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- (57) Claim

1. Opalescent glass having a continuous glass phase and a discontinuous glass phase dispersed therein, and comprising the following components:

Component	Wt.%
SiO ₂	48.0 to 66.0
B ₂ O ₃	0 to 1.0
Me (III) ₂ O ₃	5.8 to 20.0
Me (I) ₂ O	6.0 to 22.0
Me (II)O	2.6 to 16.0
Me (IV)O ₂	0.5 to 10.0
P ₂ O ₅	0.5 to 5.0
CeO ₂	0 to 3.0

where

- a) the quantity of Me (III)₂O₃ quoted is formed of 5.8 to 20.0 wt.% Al₂O₃ and 0 to 6.0 wt.% La₂O₃;
- b) the quantity of Me (I)₂O quoted is formed of 3.0 to 15.0 wt.% K₂O, 3.0 to 12.0 wt.% Na₂O and 0 to 2.5 wt.% Li₂O;
- c) the quantity of Me(II)O quoted is formed of 0 to 10.0 wt.% CaO, 0 to 7.5 wt.% BaO, 0 to 9 wt.% MgO, 0 to 3.5 wt.% ZnO and 0 to 8.5 wt.% SrO; and
- d) the quantity of Me (IV)O₂ quoted is formed of 0 to 5.0 wt.% TiO₂ and

0 to 5.0 wt.% ZrO₂.

with the exception of opalescent glass comprising at least 2.0 wt.% PbO.

3. Opalescent glass according to claim 1 or 2, comprising the following components:

Component	Wt.%
SiO ₂	53.0 to 62.0
B ₂ O ₃	0 to 0.9
Al ₂ O ₃	10.0 to 17.0
K ₂ O	6.0 to 15.0
Na ₂ O	5.0 to 11.0
CaO	2.0 to 7.0
BaO	0 to 5.5
SrO	0 to 8.5
TiO ₂	0.2 to 2.0
ZrO ₂	0 to 3.0
P ₂ O ₅	2.0 to 5.0
CeO ₂	0 to 1.0

4. Process for the production of opalescent glass according to any one of claims 1 to 3, wherein a glass is prepared which contains the components according to any one of claims 1 to 3, and the prepared glass is optionally subjected to a heat treatment in the temperature range from 950 to 1100°C.
5. Process according to claim 4, wherein the heat treatment is carried out for 15 minutes to 4 hours.
8. Opalescent glass according to any one of claims 1 to 3 when used as dental material or as additive to or constituent of dental material.

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT



Invention Title:





"OPALESCENT GLASS"

The following statement is a full description of this invention including the best method of performing it known to us:-

The invention relates to opalescent glass and particularly to opalescent glass which, as a result of its chemical resistance and its processing properties, can be used in the dental field.

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The property of a material of appearing bluish-white in reflected light and red in transmitted light is called opalescence. A more exact treatment of this effect can be found for example in W. Vogel: Glaschemie, Verlag für Grundstoffindustrie, Leipzig, 1971.

To achieve the opalescence effect with industrial glass, an opacifier is often added to them. Fluorides, phosphates and borates are primarily used as opacifiers.

10

Opal glasses are for example known from DE-OS 1 496 646. The glasses described there are distinguished through a content of crystallized TiO_2 which forms its own phase and causes a clouding of the glass. The glasses are principally used as pigments in varnishes and paints and as fillers in papers, plastics and chemical fibres.

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Known from DE-PS 33 06 648 is a bioactive glass ceramic in whose micro-structure there are apatite and mica crystal phases. The glass ceramic contains no TiO_2 or ZrO_2 . It is intended in particular for prosthetic purposes, namely as bone replacement material.

