USE OF THE FINING METHOD IN THE PRODUCTION OF CERAMIC FRITS

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ABSTRACT

The removal of bubbles from a glass melt is one of the major technological problems in glass melting. It is usually solved by holding the glass for some time at a temperature somewhat bellow the highest melting temperature, and by adding certain minor constituents to the original glass batch, what is called fining. *Bubbles can be removed from a melt by two ways: they can rise to the surface or the gas in them can dissolve in the glass.*

1. INTRODUCTION

The solubility of carbon dioxide in sodium silicate glasses increases rapidly below about 1100°C or 1200°C, depending on composition[1-3]. Above these temperatures, the solubility did not change as much with temperature and for several glasses is about 10-4wt%/atm, which is the amount of physical solubility expected. The entity formed in the glass is probably not a simply sodium carbonate molecule, but some more complex combination of these ions with the silicate lattice[4]. The solubility of carbon dioxide in a $Na_2O_2SiO_2$ melt is proportional to pressure bellow atmospheric pressure. There is a large increase in solubility of carbon dioxide as the amount of Na_2O in the melt is increased above 25%. The increase for melts above 35% Na_2O is much greater. Apparently in melts of higher Na_2O, the Na_2O activity increases sharply. This increase can also be deduced from the sharp increase in the volatility of soda in these melts[1,5]. The reaction of carbon dioxide with sodium borate melts shows a similar increase in solubility as the temperature decreased; however, the enthalpy of solution is considerably lower than for the silicates[1,6].

Sulfur dioxide also dissolves in silicate melts. Its reaction to an alkali sulfate is complicated by the need for oxygen to form the sulfate from sulfur dioxide. Thus its solubility in alkali silicates increases as the alkali concentration increases[1,2-7-9] and decreases as the temperature increases; however, under reducing conditions the solubility is much reduced. It has long been known that furnace gases are beneficial for the weathering properties of glass. These effects arise from the reaction of sulfur dioxide in the gases with the glass surface. Water and oxygen, as well as sulfur dioxide, must be present. The "dealkalization" reaction is an ion exchange that is made possible by the removal of the sodium ion as sodium sulfate[1,10]. The rate of formation of sodium sulfate is proportional to the square root of time, and is controlled by the interdiffusion of hydrogen and sodium ions in the glass. The rate of weathering of a glass with a dealkalized layer is less because weathering requires ion exchange with sodium ions.

Fining, or the removal of bubbles from a glass melt, is one of the major technological problems in glass melting. It is usually solved by holding the glass for some time at a temperature somewhat bellow the highest melting temperature, and by adding certain minor constituents to the original glass batch. Bubbles can be removed from a melt by two ways. They can rise to the surface or the gas in them can dissolve in the glass. The rate of rise is given by[1]:

$$dh/dt = 2\rho g R^2 / 9\eta \qquad (1)$$

Where ρ is the density of glass, g is the gravitational constant, R is the bubble radius, and η is the viscosity of the glass. For a viscosity of 100P, typical for melting temperatures, the rate of rise of bubbles 0.1mm in diameter is about 10cm/day, which is too small to eliminate them from a normal glass furnace. Thus small bubbles can be removed from glass melts only by dissolution of their gas into the glass melt, although larger bubbles can rise to the surface[1].

Arsenic oxide is a common fining agent added to glass to help remove bubbles. For many years it was thought that the arsenic released oxygen at glass melting temperatures, which swept out the bubbles in the glass. But such a mechanism would not eliminate small bubbles, and the objective of arsenic and antimony oxide additions to the glass is to aid in removal of fine bubbles, rather to generate more gas[1,11-13]. In actual glass-melting practice carbonates are the usual source of sodium and calcium oxides. So carbon dioxide may be present in bubbles in glass as well as oxygen and nitrogen from air. Potassium and sodium nitrates decompose complete to the oxides between 400°C and 800°C, but only above 900°C the arsenic compound begin to decompose[1]. The role of the added nitrates is probably to increase the amount of oxygen in the bubbles at the expense of nitrogen. The nitrates decompose before the glass becomes molten, increasing the proportion of oxygen in the mixed batch materials and consequently in the bubbles of entrapped gas. Nitrates in the glass batch improve fining rates by replacing nitrogen in entrapped gas by oxygen[1].

Sulfates are often used as fining agents. In soda-lime glasses sulfate additions can either speed or retard fining, depending on the composition of the glass[14]. When the ratio Na_2O/SiO_2 is great, fining is retarded, whereas for lower ratios it is enhanced, at least for silica concentrations from 69% to 76%. The presence of sulfide in the more reduced glasses means it can react with oxygen and carbon dioxide from bubbles and therefore enhance their removal from the bubbles[15]. An increase in the sulfate level in a soda-lime glass reduces the retentions of nitrogen[16]. However, when the sulfate is replaced by sulfide (more reducing conditions) nitrogen retention increases, showing the effect of state of oxidation of the glass on reaction of nitrogen with it, and indicating that sulfide also helps to remove nitrogen from bubbles[1].

