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(54) **Title**: NOVEL GLASSES

(57) **Abstract**: Glasses are disclosed having a composition comprising the following oxides (in weight %): SiO_2 61 to 70%, Al_2O_3 0 to 9%, Na_2O 10 to 13%, K_2O 0 to 1%, MgO 2 to 6%, CaO 6 to 16%, SrO 0 to 1%, ZrO_2 0 to 1%, TiO_2 2 to 15%, the glasses having a strain point greater than 570° C. The glasses have good dimensional stability at high temperatures, making them suitable for fire protection glazings and substrates which are processed at elevated temperatures, e.g. substrates for display panels, information storage discs and semiconductor devices, including photovoltaic cells. Physical properties of the glasses, such as thermal expansion coefficient, density and refractive index, are disclosed, as are the melting and liquidus temperatures. The glasses are suitable for manufacture by the float process, yielding flat glass in the form of sheets.

NOVEL GLASSES

The present invention relates to glass, more specifically to novel glasses, novel glass compositions and to substrates composed of the novel glass compositions. The novel glass compositions are soda lime silica glasses, but possess relatively high strain points compared with known soda lime silica glasses, in particular those soda lime silica glasses which are in common use to produce flat glass by the float process. Consequently, the novel glasses of the invention are suited to applications requiring good dimensional stability at high temperatures, such as fire protection glazings and substrates for processing at high temperature. The substrates are suitable for the deposition of coatings and the manufacture of display panels, discs, e.g. magnetic recording discs, semiconductor devices, including photovoltaic cells, especially solar cells, amongst other applications.

While normal soda lime silica glass (i.e. soda lime silica glass compositions in common use for windows and other glazings for buildings and vehicles) has suitable properties at room temperature for many of the above applications, the applications may require processing of the glass at high temperatures, i.e. at temperatures which are above the strain point, or the annealing point, or even the softening point of the glass. Processing the glass at such elevated temperatures would result in the creation of permanent internal stresses in the glass, possibly leading to distortion or fracture of the glass. The glass may even become distorted or deformed during processing. Attempts have therefore been made to provide glasses which are more suited to high temperature processing, i.e. which possess improved high temperature stability by virtue of having relatively high strain points.

The strain point (which is defined as the temperature at which the viscosity of the glass is $10^{14.5}$ poise, denoted T log 14.5 poise) of soda lime float glass in common use is in the region of about 510° C to 540° C, depending on the precise composition. However, many glasses with higher strain points are known. One group of glasses with high strain points is the so-called alkali-free glasses. Unfortunately, these glasses are difficult and expensive to produce, owing to the lack of alkali which acts as a flux. Many of these glasses are also unsuitable for forming by the float process. The use of alternative forming processes generally adds further to the cost, and may result in inferior flatness or smoothness of the surface. A further problem with alkali-free glasses is that they tend to have very low coefficients of thermal expansion, which renders them unsuitable for some applications.

Another group of glasses with relatively high strain points contains increased potash and reduced soda, compared with common or “normal” soda lime silica float glass.

TiO_2

Unfortunately, high potash glasses are themselves difficult to produce in the open regenerative furnaces generally employed in float plants, because high potash glasses may be difficult to refine in such furnaces.

A number of attempts have been made to provide a soda lime silica glass composition having a higher strain point than common float glass. US 5,599,754 discloses a glass composition for a substrate, which is useful for flat display panels, particularly for plasma display panels. The claimed compositions contain from 6 to 9% SrO, which is expensive, and adds significantly to the cost of raw materials when used at these relatively high levels.

US 6,905,991 is an example of a soda lime silica glass composition containing relatively low levels of soda (from 2 to 8% Na_2O) and relatively high levels of potash (from 0-8%, but all of the Examples contain at least 3.5% K_2O). The resulting glasses may be used for producing fireproof glazing panels or for substrates for display panels.