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DE-PS 2 313 074 discloses phosphate-opacified opal glasses based on SiO_2 - B_2O_3 - Al_2O_3 - K_2O . It is a disadvantage with these glasses that the opalescence disappears partly or completely when the Al_2O_3 content is increased to more than 5 wt.%.
25

Finally, known from DE-PS 1 909 187 are opal glasses which are likewise free from TiO_2 and ZrO_2 . The opalescence effect of these glasses appears to be attributable to the fact that, after the desired glass objects have been formed, an in-situ phase separation takes place by heat treatment.
30

The known opal glasses do not however satisfy the requirements which are placed on a dental material. Admittedly, their opalescence effect is sufficient in many cases to imitate the opalescence of natural teeth, but they do not satisfy other requirements for dental materials. For one thing, the conventional glasses frequently contain components which are not completely safe from a physiological point of view. For another, the chemical resistance of the opal glasses is insufficient in many cases for application in the dental field. Finally, the opal glasses known to date have the disadvantage that they do not withstand usual dental processing without losing their original opalescence effect. During the dental processing, the opal glass is comminuted to give a granulate with a particle size of less than 90 μm and the granulate is then sintered at a temperature of up to 1100°C to give a dense product. Further thermal treatments are optionally carried out at up to 1100°C. After undergoing such processing, conventional opalescent glasses either become completely transparent or they crystallise out very quickly to give a white opaque material. In both cases the desired opalescence effect is completely lost.

It is therefore the object of the invention to provide an opalescent glass, a process for its production and its use, which opalescent glass has a high opalescence and an excellent chemical resistance and, moreover, can withstand the aforementioned dental processing without considerable loss of the original opalescence effect and can therefore be used as dental material.

This object is surprisingly achieved by the opalescent glass according to claims 1 to 3 and the process for its production according to claims 4 to 7 and its use according to claims 8 to 10.

~~The opalescent glass according to the invention is characterized in that it has a continuous glass phase and a discontinuous glass phase dispersed therein and comprises the following components:~~

In one aspect, the present invention is directed to opalescent glass having a continuous glass phase and a discontinuous glass phase dispersed therein and comprises the following components:

Component	Wt.%
SiO ₂	48.0 to 66.0
B ₂ O ₃	0 to 1.0
Me (III) ₂ O ₃	5.8 to 20.0
Me (I) ₂ O	6.0 to 22.0
Me (II)O	2.6 to 16.0
Me (IV)O ₂	0.5 to 10.0
P ₂ O ₅	0.5 to 5.0
CeO ₂	0 to 3.0

5 where

- a) the quantity of Me (III)₂O₃ quoted is formed of 5.8 to 20.0 wt.% Al₂O₃ and 0 to 6.0 wt.% La₂O₃;
- b) the quantity of Me (I)₂O quoted is formed of 3.0 to 15.0 wt.% K₂O, 3.0 to 12.0 wt.% Na₂O and 0 to 2.5 wt.% Li₂O;
- 10 c) the quantity of Me(II)O quoted is formed of 0 to 10.0 wt.% CaO, 0 to 7.5 wt.% BaO, 0 to 9 wt.% MgO, 0 to 3.5 wt.% ZnO and 0 to 8.5 wt.% SrO; and
- d) the quantity of Me (IV)O₂ quoted is formed of 0 to 5.0 wt.% TiO₂ and 0 to 5.0 wt.% ZrO₂.

15 with the exception of opalescent glass comprising at least 2.0 wt.% PbO.
All weight percentage data are relative to the glass.

It is preferred that the glass contain 0 to 0.9 wt.% B₂O₃. Particularly preferred are glasses which contain the following components:

Component	Wt.%
SiO ₂	53.0 to 62.0
B ₂ O ₃	0 to 0.9
Al ₂ O ₃	10.0 to 17.0
K ₂ O	6.0 to 15.0
Na ₂ O	5.0 to 11.0
CaO	2.0 to 7.0
BaO	0 to 5.5
SrO	0 to 8.5
TiO ₂	0.2 to 2.0
ZrO ₂	0 to 3.0
P ₂ O ₅	2.0 to 5.0
CeO ₂	0 to 1.0

