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### A NEW SERIES OF X-RAY-OPAQUE REINFORCING FILLERS FOR COMPOSITE MATERIALS

by

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## A NEW SERIES OF X-RAY-OPAQUE REINFORCING FILLERS FOR COMPOSITE MATERIALS

There has been a continued interest in having composite restorative materials that are radiopaque. This property would facilitate the detection of associated caries or underlying decalcified dentin and would call attention to overhanging margins, voids or other defects, should they occur in the restoration.

The presence of major proportions of inorganic reinforcing fillers in direct filling, polymeric materials,<sup>1</sup> now called composite materials,<sup>2</sup> suggested the possibility of making such dental materials opaque to X-rays. This can be done by the incorporation of an element of relatively high atomic weight into the glass that constitutes part or all of the reinforcing filler. Many of the heavier elements, such as those containing partly-filled d orbitals ( $\text{Zn}^{2+}$  being an exception),<sup>3</sup> are not suitable because of the color they impart to the glass or, in the case of lead, because of the possibility of discoloration through the formation of sulfides.

Tensile stresses develop in composites upon hardening,<sup>4</sup> and water penetrates such materials.<sup>5</sup> Alkaline elements in silicate glasses make them more hygroscopic<sup>6</sup> and tend to form a strongly alkaline water film.<sup>7</sup> Assuming that these alkaline elements are washed<sup>7</sup> or otherwise removed from the surface of the filler before it is treated with an appropriate organofunctional silane coupling agent,<sup>8</sup> it is reasonable to expect that diffusion from the interior of the glass to the surface (or silane interface region) would be more probable for smaller, monovalent ions than for larger polyvalent ions.

Alkaline conditions at the interface generated by alkali elements, as well as the presence of fluoride ion might catalyze the hydrolysis (depolymerization) of the interfacial silica, polysiloxane or both.<sup>9,10</sup> Thus, in the presence of moisture and internal residual tensile stresses (and other stresses exerted on surface particles), a form

of stress corrosion<sup>7</sup> might increase the rate of surface material loss, due to normal wear and tear, and decrease the bulk strength of the composite material.<sup>11</sup>

The known commercially-available glasses containing barium have refractive indexes that are above those desirable for the purposes of this application, contain alkali elements, such as sodium, potassium, or lithium, or have such a high barium content so as to warrant mechanical admixture with other filler materials.<sup>12</sup> Consequently, it was important to determine whether clear, radio-paque glasses having the proper refractive index could be formulated for use as the sole or major reinforcing filler, using only polyvalent elements. The purpose of this paper is to describe barium-containing glasses, some of which contain no monovalent elements, developed since a previous report<sup>12</sup> of this continuing study.



Materials and Methods\*

The formulations of the glasses are given in the tables. The glasses were melted in an electric furnace in a platinum crucible 6.35 cm in diameter by 7.62 cm deep. After the batch was melted, the melt was stirred with a motor-driven platinum 10%-rhodium double-bladed propeller-type stirrer to obtain homogeneity. The time of melting and fining depended on the characteristics of the melts as did the maximum temperature used. Usually about 1.5 hours was required to fill the crucible and about the same length of time was required for stirring the melt. The maximum temperature used was about 1650°C. When possible, a small amount of the molten glass was poured into a metal mold and the rest was poured into clean water to quench the glass and break it up into small pieces so that it could be conveniently ground in a jar mill (dry gaged).

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\* Certain commercial references are made in this paper to specify adequately the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards.

The refractive indexes were determined with a microscope by the oil-immersion method. The coefficients of thermal expansion (between about 40 and 100°C) were measured on an automatic recording apparatus.<sup>13</sup>

The powder of one of the glasses (M17-1445) was passed through an oxygen-acetylene flame, converting the irregular shaped particles into spheres. This was done because the use of rounded particle shapes and an intermittent size-distribution (gap grading) has been shown<sup>14</sup> to give an increase in the powder-to-liquid ratio, resulting in composites with lower thermal expansion coefficients, higher moduli of elasticity, and other desirable properties.

### Results

The data given in the tables demonstrate that clear and colorless glasses can be prepared having refractive indexes close to those of the polymeric binders of current and experimental composite materials with  $n_D^{25}$  about 1.54 to 1.55. The refractive index of the polymeric binders varies somewhat depending on its chemical composition, extent of polymerization, water content, and other factors.

Glasses containing about 7 mole percent of barium (Table 1), if used as the sole reinforcing filler for a dental composite material, would yield restorations with about the same minimal radiopacity as did the mixture of fillers utilized in a previous clinical study.<sup>15</sup> Voids in such restorations might be misdiagnosed as caries.<sup>15</sup> This, and the need to add other ingredients such as zinc oxide (Table 1) to obtain the desired refractive index, suggested the use of an increased barium content to give the desired refractive index (Tables 1 and 2) and an increased radiopacity.