WO 98/49111 discloses a glass composition for a plasma display panel, the glass having a lower density than previous glasses for plasma display panels. The total amount of BaO and SrO included in the total alkaline earth metal oxides in the glass lies in the range of 1 to 8%. Again, these oxides are expensive.

US 6,087,284 relates to an aluminosilicate glass which is suitable for use in display technology. This patent seeks to find a glass which has a high transition temperature, low density and is solarisation-stable. Preferably the glass contains MgO in trace levels at most, or not at all. It therefore represents a substantial departure from the composition of normal or common float glass.

US 7,273,668 relates to a glass composition having high heat resistance which is suitable for chemical strengthening. The composition may be used to produce glass substrates for magnetic recording media, e.g. hard disk drives. Unfortunately this glass is prone to devitrification, which can make manufacturing difficult, and reduce yields.

KR 2009 0111680 A discloses a glass composition for display panels, which seeks to improve reactivity and failure rate of electrode patterns.

JP 2010 143790 A discloses a method for producing a glass substrate for a solar cell in which waste glass can be efficiently recycled. The waste glass is used as part of the glass raw material, which is then melted in a glass melting furnace and formed into the glass substrate.

US 8,828,897 relates to aluminosilicate glasses having high thermal stability and low processing temperatures. The glasses may be used as substrate glass, superstrate glass and/or cover glass for photovoltaic applications and other solar technology applications.

US 8,895,463 relates to a glass substrate for a solar cell such as a Cu-In-Ga-Se ("CIGS) solar cell. The glass compositions of the invention deviate significantly from common soda lime silica glass, being low in soda and high in potash.

US 2013/0306145 A1 also relates to a glass substrate for a CIGS solar cell, and again, the glass compositions are low in soda and high in potash.

US 2013/0313671 A1 relates to glass substrates for solar cells, such as CdTe or CIGS cells. It is stated that the content of SrO, BaO, B_2O_3 and/or ZrO_2 is advantageously zero in order not to penalise the cost of the glass sheet. However, judging by the Examples provided, this approach yields only modest increases in strain point compared with common soda lime silica glass.

It would be desirable to provide novel glasses which achieve a substantial increase in strain point without a substantial increase in the cost of the glass. The cost of glass comprises the cost of the raw materials together with the cost of converting them into finished glass sheets, which itself comprises elements such as the cost of fuel, labour, the plant employed, its level of efficiency, the yields obtained, etc. It would therefore further be desirable to provide novel glass compositions which achieve a substantial increase in strain point and are also able to be readily manufactured by the float process, since this process is a very efficient way of making flat glass. The desired novel glass compositions are therefore ones which lend themselves to economic manufacture.

It has surprisingly been found that the addition of TiO_2 to a normal float glass composition yields a substantial increase in the strain point of the glass.

According to the present invention there is provided a glass having a composition comprising the following oxides (in weight %):

SiO_2	61 to 70%
Al_2O_3	0 to 9%
Na_2O	10 to 13%
K_2O	0 to 1%
MgO	2 to 6%
CaO	6 to 16%
SrO	0 to 1%
ZrO_2	0 to 1%
TiO_2	2 to 15%

the glass having a strain point greater than 570° C.

It has also been found that increasing the amount of Al_2O_3 in the glass composition, in addition to increasing the amount of TiO_2, further increases the strain point of the glass.

Glasses according to the invention are suitable for processing at higher temperatures than normal float glass. The inventive glasses are less susceptible to deformation or distortion at elevated temperatures, and so have higher dimensional stability and improved heat resistance.

Preferably, the glass comprises certain oxides in the following ranges (in weight %):

SiO_2	61 to 69%
Al_2O_3	0 to 8%
CaO	7 to 13%
TiO_2	2 to 13%.

