

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 September 2010 (10.09.2010)

(10) International Publication Number
WO 2010/100416 A1

(51) International Patent Classification:

C03C 3/091 (2006.01) C03C 4/02 (2006.01)
C03C 3/093 (2006.01) C03C 12/00 (2006.01)

(21) International Application Number:

PCT/GB2010/000376

(22) International Filing Date:

2 March 2010 (02.03.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0903460.4 2 March 2009 (02.03.2009) GB

(72) Inventor; and

(71) Applicant : WATKINSON, Charles [GB/GB]; Bridge Cottage, Long Lane, Great Heck, Goole DN14 0BE (GB).

(74) Agent: HARRISON, Michael; Harrison IP Limited, Marlborough House, Westminster Place, York Business Park, Nether Poppleton York YO26 6RW (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



WO 2010/100416 A1

(54) Title: COLOURED GLASS FLAKES

(57) Abstract: A glass flake having a thickness below 10µm and being coloured through the bulk of the material. The flake may be at least partially crystalline and/or include one or more clusters. A method of producing such flake comprises incorporating a nucleating agent and a colouring agent and heating the flakes to change the extent and/or nature of their crystallisation and/or clustering.

COLOURED GLASS FLAKES

Field of the invention

This invention relates to powdered glass comprising small particles or flakes of glass, hereinafter referred to as glass flake (GLASSFLAKE is a registered trade mark of
5 Corrocoat Ltd).

Background to the Invention

A method of producing glass flakes is known which makes use of a spinning cup to produce a flat film of molten glass emanating radially from the rim of a rotating cup.
10 The film is fed between two plates, forming an annular venturi and is super-cooled with forced air. The film is broken up due to the high velocity air stream and the drag (frictional resistance) imparted by it. Such a method and apparatus to perform it is the subject of EP 0 289 240.

15 The parameters involved in the successful production of a flat glass flake of even thickness, according to the method described in EP 0 289 240 are varied and complex. They have been found to include the following:-

- glass composition, melt temperature and viscosity
- temperature of glass in the melt tank
- 20 • mass flow of glass leaving the tank and entering the cup
- temperature of the glass entering the cup
- distance between the outlet of the glass tank and entry to the cup
- diameter and depth of the cup
- heat dissipation properties of the cup
- 25 • rotational speed of the cup
- distance between the rim of the cup and entry to the radial venturi
- distance between the plates forming the radial venturi
- diameter of the venturi plates
- volume and pressure of air being drawn between the venturi plates
- 30 • temperature of the air flowing between the venturi plates
- diameter and construction of the cyclone collector

These parameters can all be varied with the result that the glass flakes either are or are not produced. Flakes, if produced, may be flat or wavy. The flakes may have a substantial variation in thickness or be very consistent in thickness. The flakes may be large or small in cross-section and/or thickness.

5

Using the said method and with appropriate control of the above mentioned parameters it is possible to produce a mean thickness range below 10 μ m and, indeed, below 200nm and even down to 10nm or less.

10 Examples of glasses which may be used to produce such glass flake are ECR glass, C glass, E glass and LA glass.

In general, such glass flake is colourless or white. Attempts have been made to produce coloured flake but they have been unsuccessful. For instance, formulations
15 were based on a standard C-glass (Table 1) but with the addition of colouring agents used in sheet glass such as iron oxide, copper oxide and graphite at high levels (> 5% by weight).

Oxide	Wt (%)
SiO ₂	< 63
Na ₂ O	8
Al ₂ O ₃	> 5
K ₂ O	8
CaO	14
MgO	5
B ₂ O ₃	> 5.9
Other	< 1

20 *Table 1 C-glass composition*

Although the additives mentioned give strong colour to glass in thickness of circa 10 μm and above they merely serve to change, very slightly, the refractive index of the glass and produce a slight greying or change in brightness in flake below circa 2 μm even though in the thick sections of glass very strong colouring was observed to the extent that the glasses became opaque.

There is interest in producing coloured glass flakes that retain their colour and light scattering properties when produced at sub-micron thickness.

Statements of the Invention

According to the present invention, there is provided glass flake having a thickness below 10 μm and being coloured through the bulk of the material. The colour is not just on the surface of the material but extends throughout the flake.

Preferably, the glass flake is at least partially crystalline and/or includes one or more clusters. Clustering is a phenomenon occurring at or on an atomic scale and is discussed in Greaves, G.N and Sen, S. (2007) "Inorganic glasses glass-forming liquids and amorphizing solids", *Advances in Physics*, 56:1, 1-166.