The opalescent glass according to the invention is formed in a conventional manner and in particular by melting suitable starting materials at a temperature of 1400 to 1650°C, with the formation of a homogeneous glass melt. If the opalescence effect of the glass produced in this way is sufficient, subsequent heat treatment need not be carried out. Since, however, the intensity of the opalescence effect can in general be increased by means of the heat treatment mentioned hereinafter, treatment of this kind is preferably to be carried out. During the heat treatment, the prepared glass melt is kept for a certain period of time in the temperature range from 950 to 1100°C, after or without prior cooling to room temperature. This treatment preferably lasts 15 minutes to 4 hours.

By means of scanning electron microscopic investigation, it was proven that the glass according to the invention has a microheterogeneous structure, displaying a continuous glass phase in which a discontinuous glass phase is dispersed. The discontinuous glass phase exists in the form of drops which have an average size of about 150 to 250 nm, relative to the number

of drops. The investigations likewise showed that the size distribution of the drops is narrow.

5 Surprisingly, it is possible to expose the glass according to the invention to the conditions which prevail during dental processing without the opalescence effect becoming impaired. The dental processing of the glass according to the invention as dental material involves that a granulate with a particle size of preferably less than 90 μm is formed from the glass and this granulate is then sintered together at temperatures of up to 1100°C, preferably 880 to 1070°C. Two to four further thermal treatments at temperatures of up to 1100°C can be appended to this sintering together. Surprisingly, the glass according to the invention survives all these conditions without loss of the opalescence effect. Rather, it was established that in some cases the conditions of the dental processing even led to an increase in the opalescence effect. The glass according to the invention is therefore clearly superior to the glasses known to date which, under the dental processing conditions described, become completely transparent or very quickly crystallize out to a white opaque material, the result in both cases being a loss in the opalescence.

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25 The high opalescence of the glasses according to the invention is all the more surprising since they contain relatively large quantities of Al_2O_3 , namely 5.8 to 20.0 wt.%. With the silicate glasses known from DE-PS 2 313 074, such quantities of Al_2O_3 lead to a reduction or a complete disappearance of the opalescence effect.

30 In addition to a stable opalescence effect, the glasses according to the invention are also characterized by an excellent chemical resistance and by a linear expansion coefficient suitable for dental applications. The glasses according to the invention can therefore be used in an advantageous manner for dental applications. For this, the glasses can themselves be used as

5 dental material or as a component of or additive to dental materials. The glasses according to the invention are particularly preferably used together with silicate glasses and silicate glass ceramics. Alone or combined with other compatible additives, the glasses according to the invention can be granulated as described and then sintered to give dense dental products, such as inlays, onlays, crowns or coating ceramics on metal. It is also possible to use the opalescent glass according to the invention as a filler for inlays, onlays or those moulded articles from which computer-milled dental replacement parts are produced.

10 The invention is further explained with reference to the following examples.

Examples

Examples 1 to 24

15 27 opalescent glasses according to the invention, which had the compositions shown in the following Table I, were prepared by melting at temperatures from 1400 to 1650°C, cooling to temperatures from 1100°C to room temperature and optionally by subsequent heat treatment for 15 minutes to 4 hours in the temperature range from 950 to 1100°C.

20 Glasses 5, 8, 9, 14, 15, 20 and 22 and glasses 25, 26 and 27 are preferred.

Composition of the glasses

Glass no.