Advantageously, the glass comprises from 3 to 12% TiO_2, preferably from 3 to 11% TiO_2, more preferably from 4 to 10% TiO_2, still more preferably from 4 to 9% TiO_2, yet more preferably from 4 to 8% TiO_2, most preferably from 4 to 7% TiO_2. Particularly suitable glass compositions may contain from 4 to 6% TiO_2. Optionally, such glass compositions may also contain from 3 to 8% Al_2O_3, preferably from 4 to 7% Al_2O_3, more preferably from 5 to 6% Al_2O_3. Since titania (TiO_2) is more expensive than other raw materials employed in the manufacture of float glass, this allows glasses according to the invention to be tailored to achieve the desired balance between performance and cost.

Optionally, the glass is free of any one, or any number, of the following oxides: As_2O_3, BaO, B_2O_3, BeO, CeO_2, Er_2O_3, GeO_2, Li_2O, P_2O_5, PbO, Sb_2O_3, SnO_2, SrO, V_2O_5, ZnO, ZrO_2. These oxides may be objectionable for reasons of toxicity, cost or their adverse effect on the furnace structure. However, traces of these oxides may be present as a result of impurities in the raw materials. In particular, the glass composition may contain from 0 to 1% BaO or B_2O_3. In many of the applications contemplated, it is not necessary or not desirable to tint the glass, so in such cases the glass is free of colourants, e.g. CdO, CeO_2, CoO, Co_3O_4, Cr_2O_3, CuO, Er_2O_3, MnO_2, Nd_2O_3, NiO, Se, V_2O_5.

Preferably, a glass according to the invention has a strain point greater than 580° C, preferably greater than 585° C, more preferably greater than 590° C. As mentioned above, it is desirable to provide glasses which are readily manufactured by the float process. Therefore, while increasing the strain point of a glass, it is also important to take account of other properties of the glass, such as melting temperature, liquidus temperature and working range, which determine how readily the glass may be melted and formed. Surprisingly, the inventors were able to tailor all these properties simultaneously, to provide glasses with high strain points and favourable manufacturing properties.

Preferably, a glass according to the invention has a melting temperature (defined as the temperature at which the viscosity is 100 poise, i.e. log 2 poise, denoted T log 2 poise) less than 1500° C, preferably less than 1480° C, more preferably less than 1460° C. This allows the raw materials to be melted and turned into glass without excessive fuel usage and without causing undue wear to the structure of the furnace in which the glass is melted.

Advantageously, a glass according to the invention has a liquidus temperature less than 1200° C, preferably less than 1180° C, more preferably less than 1160° C, yet more preferably less than 1140° C, still more preferably less than 1120° C, most preferably less than 1100° C. A lower liquidus temperature reduces the risk of devitrification in molten glass in the cooler regions of the furnace. The term “devitrification” refers to the formation of crystals such as wollastonite (abbreviated to “Woll.” in Table I below) or diopside in the glass, which is undesirable because such crystals may end up in the final product, causing it to be rejected.

Desirably, a glass according to the invention has a working range (defined as the forming temperature, i.e. T log 4 poise, minus the liquidus temperature) greater than -100° C, preferably greater than -80° C, more preferably greater than -60° C, yet more preferably greater than -40° C, still more preferably greater than -20° C, most preferably greater than 0° C, i.e. preferably the working range is positive. Some glass forming processes are more tolerant of a negative working range than others, and the float glass process is able to operate with a negative working range. A less negative, or more positive, working range facilitates forming of the molten glass into a product (e.g. a ribbon of flat glass) without devitrification occurring.

It is advantageous for the physical properties of the final product (e.g. sheet of glass, glass substrate, display panel, disc, etc) to be suited to the particular application for which the glass is intended. For some of these applications, normal soda lime silica glass possesses suitable physical properties at room temperature, but, as mentioned previously, it cannot be processed at sufficiently high temperatures without negative effects. According to an additional aspect of the invention, glasses are provided which not only have increased strain points, and lend themselves to economic manufacture, but also retain suitable physical properties at room temperature.

For instance, according to this aspect of the invention, a glass is provided having a coefficient of thermal expansion from 70 to 90 x 10^{-7} °C^{-1} (50-350° C), preferably from 72 to

88 x 10^{-7} °C^{-1} (50-350° C), more preferably from 74 to 86 x 10^{-7} °C^{-1} (50-350° C), and most preferably from 76 to 84 x 10^{-7} °C^{-1} (50-350° C).

