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(54) PROCESS TO OBTAIN TRANSPARENT COLOURLESS GLASS-CERAMICS AND GLASS-CERAMICS THUS OBTAINED

(71) We, CORNING GLASS WORKS, a Corporation organised and existing under the laws of the State of New York, United States of America of Corning, County of Steuben, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with the decolorizing of glass-ceramics, and particularly a means for decolorizing transparent glass-ceramics containing titanium-dioxide.

It is known that numerous glass compositions can give, after a well chosen thermal treatment, a transparent glass-ceramic. As examples, some of these compositions are described in French patents 1 221 174 and 1 562 377. These transparent glass-ceramics are composed of a residual glassy matrix encompassing very small crystals. Depending on the glass composition and thermal treatment these crystals may be mixed crystals having the structure of beta-quartz (or mixed crystals of beta-eucryptite), spodumene, zinc spinel, celsian, aluminium titanate, zirconia, rutile and some others.

In these transparent glass-ceramics, one often finds a certain amount of titanium oxide, this last playing a role of prime importance in the forming of crystalline nuclei which are necessary to obtain the desired crystalline structures. Titanium oxide presents the drawback of giving to transparent glass-ceramics containing it an amber tint that can be considered as unpleasant for some applications. For instance, when used in the manufacture of ware such as casseroles, coffee-pots, etc., the amber tint may change the colour aspect of food and drinks contained in the vessel unpleasantly. In this sort of article, the problem becomes particularly acute because production cost constraints lead to the use of impure raw materials containing a certain quantity of iron oxide and the interaction of these two oxides, of iron and of titanium, increases the amber tint of the glass-ceramic.

Some compositions have been proposed to avoid this tinting, by suppressing TiO_2 or reducing its amount to a very low value. For example, there are the glass-ceramics described in French patents 1 337 180 and 1 421 662. These compositions are not entirely satisfactory because the replacement of TiO_2 by other oxides, such as ZrO_2, is accomplished to the detriment of manufacturing conditions: melting, forming, ceramicing time, or of some especially useful properties of the material: low coefficient of thermal expansion, low diffusion of light etc. This demonstrates the interest to be found in neutralizing the coloration arising from the presence of TiO_2.

In glass technology it is known that one can neutralize an undesirable tint arising from an impurity by incorporating a colouring element producing a complementary tint in the glass. As an example the yellowish tint that would be produced in lead crystal by iron oxide contained as an impurity in raw materials can be neutralized by an appropriate amount of cobalt and nickel oxides. In fact the result is a larger absorption of the light, but this absorption is balanced so as to constitute a practically neutral tint invisible.

French patent 1 474 728 describes a certain number of transparent or opaque coloured glass-ceramics and shows that the normal colouring oxides used in glass technology give unexpected colours in glass-ceramics. It can thus be anticipated that oxides used for decolorizing glasses will not give the normal decolorizing effect when one uses them in glass-ceramics.

This has been confirmed with transparent glass-ceramics wherein the predominant crystal phase is a beta-quartz solid solution, and with compositions encompassed within the following range:

SiO_2	60 to 70% by weight	LiO_2	3 to 4% by weight
Al_2O_3	15 to 25% by weight	TiO_2	2 to 6% by weight

the raw materials of which contained about 500 parts per million of Fe_2O_3. The glass before ceramicing could be made colourless with any one of the following additions, in weight percent:

Addition number 1: 0.0025 to 0.005% CoO
Addition number 2: 0.25 to 0.50 % SeO_3Zn
Addition number 3: 0.0025% CoO+0.010% CuO

However after ceramicing glass-ceramics containing additions numbers 1 and 3 display different shades of purple which may vary from pink to brown, whilst addition number 2 scarcely masks the usual amber tint of the titanium glass.

Thus none of the usual colouring agents, particularly Co, Cr, Cu, Mn, Ni V give, after ceramicing, a tint capable of masking the tint arising from titanium and iron oxides.

There is a need therefore for a process of neutralization of the tint conferred to glass-ceramics by titanium and iron oxides. The present invention is designed to satisfy that need.