Preferably, the flake comprises a nucleating agent and a colouring agent.

Preferably, the flake has a thickness below 5 μm , more preferably below 2 μm and, most preferably, below 1 μm . By way of example, the flake may have a thickness in the range from 200 to 500 μm .

The flake preferably includes, as a nucleating agent, titanium dioxide and/or zinc oxide.

Other ingredients may include the oxides of sodium, potassium and calcium. The glass may have a low borate concentration.

The flake preferably includes a colouring agent present in an amount of at least 2% by weight. Typically, transition metals and rare earth metals may be used to create colour effects. Preferred colouring agents include copper oxide, cobalt oxide, ferric oxide, manganese dioxide, nickel oxide and cerium oxide.

5

The invention also provides a method of producing coloured glass flakes having a thickness below 10 μ m, the method comprising incorporating in the glass flakes a nucleating agent and a colouring agent and heating the flakes to change the extent and/or nature of their crystallisation.

10

Detailed Description of the Invention

Clustering and Crystal Growth

A glass is formed typically from oxides of silicon, boron, aluminium, titanium or phosphorous in combination with various cationic species which typically contain sodium potassium, calcium or other suitable species. The melt viscosity of glass is determined by the polymeric nature of the structure which exists. At very high temperatures, the species which exists will be clusters of atoms: SiO_x, AlO_y, BO_z, etc. As the melt is cooled, so the size and nature of the clusters will change and reflect the thermodynamic stability of the species which can be formed from the mixture. In the case of a brittle soda glass the SiO_x can form 3D polymeric structures and the extended order is often referred to as a crystalline structure. In a mixture of SiO_x and AlO_y, compositions can be created where the Lewis acid – base nature of the components balance and a stable layer structure is created which comprises a sandwich of Si and Al oxides. The Al oxide is attached to a Si oxide and a completed structure is created at a dimension of approximately 1nm thickness. This structure is its most ideal form is found in clay. If the balance between the Si and Al is not exactly matched then a more 3D structure is formed. The Al acts as a blocking agent for the formation of the 3D polymeric structure. Addition of certain oxides will act to nucleate crystal growth; titanium and zinc oxides have this effect. The nucleation mechanism is via the formation of stable mixed oxides which control and assist the formation of the regular order entities which are associated with crystal structure in glasses.

In order to achieve colour on a sub-micron scale, it has been postulated that a semi-crystalline glass (a glass-ceramic) will enhance the colour. The colour of glass arises from light that is either reflected or transmitted (scattered) by the glass. If larger particles are present in the glass, the intensity of the scattered radiation will be increased.

It is possible to devitrify the majority of glasses if a glass is heated for a sufficient length of time at a suitable temperature. By controlling the temperature and viscosity of a glass, different crystallographic compositions of material exhibiting identical chemical compositions can be achieved and this can produce some colouration as crystallisation occurs. Crystallisation involves two basic parameters: nucleation and growth. Titanium dioxide and zinc oxide are known nucleating agents and can work in at least two different ways:

1. *As catalysts of phase separation* - one amorphous phase is produced that is more easily crystallised than the bulk glass.
2. *As nucleating agents* - they promote the formation of nucleation sites within the glass in order to achieve controlled crystallisation. In the case of coloured glass, heterogeneous nucleation occurs, as the titanium and zinc oxides provide nuclei for the growth of transition metal oxides such as iron oxide to impart colour.

In essence there are a number of factors which will influence the nature of the "structure" which is dynamically formed in the melt and which will influence the properties of the quenched solid created in the flake. These factors are the presence of nucleating species, the presence of depolymerising species and the balance of cationic to anionic species.

Titanium, zinc and aluminium are all higher temperature oxides than silica and hence should thermodynamically be more stable than silica. Titanium and aluminium form basic oxides whereas silicon forms an acidic oxide. Thus, thermodynamically there will be a bias towards formation of aluminium - silica and titanium - silica primary structures. This bias is clearly illustrated in mineral chemistry where aluminosilicates form a major part of the structure of the earth.