Moreover, properties such as density and refractive index are also important when the glass produced by a furnace is changed over from one composition to another. A changeover of particular significance is the changeover from normal float glass to a glass according to the invention. Such changeovers are carried out "on the run", i.e. the mixture of raw materials fed to the furnace is changed to the mixture which is appropriate for the new composition without draining the furnace or stopping melting. The time taken for the changeover can be reduced if both glass compositions have similar density and refractive index, since mixing of the two compositions then occurs more readily.

It is therefore also desirable to provide a glass having a density from 2.50 to 2.70 g cm^{-3} at 25° C, preferably from 2.51 to 2.69 g cm^{-3} at 25° C, more preferably from 2.52 to 2.68 g cm^{-3} at 25° C, further preferably from 2.53 to 2.67 g cm^{-3} at 25° C, yet more preferably from 2.54 to 2.66 g cm^{-3} at 25° C, most preferably from 2.55 to 2.66 g cm^{-3} at 25° C.

Similarly, it is desirable if a glass according to the invention has a refractive index from 1.50 to 1.62, preferably from 1.51 to 1.60, more preferably from 1.52 to 1.59, more preferably from 1.53 to 1.58.

The invention also encompasses glass articles having a glass composition according to the appended claims, and in particular a sheet of glass formed from glass having a glass composition as claimed herein. Additionally, the invention includes a fire resistant glazing made with one or more sheets of such glass. Furthermore, the invention also includes a glass substrate comprising glass as claimed herein, and any of the products manufactured using such a glass substrate, including but not limited to a display panel, a disc, a semiconductor device and a photovoltaic cell, especially a solar cell. Glass substrates according to the invention may be used for CdTe and CIGS (Cu-In-Ga-Se) solar cells amongst others.

The invention will now be further described with reference to the following non-limiting Examples set out in Table 1. In the table, Examples 3 to 7 are according to the invention, and Examples 1, 2 and 8 to 20 are comparative examples. In particular, Example 1 is representative of normal float glass, and has a strain point of 536° C. In contrast, Examples 2 to 20 have strain points ranging from 574° C to 595° C, and the Examples according to the invention span the same range of strain points.

It may be seen that Example 7 has the highest strain point, namely 595° C. This Example also has a very low melting temperature, namely 1290° C. In fact, this Example generally has relatively low viscosity at high temperature, including a forming temperature of only 972° C. Since the liquidus temperature of this glass is relatively high at 1171° C, this leads to a large negative working range of -199° C. Examples 5 and 6 concede only one or two degrees in terms of their strain points, and have working ranges of -91° C and -108° C respectively, which makes them better propositions from the manufacturing aspect.

Glasses having a glass composition according to the invention therefore offer a considerably increased strain point while retaining suitable manufacturing and room temperature properties, rendering it suitable for high temperature processing and other applications requiring increased dimensional stability at elevated temperatures.