The coefficients of thermal expansion of four of the glasses were 3.8, 4.1, 3.3, and 4.9 ppm/°C between 40 and 100°C for F1537, F1541, F1542, and K-17, respectively.

The portion of glass M17-1445 powder that was passed through an oxygen-acetylene flame did not change perceptibly in refractive index during the transformation into spherical particles. However, comparison of it with F1542, having the same batch composition (Table 1), again<sup>12</sup> pointed out



the sensitivity of refractive index to thermal history in glasses containing fluoride.

### Discussion

The need for a predictable and stable refractive index in a radiopaque glass, a desire to eliminate monovalent elements, and other considerations led to the study of the compositions given in Table 2. The rationale leading to the study of these particular formulations follows.

After the available information<sup>16-22</sup> bearing on the subject was brought together, the following concept emerged. At least in silica glasses, in the presence of approximately stoichiometric concentrations of elements of sufficiently low electronegativity,<sup>23</sup> including barium,<sup>20</sup> aluminum atoms are converted from a coordination of six (octahedral) to four (tetrahedral), and residually, boron atoms from a coordination of three (planar) to four (tetrahedral).

The transformation from three to four coordination in the case of boron results in a reduced thermal ex-

pansion coefficient.<sup>20</sup> In view of the similarity of the other "anomalous" characteristics in the transformation from six to four coordination in the case of aluminum,<sup>18</sup> it is reasonable to expect a similar reduction in thermal expansion coefficient. The lowest possible thermal expansion coefficient is desirable in the reinforcing filler since this helps lower the thermal expansion of the composite material.<sup>14</sup>

Present evidence<sup>16-22</sup> suggests that in the four-coordinated configurations, aluminum and boron oxides can enter into the tetrahedral silicon-oxide framework of the glass structure. This might be expected to localize the large, interstitial, eight-coordinated  $Ba^{2+}$  ions to maintain electrical balance with the  $[AlO_4]^-$  and  $[BO_4]^-$  segments. It is hoped that this effect will provide hydrolytic stability to this type of glass and to its products.

These considerations led to the stoichiometric formulations seen in Table 2 and Figure 1. What was left to determine, on an empirical basis, was the best  $BaO \cdot B_2O_3$  to  $BaO \cdot Al_2O_3$  ratio

along an isofract of the desired refractive index. A promising region was found between the extremes of maximal  $\text{BaO} \cdot \text{B}_2\text{O}_3$ , which is in a region of liquid immiscibility,<sup>24,25</sup> and maximal  $\text{BaO} \cdot \text{Al}_2\text{O}_3$ , having a high liquidus temperature<sup>26</sup> and viscosity. For example, compositions K-19 and K-17 had viscosities low enough for dry gaging,<sup>27</sup> apparently had low liquidus temperatures, and were resistant to devitrification.

Future studies should determine the feasibility of preparing spherical particles of this kind of glass and obtaining optimal size distribution.<sup>14</sup> Its resistance, after preliminary washing and silane treatment, to leaching of barium constituents should be determined, in view of the toxicity of soluble barium compounds.<sup>28</sup>

### Conclusions

X-ray-opaque glasses containing no monovalent elements can be prepared that are clear and colorless and that have refractive indexes suitable for use in translucent composite restorative materials. The batch composition in mole percent for one such glass, for example, is:  $\text{SiO}_2$ , 66;  $\text{BaO}$ , 17;  $\text{B}_2\text{O}_3$ , 11, and  $\text{Al}_2\text{O}_3$ , 6.