As the melt is cooled clusters will be formed. The size and form of the clusters will be controlled by several factors:-

- 5 • The balance between the Lewis acidic (silica) and Lewis basic (alumina). If the system were charge neutral then these components would form an infinite amorphous matrix.
- 10 • The presence of oxides such as Na_2O , K_2O , CaO etc. will inhibit the formation of the Si-O-Si, Al-O-Al or Si-O-Al bonds creating X-O⁻ terminations. If the temperature is high then the formation of the matrix will be determined by the temperature difference between that of the melt and that for the formation of the particular species. If the concentration of the positive charged species is high, then it will be possible to envisage that pseudo micelle type structures are formed. These micelles will coalesce to form an amorphous matrix as the glass is cooled. If the melt is rapidly quenched then it will be possible that these structures will be retained and will influence the physical properties which are created.
- 15 • The extent of the structure will be influenced by the presence of structure forming oxides such as zinc and titanium. These will nucleate the growth of the clusters in the melt.
- 20 • The presence of borate will limit the growth of the silica or alumina oxide structures, lowering the melting point and suppressing the growth of the clusters.

The composition of the glass will influence the nature of the structure formed.

25

If colour is associated with electronic transitions of, for instance, cobalt, in the glass, then it is reasonable to assume that will have to be in a charged state and that state will be dictated by the charge balance in the system. Theory tells us that the colour centre will usually be associated with a coordinated structure around the pigment. If the cobalt can form a lower oxidation state then it will lose the coordination and its colour. The octahedral coordination will achieve the Russell Sanders splitting usually associated with the blue colour. The coordination will be dictated by the groups which are bound to the colour centre. It is reasonable to assume that the first

30

coordination shell will be oxygen and that the second can contain silica, alumina or titanium. Which of these elements form the structure will be determined by which can form the most stable coordination shell. Silica will tend to form a tetrahedral whereas alumina will form an octahedral structure. Theory therefore suggests that for colour to be observed, it will be important that the colour centre is formed in the melt and retained during the quenching process. If the positive charge content is high then the cobalt will retain its high oxidation state. If, however, the positive charge content is low then there will be a tendency for the cobalt to be reduced to a colourless lower oxidation state.

10

Examples

Examples of methods and formulations illustrating the invention will now be given.

A golden/brown coloured glass flake was produced on several occasions when the starter formulation was based on the LAG6 formulation (Table 2) of Glassflake Ltd but with the addition of a transition metal. When standard LAG6 glass flake is produced, it is white, irrespective of thickness. However, slight modifications of the formulation, namely the addition of colouring agents such as iron oxide, manganese oxide and bismuth oxide, produce slightly coloured glass flakes (UVRB series) the strongest of which, a golden/brown flake, was produced with the addition of bismuth and titanium tioxide. Phase separation and some crystallisation are exhibited in the UVRB glass series.

20

	Oxide	Weight (%)			
		LAG6	UVRB1	UVRB2	UVRB3
	SiO ₂	70.35	68.27	64.06	58.80
5	Na ₂ O	7.98	7.17	6.95	8.76
	Al ₂ O ₃	3.15	3.22	3.57	3.79
	K ₂ O	1.93	1.76	1.75	1.91
	CaO	1.84	1.87	0.91	3.87
	MgO	1.30	1.24	0.55	1.00
10	B ₂ O ₃	11.87	10.58	7.68	7.56
	Fe ₂ O ₃	0.08	3.11	4.04	3.99
	Bi ₂ O ₃		1.33	2.00	1.96
	MnO ₂			6.35	6.27
	TiO ₂	1.51	1.33	2.01	1.96
15	ZnO		0.11	0.13	0.13
	Flake thickness (um)	1	-	0.4-1.8	0.57-2.41

20 *Table 2 UVRB compositions based on LAG6 that fabricated golden flake*

In contrast, formulations based on ECR glass flake did not produce coloured glass flake at all (Table 3). The glass flake was white.

Oxide	Weight (%)			
	ECR	UVRA1	UVRA2	UVRA3
SiO ₂	64.62	66.49	62.92	66.49
Na ₂ O	11.15	10.71	11.98	10.71
Al ₂ O ₃	4.87	4.72	4.75	4.72
K ₂ O	2.24	2.29	2.31	2.29
CaO	6.00	6.15	6.82	6.15
MgO	2.30	2.36	2.38	2.36
B ₂ O ₃	5.16	3.78	4.36	3.78
Fe ₂ O ₃	0.08	0.36	0.35	0.36
Bi ₂ O ₃		0.06	0.00	0.06
TiO ₂	0.30		1.03	
ZnO	3.28	3.08	3.10	3.08
Flake thickness (um)	1.0	0.8	0.32-0.5	0.3-0.5

5

Table 3 UVRA compositions based on ECR that produced white flake

Powder X-ray diffraction was performed on standard ECR glass flake and UVRB2 glassflake after grinding the flake to fine powders. Results show that ECR glass flake is completely amorphous, whilst UVRB2 glass flake is partially amorphous and partially crystalline. This suggested that the crystallinity of UVRB2 is the significant factor in the colouring of the flake.