Table 1

Example Number	1	2	3	4	5	6	7
Composition (wt %)							
SiO2	72.8	69.7	64.2	61.5	66.6	65.4	62
Na2O	13.4	10	11.8	11.7	10.1	10.1	10.1
CaO	8.71	15.3	12.06	12.0	9.2	10.2	12.1
MgO	4.26	4.24	4.29	4.15	4.13	4.22	4.35
Al2O3	0.4	0.4	0.11	7.06	5.03	4.12	0.08
ZrO2							
TiO2			7.2	3.1	4.6	5.5	10.8
SrO							
BaO							
SO3	0.31	0.34	0.31	0.34	0.24	0.28	0.34
Fe2O3 (Trace components)	0.015	0.015	0.013	0.107	0.102	0.105	0.103
K2O	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Forming Characteristics							
Liquidus Temperature (° C)	1066	1201	1116	1157	1158	1154	1171
Working Range (liquidus minus T log 4)	-39	-179	-143	-135	-91	-108	-199
Primary Devitrification Phase	Woll.	Woll.	Woll.	Woll.	Woll.	Woll.	Woll.
Physical Properties							
Coeff. of Thermal Expansion (50°-350° C)	87.1	84.9	89.0	86.4	76.2	77.9	83.1
Young's modulus E (GNm-2)	74.8	79.9	84.1	80.8	79.2	80.8	84.5
Shear Modulus G (GNm-2)	30.5	32.5	33.8	32.9	32.5	33.3	34.3
Poisson's Ratio σ	0.23	0.23	0.25	0.23	0.22	0.21	0.23
Density (g/cm3 @ 25° C)	2.495	2.563	2.619	2.594	2.551	2.572	2.661
Refractive Index (Nad)	1.5182	1.5388	1.5688	1.5492	1.5441	1.5517	1.589
Viscosity Profile (° C)							
T log 2 poise (Melting Temperature)	1448	1389	1309	1389	1476	1431	1290
T log 2.5 poise	1304	1265	1195	1264	1336	1300	1182
T log 3 poise	1191	1167	1105	1165	1227	1197	1097
T log 4 poise (Forming Temperature)	1027	1021	973	1021	1067	1046	972
T log 5 poise	912	919	881	921	957	941	885
T log 7.6 poise (Softening Point)	732	755	734	762	782	775	747
T log 13 poise (Annealing Point)	563	600	596	613	619	619	616
T log 13.4 poise	555	592	589	606	611	612	610
T log 14.5 poise (Strain Point)	**536**	**575**	**574**	**589**	**593**	**594**	**595**

Table 1 (continued)

Example Number	8	9	10	11	12	13	14
Composition (wt %)							
SiO2	68.0	68.7	69.1	66.2	64.8	67.7	67.0
Na2O	11.7	12	12.3	10.9	11.8	11.9	11.5
CaO	9.86	8.52	7.24	6.23	11.9	6.51	11.5
MgO	4.43	4.52	4.62	4.21	4.24	4.42	4.40
Al2O3	3.47	1.88	0.28	0.08	0.03	0.08	5.20
ZrO2	2.14	4.06	6.1	6.8	6.8	8.8	
TiO2							
SrO				5.0			
BaO							
SO3	0.22	0.21	0.185	0.29	0.31	0.24	0.26
Fe2O3 (Trace components)	0.075	0.075	0.077	0.058	0.015	0.104	0.075
K2O	0.01	0.01	0.01	0.02	0.01	0.02	0.02
Forming Characteristics							
Liquidus Temperature (° C)	1148	1129	1079	1030	1149	1075	1164
Working Range (liquidus minus T log 4)	-84	-46	14	57	-105	44	-110
Primary Devitrification Phase		Diopside	Diopside	Woll.	Woll.	Woll.	
Physical Properties							
Coeff. of Thermal Expansion (50°-350° C)	81.8	80.9	79.9	78.7	84.2	76.8	84.7
Young's modulus E (GNm-2)	78.3	79.3	78.1	80.4	82.8	80	78
Shear Modulus G (GNm-2)	32.1	32.4	32.2	33.3	33.6	33.7	32.1
Poisson's Ratio σ	0.22	0.22	0.21	0.21	0.23	0.19	0.22
Density (g/cm3 @ 25° C)	2.554	2.568	2.581	2.668	2.664	2.620	2.541
Refractive Index (Nad)	1.5322	1.5347	1.5361	1.5452	1.5544	1.5436	1.5298
Viscosity Profile (° C)							
T log 2 poise (Melting Temperature)	1456	1472	1478	1453	1380	1482	1452
T log 2.5 poise	1324	1343	1352	1334	1269	1365	1317
T log 3 poise	1219	1239	1249	1237	1180	1268	1211
T log 4 poise (Forming Temperature)	1064	1082	1093	1087	1043	1118	1054
T log 5 poise	953	970	980	977	944	1007	944
T log 7.6 poise (Softening Point)	775	786	793	794	781	818	769
T log 13 poise (Annealing Point)	605	607	608	609	619	626	602
T log 13.4 poise	597	598	599	600	611	617	594
T log 14.5 poise (Strain Point)	**577**	**577**	**577**	**579**	**592**	**594**	**575**