The invention provides a process for producing a substantially colourless transparent glass-ceramic from a starting batch within the $Li_2O/Al_2O_3/SiO_2$ field which contains, on the basis of the oxide and as calculated from the batch, from 0.5 to 6% by weight TiO_2 and optionally up to 500 ppm of Fe_2O_3 which normally gives a coloured glass-ceramic, which comprises incorporating in the batch sufficient neodymium oxide within the range of from 0.03 to 0.75% by weight to render the glass-ceramic product substantially colourless. The method of forming the glass-ceramic of the invention is conventional and comprises melting the batch first to form a glass and converting the resultant glass into a glass ceramic by a thermal treatment.

The exact proportion of neodymium oxide to be incorporated will vary with the particular composition of the glass-ceramic, particularly with the amount of TiO_2 and Fe_2O_3 present. Trials with different additions of neodymium oxide should be made for each particular composition, for example in the manner indicated in the illustrative example given hereafter.

Generally too low an addition of neodymium oxide will lead to glass-ceramics with a yellow tint, whilst too high an addition will lead to blue violet tinted glass-ceramics.

The invention relates also to a transparent substantially glass-ceramic in which β quartz constitutes the predominant crystalline phase having a base composition within the $Li_2O/Al_2O_3/SiO_2$ field which contains, on the basis of oxide and as calculated from the starting batch, 0.5 to 6% by weight TiO_2, an optional amount of Fe_2O_3 up to 500 ppm and a decolourizing amount in the range of from 0.03 to 0.75% by weight of neodymium oxide.

The following non-limiting examples are given as illustration and for a better understanding of the present invention, with reference to the drawings wherein:

Figure 1 is a graph showing light transmission curves as a function of wavelength of a base glass for glass-ceramics without additive (curve 1), with addition of cobalt oxide (curve 2) and with addition of neodymium oxide (curve 3).

Figure 2 is a graph similar to that of Figure 1, but after ceramising the base glasses.

Example 1.

A) The glass used has the following composition, in weight percent:

SiO_2	60	TiO_2	6
Al_2O_3	24	Fe_2O_3	0.02
Li_2O	3.5	P_2O_5	4

This glass is melted at 1600°C for 24 hours in a 1 litre silica crucible to avoid any influence that a crucible made of rhodium platinum could have on the tint. Its colour is characterized by transmission curve 1 of Figure 1; it can be designated as very pale yellow. A sample of this glass is treated for 2 hours at 870°C to change it into a transparent glass-ceramic containing around 90% crystal phase which is mainly a beta-quartz solid solution. The colour of this glass-ceramic is characterized by curve 1 of Figure 2: it looks amber.

B) The same base glass composition is melted with the addition of 0.004% of cobalt oxide CoO. The colours before and after ceramising are characterized by curves 2 of Figures 1 and 2 respectively. Visually the sample appears colourless before ceramising and purple after cearmising. Comparison of curves 2 of Figures 1 and 2, reveals a strong modification in the form following ceramising. Although at about 0.65 micron transmission remains unchanged it decreases by about 10% at about 0.50 micron, which explains the evolution of the tint.

C) The same base glass composition is melted with the addition of 0.3% of neodymium oxide Nd_2O_3.

The colours before and after ceramising are characterized by the curves 3 of Figures 1 and 2 respectively. Visually the sample seems colourless before and after ceramising. Comparison of curves 3 of Figures 1 and 2, reveals the low modification of the absorption bands of Nd_2O_3 following ceramising contrary to the previous case.

The thermal expansion coefficient of this glass ceramic is less than $15 \times 10^{-7}/°K$.

The phenomenon from which the present invention derives benefits for decolorizing transparent glass-ceramics containing titanium dioxide is not yet completely elucidated.

However without limiting the present invention to any theory, two hypotheses are proposed.