Titanium dioxide is an intermediate oxide, and can act as both an acid and a base. Therefore it can destabilise a single-phase glass due to co-ordination effects. Phase separation can arise due to differences in charge between principal network forming

15

ions. Based on results from the UVRA and UVRB series it is possible to form the following conclusions:

- Thickness of flake is irrelevant in production of the golden/brown flake. The thickness varies from 300 nm to 2 microns, and still remains coloured.
- 5 • Nucleating agents (TiO₂ and ZnO) are present in both types of glass. It is likely that the presence of titanium dioxide in the UVRB series has catalysed the phase separation exhibited. The phase separation is minor, and therefore it is probable that the titanium dioxide is also behaving as a nucleating agent to crystallisation. The colouring agents in these glasses are present in sufficient quantities to grow
10 crystals on the titanium dioxide nucleation sites formed. This contrasts to the UVRA series, where the colouring agents are present in insufficient quantities to be able to produce a coloured flake at a sub-micron scale, even though the flake may be partially crystalline due to the presence of nucleating agents.
- To achieve coloured glass flake, a combination of nucleating agents and sufficient
15 quantities of colouring agents must be present, because they work together, in synergy. Golden/brown flake was produced to some extent in all UVRB formulations despite the different colouring agents used. Therefore the oxidation state of the transition metal oxides must be controlled in order to produce different colours.

20

To confirm the above theory that colour arises on the sub-micron scale in glass flake due to both nucleating agents and colouring agents being present in sufficient quantities, more glasses were produced and flaked. Difficulties in melting LAG6 type batches meant that ECR formulations were used. The nucleating agents (TiO₂ and
25 ZnO) enable the glass network to atomically rearrange and create long range orders, essential for crystallisation. Colouring agents were added in sufficient (greater) amounts to grow crystals upon the nuclei. As a consequence coloured flakes were produced using the ECR formulation as a starter. Glass flakes containing copper are pale blue in colour, whilst cobalt containing glassflakes are intense blue.

30 See (Table 4).

Oxide	Wt (%)
SiO ₂	61.97
Na ₂ O	11.08
Al ₂ O ₃	4.67
K ₂ O	2.15
CaO	5.79
MgO	2.20
B ₂ O ₃	5.22
Fe ₂ O ₃	0.07
TiO ₂	0.34
CoO	2.15
ZnO	4.35
	100.00

Table 4 Formulation (based on ECR) to produce intensely coloured blue glassflake at sub-micron thickness

5

This formulation has produced glass flake that has thickness ranging from 500-200nm. It is still intensely coloured at the lower thickness. The formulation differs from the UVRA series in that it has higher levels of the colouring agent. It differs from the UVRB series as it has lower levels of TiO₂ and higher levels of ZnO, but is similar as it has high levels of colouring agent. Therefore, it is possible to conclude that **either** TiO₂ or ZnO can be used as a nucleating agent, as long as the colouring agent is present in amounts larger than ~ 2%. It is advantageous to use ZnO instead of TiO₂, as large amounts of TiO₂ increase the viscosity of the molten glass and melt temperature, and further contribute to phase separation.

15

Although two very different glasses have been used to produce a sub micron coloured glass, others may be used so long as the colouring and nucleating agents are present in appropriate quantities. Further there are some minerals such as basalt that already

have the correct balance of elements to produce colour as a starter material and only need small additions of the correct colouring agents to produce a coloured glass/ceramic at sub-micron level.

5 *Conclusions*

Previous attempt had failed to produce coloured glass flake at low and submicron levels. The lack of nucleating agents in the formulation explains why colour was not seen on these experiments.

10 Golden glass flake was produced when TiO_2 was present (~2%) and colouring agents were present (at least 3% of one colouring agent). However, white glass flakes were produced when nucleating agents were present but colouring agents were only present at low levels (<0.4%). From this, it was possible to conclude that both nucleating and colouring agents are required to produce coloured flake.

15

From research conducted, and glass flakes produced, it is possible to manufacture pale blue flake using copper oxide, and intensely coloured flake (at sub-micron thickness) using zinc oxide as the main nucleating agent (titanium dioxide is present in small quantities) and cobalt oxide as the colouring agent. Increasing the level of cobalt
20 oxide produces darker coloured glassflakes.

The ECR formulation can be taken and modified (as in Table 4) to produce a range of coloured glassflakes. It is important to control the reaction conditions and oxidation states of the transition metal oxides in order to obtain the desired colours.