Table 1 (continued)

Example Number	15	16	17	18	19	20
Composition (wt %)						
SiO2	65.8	67.7	63.9	64.0	64.8	63.3
Na2O	11.6	11.6	11.3	11.3	10.8	11.5
CaO	11.61	11.88	12.1	10.9	12.6	7.5
MgO	4.21	2.05	4.14	5.27	4.3	4.86
Al2O3	6.35	6.41	8.03	8.00	7.06	8.0
ZrO2						
TiO2						
SrO						4.3
BaO						
SO3	0.27	0.22	0.33	0.33	0.28	0.27
Fe2O3 (Trace components)	0.014	0.012	0.105	0.105	0.107	0.107
K2O	0.06	0.06	0.01	0.01	0.01	0.02
Forming Characteristics						
Liquidus Temperature (° C)	1168	1174	1178	1209	1173	1140
Working Range (liquidus minus T log 4)	-118	-107	-116	-140	-109	-69
Primary Devitrification Phase	Woll.	Woll.	Diopside	Diopside	Diopside	
Physical Properties						
Coeff. of Thermal Expansion (50°-350° C)	85.2	84.8	84.1	83.4	82.9	83.9
Young's modulus E (GNm-2)	79.8	77.2	78.9	79.1	79.7	78.7
Shear Modulus G (GNm-2)	32.8	31.5	32.8	32.4	32.6	32
Poisson's Ratio σ	0.22	0.22	0.20	0.22	0.23	0.23
Density (g/cm3 @ 25° C)	2.5478	2.5225	2.556	2.550	2.556	2.582
Refractive Index (Nad)	1.5311	1.5268	1.5321	1.5317	1.5325	1.5294
Viscosity Profile (° C)						
T log 2 poise (Melting Temperature)	1444	1495	1451	1462	1452	1472
T log 2.5 poise	1310	1347	1320	1329	1321	1337
T log 3 poise	1204	1233	1216	1224	1217	1230
T log 4 poise (Forming Temperature)	1049	1066	1062	1068	1064	1071
T log 5 poise	940	952	953	959	955	958
T log 7.6 poise (Softening Point)	768	772	780	783	782	776
T log 13 poise (Annealing Point)	604	605	615	616	617	602
T log 13.4 poise	597	598	607	608	609	594
T log 14.5 poise (Strain Point)	**578**	**579**	**588**	**589**	**590**	**574**

Claims

1. A glass having a composition comprising the following oxides (in weight %):

SiO_2	61 to 70%
Al_2O_3	0 to 9%
Na_2O	10 to 13%
K_2O	0 to 1%
MgO	2 to 6%
CaO	6 to 16%
SrO	0 to 1%
ZrO_2	0 to 1%
TiO_2	2 to 15%

the glass having a strain point greater than 570° C.

2. A glass as claimed in claim 1, comprising the following oxides (in weight %):

SiO_2	61 to 69%
Al_2O_3	0 to 8%
CaO	7 to 13%
TiO_2	2 to 13%.

3. A glass as claimed in claim 1 or claim 2, comprising from 3 to 12% TiO_2, preferably from 3 to 11% TiO_2, more preferably from 4 to 10% TiO_2, most preferably from 4 to 6% TiO_2.

4. A glass as claimed in any preceding claim having a strain point greater than 580° C, preferably greater than 585° C, more preferably greater than 590° C.

5. A glass as claimed in any preceding claim having a melting temperature (at which viscosity = log 2 poise) less than 1500° C, preferably less than 1480° C, more preferably less than 1460° C.