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TABLE 1

COMPOSITIONS AND PROPERTIES OF GLASSES ARRANGED ACCORDING TO  
DECREASING REFRACTIVE INDEXES

Glass No.	Melting tempera- ture, °C	Composition of Batch (mole %)					Refractive Index $n_D$	Appearance
		Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	BaF <sub>2</sub>	BaO	SiO <sub>2</sub>	Other	
F1539	1650+	7	--	--	7	65	7 MgO 7 TiO <sub>2</sub> 7 ZrO <sub>2</sub>	1.592± Heterogeneous
F1537	1600	7	5	--	11	63	14 ZnO	1.558 Faint trace of crystals
F1540	1500- 1600+	7	5	--	12	66	10 ZnO	1.550 Faint trace of crystals
F1541	1390- 1480	7	5	12	--	62	14 ZnO	1.546 Clear; faint trace of crystals
F1533	1550	10	--	--	17	73	----	1.543 Seeds and microcrystals
F1538	1600	7	10	--	11	63	9 ZnO	1.541 Crystals; scatter in $n_D$
F1536	1600+	7	5	--	13	69	5 ZnO	1.536 Few, if any, crystals
F1542	1500- 1580	4	4	8	--	70	14 ZnO	1.532 Clear
M17-1445*	1600	4	4	8	--	70	14 ZnO	1.514 <sup>±</sup> Opaline unless rapidly quenched
F1543	1610	5	6	11	--	78	----	1.500 Contained some crystals
F1528	1550	---	17	--	7	66	10 AlPO <sub>4</sub>	--- Did not melt
F1529	1550	2.5	17	--	7	66	7.5 P <sub>2</sub> O <sub>5</sub> <sup>†</sup>	--- Did not melt
F1530	1550	4	17	--	7	60	12 P <sub>2</sub> O <sub>5</sub> <sup>†</sup>	--- Did not melt
F1531	1550	6	17	--	7	52	18 P <sub>2</sub> O <sub>5</sub> <sup>†</sup>	1.498 Opaline <sup>‡</sup> (annealed) 1.492 Clear (quenched)



TABLE 1 (continued)

\* Melt M17-1445 prepared in the Experimental Melting Department of Corning Glass Works was larger than the prior experimental melt F1542. The larger batch was melted in a covered platinum crucible, thus probably retained more fluoride. A higher fluoride content might well explain the lower refractive index and the greater tendency to opalize.

† As  $\text{Al}(\text{PO}_3)_3$

# Had crystals of  $n_D$  about 1.53.

TABLE 2

COMPOSITIONS AND PROPERTIES OF GLASSES IN WHICH BaO IS EQUI-  
MOLAR TO  $\text{Al}_2\text{O}_3$  PLUS  $\text{B}_2\text{O}_3$

Glass No.	Melt Data		Composition of Batch (mole %)				Refractive Index $n_D$	Appearance in Microscope
	Maximum Temperature, °C	Description	$\text{Al}_2\text{O}_3$	$\text{B}_2\text{O}_3$	BaO	$\text{SiO}_2$		
F1524*	1550	Rather viscous; poured into water; seedy†	4	13	17	66	1.552±	Some birefringent particles
K-19	1585	Fluid; poured into water; free of seeds; no crystals formed in 7 days at 1100°C	6	11	17	66	1.552±	Traces of birefringence
K-20	1550	Rather viscous; poured into water; some seeds	8.5	8.5	17	66	1.550	Practically no birefringence
F1534	1550	Viscous; some seeds	10	7	17	66	1.550	Traces of birefringence
K-16	1550	Rather viscous; poured into water; seedy; crystals formed in 1.5 days at 1100°C; liquidus about 1290°C	4.5	12	16.5	67	1.549	Traces of birefringence
K-18	1575	Viscous; crucible quenched in water	9.5	7	16.5	67	1.547	Faint traces of birefringence

TABLE 2 (continued)

Glass No.	Melt Data		Composition of Batch (mole %)				Refractive Index $n_D$	Appearance in Microscope
	Maximum Temperature, °C	Description	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	BaO	SiO <sub>2</sub>		
# 5	1570	Fluid; poured into water; free of seeds; liquidus >1340°C; opaline unless very rapidly quenched	3	13	16	68	1.547	Faint traces (if any) of birefringence
F1532	1600+	Very viscous; quenched in crucible; seedy	16	--	16	68	1.547	Some birefringent particles
K-17	1550	Rather viscous; poured into water; seedy; no crystals formed in 6 days at 1100°C	7	9.5	16.5	67	1.546	Traces of birefringence
# 3	1575	Viscous; quenched in crucible; seedy	8	8	16	68	1.545±	Faint traces of birefringence
# 1	1570	Very viscous; quenched in crucible; seedy	13	3	16	68	1.544	Traces of birefringence
# 2	1600	Very viscous; quenched in crucible; seedy	11	5	16	68	1.543	Faint traces (if any) of birefringence

TABLE 2 (continued)

Glass No.	Melt Data		Composition of Batch (mole %)				Refractive Index $n_D$	Appearance in Microscope
	Maximum Temperature, °C	Description	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	BaO	SiO <sub>2</sub>		
# 4	1600	Poured into water; some seeds	5	11	16	68	1.543±	Traces of birefringence
F1535	1600+	Quenched in crucible; some seeds	8	6	14	72	1.532±	Some birefringent particles

\* The data on Glass No. F1524 were taken from the literature;<sup>1,2</sup>  
the other data have not been published previously

† Contained small bubbles (seeds)





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