25

Table 5 shows the possible combinations to give a range of colours when using the correct levels in ECR glass containing sufficient zinc oxide or titanium oxide as nucleating agents.

Colour of glass	Colouring agent required
Blue	CoO + CuO
Blue green	Fe ₂ O ₃ + CoO
Black	Fe ₂ O ₃ +MnO ₂ +NiO+CoO+CuO in oxidising conditions
Copper ruby	Cu ₂ O in reducing conditions
Rose violet	MnO ₂ +CoO in oxidising conditions
Canary yellow	TiO ₂ +CeO ₂
Green	FeO in oxidising conditions
Green-blue	FeO in oxidising conditions

Table.5 Colouring agents to be used in formulation containing nucleating agents to produce coloured glass flakes

CLAIMS

1. Glass flake having a thickness below 10 μm and being coloured through the bulk of
5 the material.
2. Glass flake according to Claim 1, wherein the glass flake is at least partially
crystalline and/or includes one or more clusters.
- 10 3. Glass flake according to Claim 1 or Claim 2, wherein the flake comprises a
nucleating agent and a colouring agent.
4. Glass flake according to any of the preceding claims, wherein the flake has a
thickness below 5 μm .
- 15 5. Glass flake according to Claim 4, wherein the flake has a thickness below 2 μm .
6. Glass flake according to Claim 4 or Claim 5, wherein the flake has a thickness
below 1 μm .
- 20 7. Glass flake according to any of Claims 4 to 6, wherein the flake has a thickness of
from 200 to 500 μm .
8. Glass flake according to any of the preceding claims, wherein the flake comprises
25 titanium dioxide and/or zinc oxide.
9. Glass flake according to any of the preceding claims, wherein the flake comprises
a colouring agent present in an amount of at least 2% by weight.
- 30 10. Glass flake according to any of the preceding claims, wherein the flake comprises
a colouring agent selected from one or more of copper oxide, cobalt oxide, ferric
oxide, manganese dioxide, nickel oxide and cerium oxide.
11. Glass flake according to Claim 1 and substantially as herein described.

12. Glass flake substantially as exemplified herein.

13. A method of producing coloured glass flakes having a thickness below 10 μ m, the
5 method comprising incorporating in the glass flakes a nucleating agent and a
colouring agent and heating the flakes to change the extent and/or nature of their
crystallisation.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000376

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C03C3/091	C03C3/093	C03C4/02
ADD. C03C12/00		
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) C03C		
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	JP 09 286633 A (NIPPON SHEET GLASS CO LTD) 4 November 1997 (1997-11-04) paragraph [0028] paragraph [0035] - paragraph [0080]	1-10, 13
X	EP 1 602 632 A1 (NIPPON SHEET GLASS CO LTD [JP]) 7 December 2005 (2005-12-07) examples paragraph [0030] - paragraph [0033]	1-10, 13
X	US 2008/090034 A1 (HARRISON DANIEL J [US] ET AL) 17 April 2008 (2008-04-17) paragraph [0091] - paragraph [0094] example 4 figure 1	1-10, 13
----- -/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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 19 May 2010		Date of mailing of the international search report 01/06/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Somann, Karsten

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000376

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 57 168963 A (DAINIPPON TORYO KK) 18 October 1982 (1982-10-18) abstract -----	1
X	JP 57 047366 A (DAINIPPON TORYO KK) 18 March 1982 (1982-03-18) abstract -----	1
X	JP 57 012053 A (DAINIPPON TORYO KK) 21 January 1982 (1982-01-21) abstract -----	1
X	JP 58 160375 A (SUZUKA TORYO) 22 September 1983 (1983-09-22) abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/GB2010/000376

Patent document cited in search report	Publication date	Publication date	Patent family member(s)	Publication date
JP 9286633	A	04-11-1997	JP 4053617 B2	27-02-2008
EP 1602632	A1	07-12-2005	CN 1720203 A	11-01-2006
			WO 2004076372 A1	10-09-2004
			JP 4295762 B2	15-07-2009
			JP 2008247736 A	16-10-2008
			US 2006048679 A1	09-03-2006
US 2008090034	A1	17-04-2008	NONE	
JP 57168963	A	18-10-1982	JP 1341154 C	14-10-1986
			JP 60044350 B	03-10-1985
JP 57047366	A	18-03-1982	JP 1054389 B	17-11-1989
			JP 1581658 C	11-10-1990
JP 57012053	A	21-01-1982	JP 1299157 C	31-01-1986
			JP 60019943 B	18-05-1985
JP 58160375	A	22-09-1983	NONE	