6. A glass as claimed in any preceding claim having a liquidus temperature less than 1200° C, preferably less than 1180° C, more preferably less than 1160° C, yet more preferably less than 1140° C, still more preferably less than 1120° C, most preferably less than 1100° C.

7. A glass as claimed in any preceding claim having a working range (defined as the liquidus temperature minus T log 4 poise) greater than -100° C, preferably greater than -80° C, more preferably greater than -60° C, yet more preferably greater than -40° C, still more preferably greater than -20° C, most preferably greater than 0° C.

8. A glass as claimed in any preceding claim having a coefficient of thermal expansion from 70 to 90 x 10^{-7} °C^{-1} (50-350° C), preferably from 74 to 86 x 10^{-7} °C^{-1} (50-350° C).

9. A glass as claimed in any preceding claim having a density from 2.50 to 2.70 g cm^{-3} at 25° C, preferably from 2.52 to 2.68 g cm^{-3} at 25° C, more preferably from 2.54 to 2.66 g cm^{-3} at 25° C.

10. A glass as claimed in any preceding claim having a refractive index from 1.50 to 1.62, preferably from 1.52 to 1.59, more preferably from 1.53 to 1.58.

11. A sheet of glass formed from glass as claimed in any preceding claim.

12. A glass substrate comprising glass as claimed in any preceding claim.

13. A photovoltaic cell comprising the glass substrate of claim 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/050812

A. CLASSIFICATION OF SUBJECT MATTER
INV. C03C3/087 H01L31/02
ADD.

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 H01L

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 practicable, 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 A	JP S61 136936 A (ASAHI GLASS CO LTD) 24 June 1986 (1986-06-24) English abstract, page 193, right column, last line; claims 1, 2; examples 1-6; table 1 -----	1-3,11, 12 4-10,13
X A	JP S63 147843 A (NIPPON SHEET GLASS CO LTD) 20 June 1988 (1988-06-20) English abstract, page 245, left column; claim 1; example 1; table 1 -----	1,2,6, 11,12 3-5, 7-10,13
A	CN 102 718 404 B (HENAN ANCAI HI TECH CO LTD) 10 December 2014 (2014-12-10) paragraph [0003] - paragraph [0006]; examples 1-10; tables 1, 2 ----- -/--	1-13

☒ 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 application or patent but published on or after the international filing date

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 3 June 2016	Date of mailing of the international search report 15/06/2016
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 Mayne, Julia

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/050812

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98/49111 A1 (PILKINGTON PLC [GB]; FYLES KENNETH MELVIN [GB]; TORR ASHLEY CARL [GB]) 5 November 1998 (1998-11-05) cited in the application page 2, paragraph 3rd - page 6, paragraph 1st; tables 1, 2 -----	1-13
A	US 2012/052275 A1 (HASHIMOTO KAZUAKI [JP] ET AL) 1 March 2012 (2012-03-01) paragraph [0053] - paragraph [0077] -----	1-13
A	US 2014/323286 A1 (AITKEN BRUCE GARDINER [US] ET AL) 30 October 2014 (2014-10-30) Paragraphs [0003], [0008]-[0027], [0102]; tables 1, 2 -----	1-13

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2016/050812

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP S61136936 A	24-06-1986	NONE	
JP S63147843 A	20-06-1988	JP H0461820 B2	02-10-1992
		JP S63147843 A	20-06-1988
CN 102718404 B	10-12-2014	NONE	
WO 9849111 A1	05-11-1998	AU 7219898 A	24-11-1998
		WO 9849111 A1	05-11-1998
US 2012052275 A1	01-03-2012	JP 2012072054 A	12-04-2012
		US 2012052275 A1	01-03-2012
US 2014323286 A1	30-10-2014	CN 105121371 A	02-12-2015
		EP 2991941 A2	09-03-2016
		KR 20160005071 A	13-01-2016
		TW 201446694 A	16-12-2014
		US 2014323286 A1	30-10-2014
		WO 2014179140 A2	06-11-2014