The first hypothesis consists in attributing the stability of the light absorption of rare earth oxides to the stability of their valence and coordination in the glass, contrary to the other colouring oxides which easily change their valence and coordination according to their surroundings. The second hypothesis consists in attributing the stability of the absorption of rare earth oxides to the ionic radius of the metallic ion. In effect the other metals used in the past to colour or to decolorize glasses have ionic radii less than 0.9 Å, which allows them, theoretically, to be substituted for lithium within the beta-quartz solid solution. We can assume that the fact of being a part of this crystal changes their electronic structure, and hence their absorption. The ionic radius of neodymium however is 1.04 Å, so that it would be obliged to remain in the glassy matrix where it would keep the same properties as in glasses.

Example 2: this example illustrates the method of determining experimentally the proportion of neodymium oxide required to be incorporated into the composition of a transparent glass-ceramic so as to obtain a colourless glass-ceramic. According as described in Example 1, a series of glass-ceramics having the basic compositions A, B, C and D indicated in the Table 1, and containing various proportions of Fe_2O_3 and Nd_2O_3 are preferred. The colours before and after ceramising are also indicated in the Table.

From the Table, it can be seen that glass-ceramics having the basic composition A at 3% TiO_2 can be decolorized by the incorporation of Nd_2O_3 at 0.20% when they contain 140 ppm Fe_2O_3 (trial 3) and by the incorporation of about 0.35% Nd_2O_3 when they contain 380 ppm Fe_2O_3 (as determined by interpolation between trials 8 and 9).

Glass-ceramics having the composition B at 1.8% TiO_2 can be decolorized by the incorporation of 0.15% Nd_2O_3 when they contain 100 ppm Fe_2O_3 (trial 14) and by an incorporation of 0.25% Nd_2O_3 when they contain 350 ppm Fe_2O_3 (trial 19). Glass-ceramics having the basic composition C with 6% TiO_2 and a rather high amount of P_2O_5 can be decolorized by the incorporation of about 0.40% Nd_2O_3 when they contain 160 ppm Fe_2O_3 (as determined by interpolation between trials 22 and 23). Glass-ceramics having the basic composition D with 4.0% TiO_2 and a rather high amount of P_2O_5 can be decolorized by the incorporation of 0.25% Nd_2O_3 when they contain 160 ppm Fe_2O_3 (trial 25) and by the incorporation of 0.32% Nd_2O_3 when they contain 440 ppm Fe_2O_3 (as determined by interpolation between trials 27 and 28).

As can be seen from the above results, the proportion of neodymium oxide required to be incorporated in the basic composition to obtain a colourless transparent glass-ceramic varies with the amount of titanium dioxide and with the amount of ferric oxide (present as impurities in raw materials or refractories used in manufacturing equipment) and with the base composition of the glass-ceramic. It is practically impossible, therefore, to forecast exactly what proportion of Nd_2O_3 will have to be added to a glass composition to obtain a colourless glass-ceramic. It will be generally necessary therefore, to prepare a series of compositions with increasing additions of Nd_2O_3 to be able to determine, either directly from the results obtained, or by interpolation, the appropriate amount of neodymium oxide to be incorporated to get the desired decolorizing effect.

Obviously the decolorizing effect could be obtained with compositions of glass-ceramics different from those specifically described in the above examples and the invention is not limited to those particular compositions.

Generally, the invention can be applied to all transparent glass-ceramic compositions containing titanium dioxide and optionally other colouring materials such as Fe_2O_3, whether these materials have an accidental origin or they have been intentionally introduced in order to improve certain properties of the glass-ceramics.