Component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
SiO_2	57,7	57,7	53,1	59,4	56,0	48,9	55,0	56,0	55,6	55,5	49,0	60,6	62,0	55,1	55,3	56,1	54,9	56,1	57,8	61,6	54,8	53,6	59,3	65,3	53,4	53,9	55,9
H_2O_3	---	1,0	---	1,0	0,2	1,0	---	---	0,9	1,0	---	---	---	0,4	0,2	-	1,0	-	-	---	0,9	1,0	---	0,2	0,2	0,2	
Al_2O_3	13,5	13,7	12,8	14,3	15,8	13,9	12,8	10,4	13,1	5,9	19,3	12,8	14,0	12,8	16,1	13,3	13,2	12,5	13,6	14,5	12,9	12,6	13,9	5,8	16,5	16,6	16,6
La_2O_3	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	6,0	---	---	---	---	---	---	---	---	---
K_2O	7,1	7,3	7,0	7,8	11,0	7,3	7,0	10,0	7,0	8,0	3,1	3,0	7,9	6,9	11,9	7,1	7,9	7,2	7,4	7,9	7,0	6,9	7,6	3,3	14,5	14,3	10,3
Na_2O	5,9	5,9	5,6	5,9	9,6	5,9	11,0	7,7	5,8	6,7	3,6	3,0	4,8	10,6	9,1	5,8	5,7	5,8	5,8	6,4	5,7	5,6	7,3	4,4	7,1	7,5	7,6
Li_2O	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	2,5	---	---	---	---	---	---	---	---
CaO	5,9	5,9	5,8	---	2,6	5,9	5,6	5,3	5,8	10,0	7,6	7,7	6,4	5,6	2,6	5,8	5,7	5,9	6,1	6,5	5,8	5,7	3,5	---	2,6	2,6	5,6
BaO	4,7	4,7	4,5	4,8	---	4,7	---	4,2	4,9	5,9	7,5	4,4	---	---	---	4,9	4,8	---	---	---	4,6	---	---	4,8	---	---	---
MgO	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	8,2	---	---	---
SrO	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	8,5	---	---	---	---	---
TiO	---	---	3,5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
TiO_2	---	1,3	1,8	1,4	0,3	5,0	1,2	1,8	1,4	1,5	2,4	1,7	1,4	1,1	0,3	1,4	1,4	1,3	1,4	0,5	1,3	1,3	1,4	1,9	0,3	0,3	0,3
ZrO_2	2,6	---	3,0	2,7	1,9	5,0	2,4	2,4	2,8	2,9	5,0	3,3	2,8	2,5	1,9	2,8	2,7	2,6	2,7	---	2,6	2,5	2,8	3,6	1,9	1,9	0,9
P_2O_5	2,4	2,5	2,9	2,7	2,6	2,4	5,0	2,2	2,7	2,7	2,5	3,5	0,6	5,0	2,6	2,8	2,7	2,5	2,6	2,7	2,4	2,4	3,3	2,7	2,6	2,6	2,6
CaO_2	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	3,0	---	---	---	0,9	---

The properties of different selected glasses according to the invention are detailed in the following Table II.

Table II
Properties of selected glasses

Glass no.	Heat treatment of the starting glass after pouring of the melt [°C/h]	Sintering temperature range for the production of rods for α -measurement [°C]	Linear expansion coefficient α (100-500°C) [°C ⁻¹]	T _g [°C]	T _f [°C]
4	none	1000 / 1020	8.1 x 10 ⁻⁶	677	778
5	950/0.5 h	960 / 980	15.1 x 10 ⁻⁶	553	670
6	none	960 / 980	9.1 x 10 ⁻⁶	677	750
8	none	900 / 920	10.3 x 10 ⁻⁶	598	664
9	950/1 h	1020 / 1020	8.5 x 10 ⁻⁶	654	740
9	1060/1 h	1020 / 1020	8.4 x 10 ⁻⁶	657	745
13	1050/2 h	960 / 980	8.6 x 10 ⁻⁶	672	748
14	none	960 / 980	10.8 x 10 ⁻⁶	634	710
15	1000/1 h and 900/1 h	960 / 980	16.8 x 10 ⁻⁶	552	697
16	1000/1 h	1020 / 1020	8.7 x 10 ⁻⁶	682	766
18	none	1030 / 1050	8.6 X 10 ⁻⁶	699	788
19	none	840 / 860	9.5 x 10 ⁻⁶	561	629
20	none	1000 / 1020	8.6 x 10 ⁻⁶	657	745
26	1040/1 h	980 / 1000	18.2 x 10 ⁻⁶	580	770
27	950/0.5 h	960 / 980	17.6 x 10 ⁻⁶	628	800

