known that polyesters exhibit a dramatic improvement in physical properties when mechanically stretched, or oriented. During the SBM process with a crystallizable polymer, this mechanical stretching occurs when the preform is blow molded into the final bottle shape. Preform design and SBM processing conditions are used to impart the desired level of mechanical stretching (stretch ratio) to the bottle sidewalls and base; and thus determine many of the bottle physical properties. These physical properties are generally much improved over those found in containers which have not been mechanically oriented, such as those containers made from an amorphous polymer. Planar stretch ratios ranging from approximately 11 to 13 are commonly used in polyester bottles that require excellent physical properties, and are considered standard practice in the industry.

To gain the advantages of increased mechanical orientation and to reduce raw material costs, bottle manufacturers and equipment suppliers are beginning to investigate methods and equipment for producing large SBM containers in sizes ranging from 1 to 10 gallons. However, the tendency of standard PET bottle polymer to form crystalline haze during the injection molding of thick walled preforms, and the tendency to form crystalline haze at the high blow molding temperatures needed to achieve the desired stretch ratios during the blow molding of large containers have limited the use of PET in these large SBM applications. Bottle producers have been forced to use amorphous polymers, such as polycarbonate, in the SBM process, which results in significantly higher raw material costs and little or no increase in physical properties typically derived from mechanical orientation.

The efforts to produce very large containers using the stretch blow molding process have been hampered not only by the crystallization characteristics, but also by the stretching characteristics of standard PET formulas and their effect on processing. In order to make a very large PET container, the preform must be designed with the correct range of dimensions that allow the production of a bottle with the desired material distribution and thickness, and also give an acceptably wide processing window in both the injection molding and blow molding steps. The PET preform can be said to have a "natural stretch ratio", or NSR at a given blow molding temperature; at which point the PET begins to self-level and strain harden. Stretching beyond the NSR at a given blow molding temperature imparts improved physical properties, but too much stretching causes a loss of clarity and delaminating (typically called pearlesence, or pearl point). The stretching characteristics of PET are highly dependent on several resin factors, primarily: IV (molecular weight), and copolymer content. In general, as the IV decreases and copolymer content increases, the NSR and the temperature at which pearlesence begins increases. By increasing the NSR of PET for use in large SBM containers, it is then possible to achieve proper material distribution and mechanical orientation at a lower blow molding temperature than would be expected with standard PET bottle polymers. This results in the ability to use optimally designed preforms and to avoid the formation of crystalline haze during the blow molding process for large SBM containers.

The polyesters of the present invention display superior crystallization (reduced crystallization rate, haze formation, etc.) and stretching characteristics (higher natural stretch ratio, increased freeblow volume, etc), which permit (or increase the processing window for) the production of large stretch blow molded (mechanically oriented) PET bottles using stretch blow molding (SBM) equipment or SBM equipment technology. The bottles of the present invention display increased clarity , improved physical properties, and improved processability which allows the production of large containers.

Large bottles which have surprisingly good physical properties and clarity are also disclosed. Accordingly, the present invention further relates to containers which are made from polyester formed by balancing the IV with copolyester modification and preferably, comprising an IV of about 0.75 to about 0.85 dl/g and from about 3.5 mol % up to about 20 mol % copolymer modification. The bottles of the present invention display surprisingly good physical properties and the desired level of clarity, as well as improved processing characteristics and production output.

The reduction of crystallization rate allows the use of crystallizable polyesters in the production of extremely large containers on stretch blow molding equipment; which results in an opportunity to improve physical properties by increased mechanical stretching, or orientation, while maintaining the desired container clarity. The increased copolymer modification not only decreases the crystallization rate, but also increases the natural stretch ratio at lower blow molding temperatures. This increase in natural stretch ratio is important in order to optimize the preform design for good material distribution and acceptable orientation, while keeping the blow molding temperature low enough to avoid the formation of crystalline haze during the blow molding stage of production.

Specifically the present invention relates to a large container which is crystallized and biaxially oriented, such as by strectch blow molding and formed from the above disclsosed polyester.

The present invention further relates to a process for forming large containers comprising providing a polyester having the above defined composition, a hoop stretch ratio at 212°F of greater than about 5.0 and a crystallization halftime sufficient to injection mold a thick walled preform without the formation of crystalline haze. The process further comprises the step of stretch blow molding said preform under conditions suitable to form said bottle without forming crystalline haze during said blow molding step.

WE CLAIM:

1. A clear, stretch blow molded polyester container weighing greater than about 200 grams.

2. The container of claim 1 wherein said polyester is formed from a diacid component comprising up to about 96.5 mol % terephthalic acid or naphthalene dicarboxylic acid and a glycol component, wherein said polyester possesses an IV of about 0.75 to about 0.85.

3. The container of claim 2 wherein said dacid component further comprises from about 6 mol % to about 17 mol % IPA.

4. The container of claim 2 or 3 wherein said glycol component further comprises ethylene glycol.

5. The container of claim 4 wherein said glycol component further comprises from about 4 mol % to about 10 mol % CHDM.

6. The container of claim 3 wherein said diacid further comprises up to about 50 mol % of modifying dibasic acids other than IPA.

7. The container of claim 3 wherein said diacid further comprises up to about 20 mol% of modifying dibasic acids other than IPA.