TABLE

Basic composition, weight %	Amount Fe_2O_3 ppm	ND_2O_3 wt. %	Trial	Colour before ceramising	Colour after ceramising
A SiO_2 69.4 Al_2O_3 18.7 Li_2O_3 3.5 MgO 1.8 BaO — ZnO 0.8 TiO_2 3.0 ZrO_2 2.0 P_2O_5 — As_2O_3 0.8	140	0	1	yellow	yellow
		0.1	2	pale yellow	yellow
		0.2	3	colourless	colourless
		0.3	4	very pale violet to pink	very pale violet to very pale pink
		1.0	5	pale violet	pale violet
	380	0	6	yellow	dark yellow
		0.2	7	yellow	yellow
		0.3	8	very pale yellow	very pale yellow
		0.4	9	colourless to very pale pink	colourless to very pale pink
		1.0	10	pale violet	pale violet
B SiO_2 62.0 Al_2O_3 21.3 Li_2O 2.7 MgO 1.0 BaO 1.3 CaO 0.5 ZnO 6.0 TiO_2 1.8 ZrO_2 2.0 P_2O_5 0.7 As_2O_3 0.7	100	0	11	pale yellow	yellow
		0.05	12	pale yellow	yellow
		0.1	13	very pale yellow	very pale yellow
		0.15	14	colourless	colourless
		0.30	15	pale violet	pale violet
	350	0	16	yellow	darker yellow
		0.1	17	pale yellow	yellow
		0.2	18	very pale yellow	pale yellow
		0.25	19	colourless	colourless
		0.40	20	pale violet	pale violet

TABLE (Continuation)

Basic composition, weight %	Amount Fe_2O_3 ppm	Nd_2O_3 wt. %	Trial	Colour before ceramising	Colour after ceramising
C SiO_2 61.0 Al_2O_3 23.0 Li_2O 3.5 MgO 0.1 ZnO 0.3 TiO_2 6.0 ZrO_2 1.5 P_2O_5 4.0 As_2O_3 0.6	160	0	21	yellow	yellow
		0.35	22	colourless	very pale yellow to colourless
		0.5	23	pale violet	pale violet
D SiO_2 61.2 Al_2O_3 24.0 Li_2O 3.4 MgO — ZnO 0.5 TiO_2 4.0 ZrO_2 2.0 P_2O_5 4.2 As_2O_3 0.7	160	0	24	pale yellow	yellow
		0.25	25	colourless	colourless
		0.35	26	pale violet	pale violet
	440	0.25	27	pale yellow	pale yellow
		0.35	28	colourless	colourless to very pale violet
		0.50	29	pale violet	pale violet

WHAT WE CLAIM IS:—

1. A process for preparing a substantially colourless transparent glass-ceramic from a starting batch within the $Li_2O/Al_2O_3/SiO_2$ field, which contains on the basis of the oxides and calculated on the batch, from 0.5 to 6 wt.% titanium dioxide which normally gives a coloured glass-ceramic, which comprises incorporating in the batch sufficient neodymium oxide within the range of from 0.03 to 0.75% by weight to render the glass-ceramic product substantially colourless.

2. A process according to claim 1 wherein the base starting batch composition contains ferric oxide in an amount of up to 500 ppm.

3. A substantially colourless transparent glass-ceramic in which β-quartz, constitutes the predominant crystalline phase and having a composition within the $Li_2O/Al_2O_3/SiO_2$ field and which contains, on the basis of oxides and calculated on the starting batch, 0.5 to 6% titanium dioxide and a decolourizing amount in the range of from 0.03 to 0.75% by weight of neodymium oxide.

4. A glass-ceramic according to claim 3 which also contains ferric oxide in an amount of up to 500 ppm.

5. A glass-ceramic according to claim 3 or claim 4 whose thermal expansion coefficient is lower than $15 \times 10^{-7}/°K$.

6. A process as claimed in claim 1 for preparing a substantially colourless transparent glass-ceramic, the process being substantially as described in Example 1 or 2.