T_g = Transformation temperature
T_f = Softening temperature

Test-rods were prepared for the determination of the linear thermal expansion coefficient α . To this end, the selected glasses according to the invention were granulated to particle sizes of < 90 μm and the obtained glass granulate sintered within the temperature ranges given in Table II to give rods. As Table

5 II shows, the expansion coefficient can be controlled, depending on the glass composition, between 8.1×10^{-6} and $18.2 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, measured in the temperature range of 100 to 500°C. Depending on the dental application, for example if the glass is to be used as additive for a baked-on ceramic or as additive for a pressed glass ceramic, it is therefore possible to produce a glass with a compatible expansion coefficient.

10
15 In this connection, glasses 5, 15, 25, 26 and 27 are to be emphasized in particular. Despite a very high expansion coefficient, they characterize themselves through an adequate to very good opalescence. With traditional glasses, high expansion coefficients can frequently only be attained with very marked losses of the opalescence effect. The glasses according to the invention, however, combine both properties in an advantageous way.

20 Table II also shows that the transformation ranges of the glasses lie between approximately 550 and 700°C and the softening temperatures between approximately 620 and 800°C.

Quoted in the following Table III are qualitative values for the opalescence effect of the glasses according to the invention and values for their chemical resistance.

Table III
Properties of selected glasses

Glass no.	Heat treatment of the starting glass after pouring of the melt [°C/h]	Sintering temperature range for the production of small test plates [°C] (holding time 1 min)	Mass loss after treatment with acetic acid (according to ISO 6872-1 ⁸⁴) [%]	Opalescence
4	none	1020 / 1040	0.0059	good
5	960/1 h	980 / 1020	0.0198	adequate
6	none	980 / 1000	0.0143	adequate
8	none	920 / 940	0.0058	adequate
9	950/1 h	1000 / 1000	0.0052	adequate
9	1060/1 h	1000 / 1020	0.0084	very good
13	1050/2 h	1000 / 1020	0.0153	adequate
14	none	1000 / 1020	0.0092	very good
15	950/1 h	980 / 970	0.0057	very good
16	1000/1 h	1020 / 1000	0.0081	good
18	none	1050 / 1070	0.0060	adequate
19	none	880 / 900	0.0090	good
20	none	1020 / 1040	0.0063	very good
26	1040/1 h	1010 / 1030	0.0348	adequate
27	950/0.5 h	980 / 1000	0.0218	good

For the determination of the chemical resistance of the glasses according to the invention and their opalescence, small test plates were produced from the opalescent glass by sintering together granulate with a particle size of less than 90 µm within the temperature ranges given in Table III to give small plates with a diameter of 12 mm and a thickness of 1 mm. The granulate was held at the sintering temperature for 1 min.

5

5 To estimate the chemical resistance, the mass loss of the small test plates was determined after treatment with 4 % acetic acid in a Soxhlet apparatus according to ISO 6872 - 1984. As the values given in Table III show, all glasses satisfied the standard of less than 0.05 % mass loss. In view of a very low mass loss, the glasses preferred are nos. 4, 8, 15, 18 and 20.

10 The opalescence effects of the individual glasses were compared with one another and appraised qualitatively. The results of the appraisal are to be found in Table III. Because of their high opalescence, the glasses preferred are nos. 5, 9 (with heat treatment), 14, 15 and 20.

15 In order to also be able to determine quantitatively the opalescence of the glasses according to the invention, the so-called contrast value (CR-value) was determined for three different glasses according to British Standard Institution BSI 5612, 1978, paragraph 8.11. To this end, a light-optical measurement, compared with a white and black standard sample was carried out with a Minolta CR-300 apparatus on glass test plates having a diameter of 12 mm and a thickness of 1 ± 0.025 mm.