8. The container of claim 3 wherein said diacid further comprises up to about 10 mol % of modifying dibasic acids other than IPA.

9. The container of claim 3 wherein said modifying dibasic acid is selected from the group consisting of aromatic dicarboxylic acids having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms.

10. The container of claim 9 wherein said modifying dibasic acid is selected from the group consisting of phthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and mixtures thereof.

11. The container of claim 3 wherein said glycol component further comprises modifying glycols selected from the group consisting of cycloaliphatic diols having 6 to 20 carbon atoms or aliphatic diols having 3 to 20 carbon atoms.

12. The container of claim 11 wherein said modifying glycol is selected from the group consisting of diethylene glycol, triethylene glycol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane and mixtures thereof

13. A method comprising forming a preform from between about 200 and about 800 grams of a polyester formed from a diacid component comprising up to about 96.5 mol % terephthalic acid or naphthalene dicarboxylic acid and a glycol component, wherein said polyester possesses an IV of about 0.75 to about 0.85; and stretch blow molding said preform into a container.

14. The method of claim 13 wherein said dacid component further comprises from about 6 mol % to about 17 mol % IPA.

15. The method of claim 13 or 14 wherein said glycol component further comprises ethylene glycol.

16. The method of claim 15 wherein said glycol component further comprises from about 4 mol % to about 10 mol % CHDM.

17. The method of claim 14 wherein said diacid further comprises up to about 50 mol % of modifying dibasic acids other than IPA.

18. The method of claim 16 wherein said glycol component further comprises modifying glycols selected from the group consisting of cycloaliphatic diols having 6 to 20 carbon atoms or aliphatic diols having 3 to 20 carbon atoms.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 98/15467

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/185 C08G63/189 B29C49/08 B65D1/02

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 6 C08G B29C B65D

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 217 128 A (STENGER DONALD R) 8 June 1993 see column 3, line 22-26 see column 3, line 46-47 see column 3, line 61-62 see column 4, line 56-57; figures 1-3	1
Y		2-18

Y	WO 91 08247 A (EASTMAN KODAK CO) 13 June 1991 see page 4, paragraph 2; claim 1	2-18

A	WO 95 03977 A (PETROU NICOLEON) 9 February 1995 see page 5, line 9-11	1
	--- -/--	

☒ 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
30 September 1998

Date of mailing of the international search report
09/10/1998

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
Voigtländer, R

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 98/15467

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 278 403 A (MITSUBISHI GAS CHEMICAL CO) 17 August 1988 see page 5, line 55 - page 6, line 8; example 3 ---	2-18
Y	WO 90 03993 A (EASTMAN KODAK CO) 19 April 1990 see claims 1,2 ---	2-18
Y	WO 96 33062 A (MUKHERJEE SUMIT ;BREWSTER GARY (US); COCA COLA CO (US); STEELE SCO) 24 October 1996 see page 14, line 14-15 see page 9, line 5-8 see page 11, line 29-30 ---	2-18
Y	WO 94 01268 A (CONTINENTAL PET TECHNOLOGIES) 20 January 1994 see page 16, last paragraph see page P28, line 11-12 -----	2-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 98/15467

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5217128 A	08-06-1993	NONE	
WO 9108247 A	13-06-1991	US 4983711 A	08-01-1991
		AT 111125 T	15-09-1994
		AU 634126 B	11-02-1993
		AU 6897591 A	26-06-1991
		CA 2069498 C	21-11-1995
		DE 69012347 D	13-10-1994
		DE 69012347 T	05-01-1995
		DK 504227 T	14-11-1994
		EP 0504227 A	23-09-1992
		ES 2059108 T	01-11-1994
		JP 5502684 T	13-05-1993
WO 9503977 A	09-02-1995	AU 7405594 A	28-02-1995
EP 0278403 A	17-08-1988	JP 2099760 C	22-10-1996
		JP 8025220 B	13-03-1996
		JP 63203540 A	23-08-1988
		JP 1139334 A	31-05-1989
		AU 610555 B	23-05-1991
		AU 1124188 A	18-08-1988
		AU 7206491 A	30-05-1991
		CA 1288912 A	17-09-1991
		DE 3867858 A	05-03-1992
		US 4994313 A	19-02-1991
WO 9003993 A	19-04-1990	EP 0368690 A	16-05-1990
		EP 0437496 A	24-07-1991
		JP 4500982 T	20-02-1992
WO 9633062 A	24-10-1996	AU 695546 B	13-08-1998
		AU 5560996 A	07-11-1996
		EP 0821645 A	04-02-1998
WO 9401268 A	20-01-1994	AU 674528 B	02-01-1997
		AU 4664293 A	31-01-1994
		CA 2139764 A	20-01-1994
		CN 1092352 A	21-09-1994
		EP 0653981 A	24-05-1995

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte   nal Application No
PCT/US 98/15467

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9401268 A		HU 71921 A,B	28-02-1996
		SG 45429 A	16-01-1998
		SK 1495 A	09-08-1995
		US 5628957 A	13-05-1997
		US 5728347 A	17-03-1998
		US 5759656 A	02-06-1998
		MX 9304091 A	31-05-1994

Form PCT/ISA/210 (patent family annex) (July 1992)