7. A glass-ceramic whenever produced by a process as claimed in any of claims 1, 2 and 6.

8. A glass-ceramic as claimed in claim 3, substantially as hereinbefore described in Example 1 or 2.

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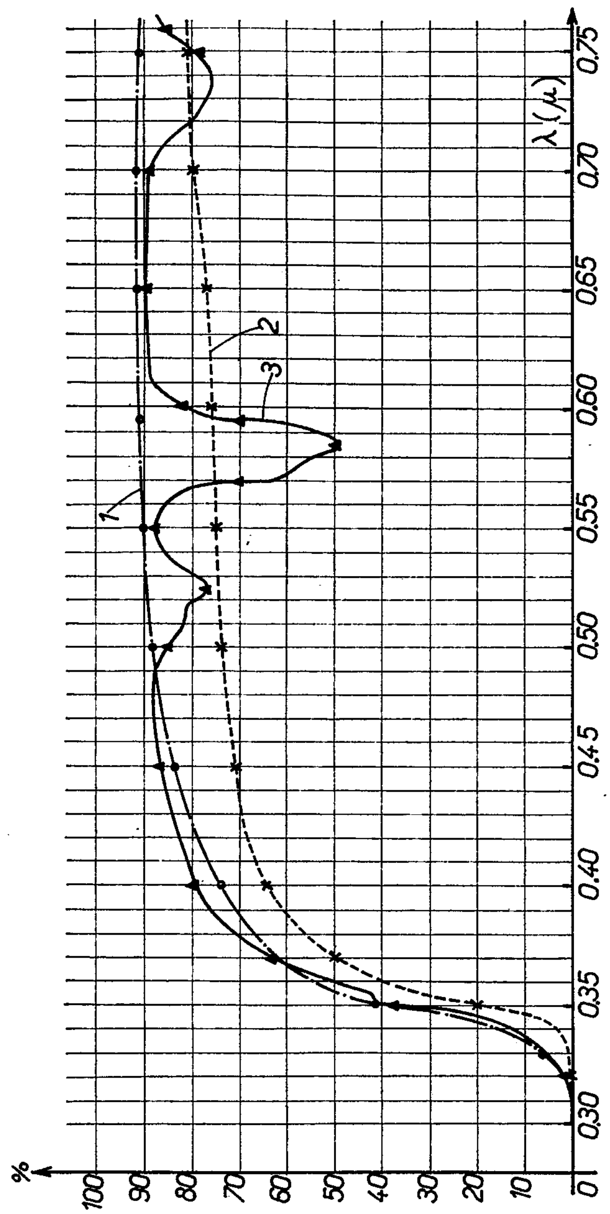
FIG.:1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λ (μ)
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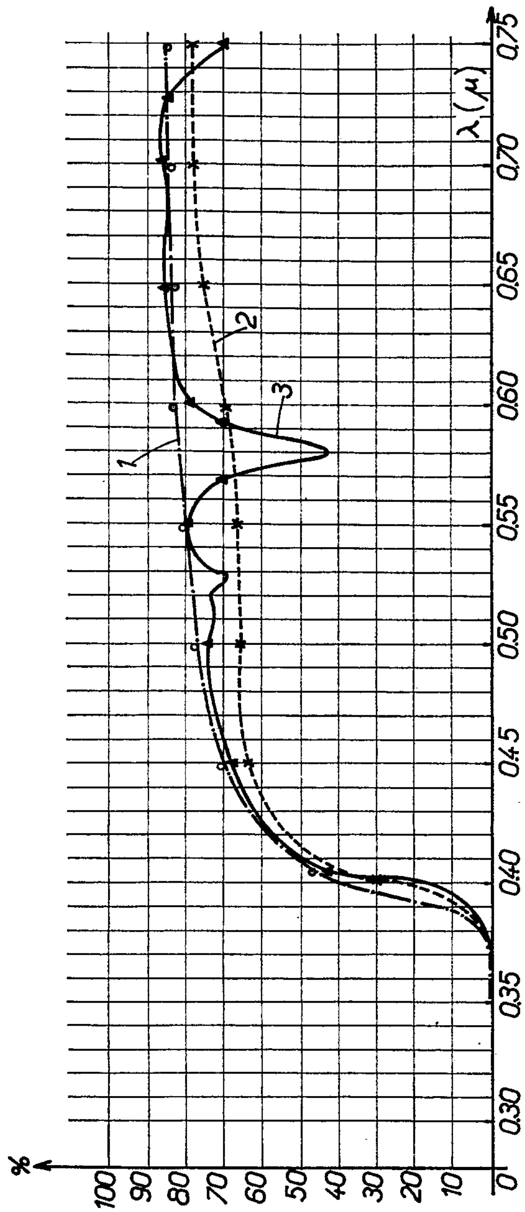
2
3

FIG.:2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