20 The small glass test plates were again produced by sintering the glass granulate, and the measured contrast value and the qualitatively estimated opalescence are given in the following Table IV.

Table IV

Glass no.	Heat treatment of the starting glass [°C/h]	Sintering conditions for the production of small test plates [°C/min]	CR-value	Opalescence qualitatively
15	1000/0.25	1020/1	0.8559	very good
16	1000/1	1020/1	0.7267	good
17	1000/1	1020/1	0.8524	very good

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Opalescent glass having a continuous glass phase and a discontinuous glass phase dispersed therein, and comprising the following components:

Component	Wt.%
SiO ₂	48.0 to 66.0
B ₂ O ₃	0 to 1.0
Me (III) ₂ O ₃	5.8 to 20.0
Me (I) ₂ O	6.0 to 22.0
Me (II)O	2.6 to 16.0
Me (IV)O ₂	0.5 to 10.0
P ₂ O ₅	0.5 to 5.0
CeO ₂	0 to 3.0

5 where

- a) the quantity of Me (III)₂O₃ quoted is formed of 5.8 to 20.0 wt.% Al₂O₃ and 0 to 6.0 wt.% La₂O₃;
- b) the quantity of Me (I)₂O quoted is formed of 3.0 to 15.0 wt.% K₂O, 3.0 to 12.0 wt.% Na₂O and 0 to 2.5 wt.% Li₂O;
- 10 c) the quantity of Me(II)O quoted is formed of 0 to 10.0 wt.% CaO, 0 to 7.5 wt.% BaO, 0 to 9 wt.% MgO, 0 to 3.5 wt.% ZnO and 0 to 8.5 wt.% SrO; and
- d) the quantity of Me (IV)O₂ quoted is formed of 0 to 5.0 wt.% TiO₂ and 0 to 5.0 wt.% ZrO₂,

15 with the exception of opalescent glass comprising at least 2.0 wt.% PbO.

2. Opalescent glass according to claim 1, comprising 0 to 0.9 wt.% B₂O₃.

3. Opalescent glass according to claim 1 or 2, comprising the following components:

Component	Wt.%
SiO ₂	53.0 to 62.0
B ₂ O ₃	0 to 0.9
Al ₂ O ₃	10.0 to 17.0
K ₂ O	6.0 to 15.0
Na ₂ O	5.0 to 11.0
CaO	2.0 to 7.0
BaO	0 to 5.5
SrO	0 to 8.5
TiO ₂	0.2 to 2.0
ZrO ₂	0 to 3.0
P ₂ O ₅	2.0 to 5.0
CeO ₂	0 to 1.0

4. Process for the production of opalescent glass according to any one of claims 1 to 3, wherein a glass is prepared which contains the components according to any one of claims 1 to 3, and the prepared glass is optionally subjected to a heat treatment in the temperature range from 950 to 1100°C.

5 5. Process according to claim 4, wherein the heat treatment is carried out for 15 minutes to 4 hours.

6. Process according to claim 4 or 5, wherein the prepared glass is granulated and the granulate is sintered together at temperatures of up to 1100°C.

10 7. Process according to claim 6, wherein the sintering together is effected by heating the granulate to 880 to 1070°C.

8. Opalescent glass according to any one of claims 1 to 3 when used as dental material or as additive to or constituent of dental material.

15 9. Opalescent glass according to claim 8 when used as additive to silicate glasses or silicate glass ceramics.

10. Opalescent glass according to claim 8 or 9 when used as a constituent of inlays, onlays, bridges or crowns.

Dated this 22nd day of January 1997

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Abstract

An opalescent glass is described which is characterized by a continuous glass phase and a discontinuous glass phase dispersed therein, and which can be used as dental material or as a constituent of dental materials.