2. MATERIALS AND METHODS

Quartz, feldspar, calcite, kaolin, boric acid and ZnO were used as raw materials in the melting of the frit. The compositional formula is shown in table 1 (std.). Potassium nitrate and sodium sulfate were used as the fining agents over the compositional formula of the standard frit. Eight frits were melted: the standard and seven frits using the fining agents, table 1. The frits were melted at 1500°C for 1h and quenched in water. Each frit was ground in eccentric mill (35min milling time, 6% residue on a 45μm sieve) with the addition of 9% of kaolin, 0.2% of sodium tripolyphosphate, 0.2% of carboxymethylcellulose and 40% of water, forming glaze slurries with controlled density (1.80g/cm^3) and viscosity of (40s flowing time in *Ford cup n° 4*). The glazes were applied in layers of 0.6mm thickness over previously engobed tiles and fired at 1140°C for 30min in an industrial roller kiln ("monoporosa" fast firing heat treatment). The surface aspect of all glazes was analyzed by spectrophotometry (400nm to 700nm, D65, 10°) and the thermal behaviour by dilatometry (10°C/min on air). The Kubelka-Munk theory was used to determine the covering capacity of the glazes.

COMPOSITION (wt%)	STD.	A	B	C	D	E	F	G
SiO_2	63.5	63.5	63.5	63.5	63.5	63.5	63.5	63.5
CaO	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4
Al_2O_3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3
$B2O_3$	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Na_2O	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
K2O	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
ZnO	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4
MgO	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Na_2SO_4	-	0.1	0.5	0.25	0.1	0.5	0.5	-
KNO_3	-	4.0	1.5	2.5	1.5	4.0	-	4.0

Table 1. Compositional formulas

3. RESULTS AND DISCUSSION

Figure 1 shows the reflectance curves for all glazes formed from the standard and modified frits and for the engobe. As expected the engobe is the whiter sample, with the higher reflectance for all wavelengths. The standard glaze shows an intermediate reflectance, with 59% of average reflectance.

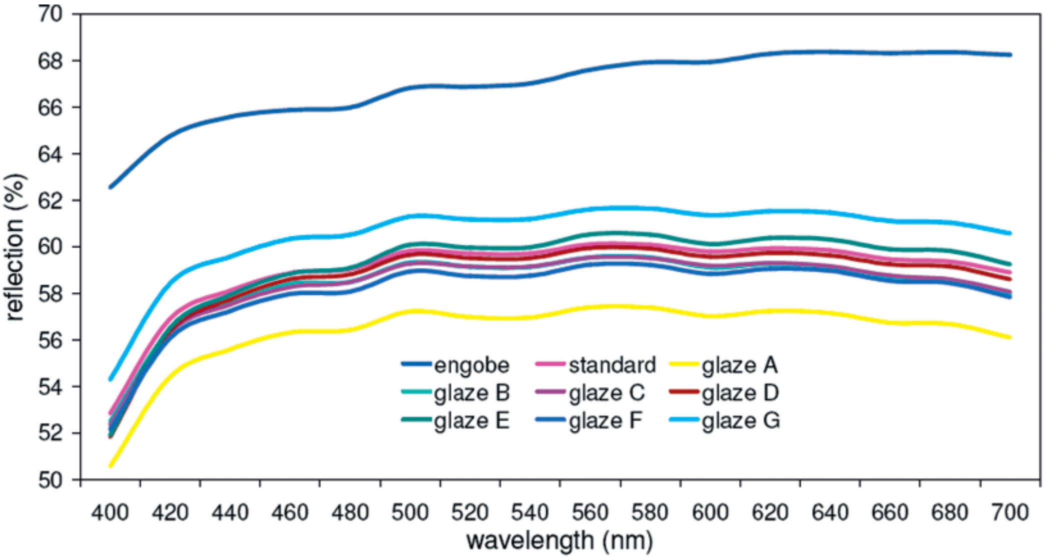

Figure 1. Reflectance spectra for engobe, standard glaze and test glazes

Except glazes E (0.5% Na_2SO_4 and 4.0% KNO_3) and G (4.0% KNO_3) all glazes show a lower reflection when compared with the standard glaze, figure 1. Figure 2 shows the K/S ratio spectra for all glazes. Once again except glazes E and G all glazes show higher values for the K/S ratios in relation to the standard glaze and the engobe. Small values for the K/S ratios mean a higher relation between absorption and scattering of light in the object, i.e., the object is more opaque with a higher covering effect.

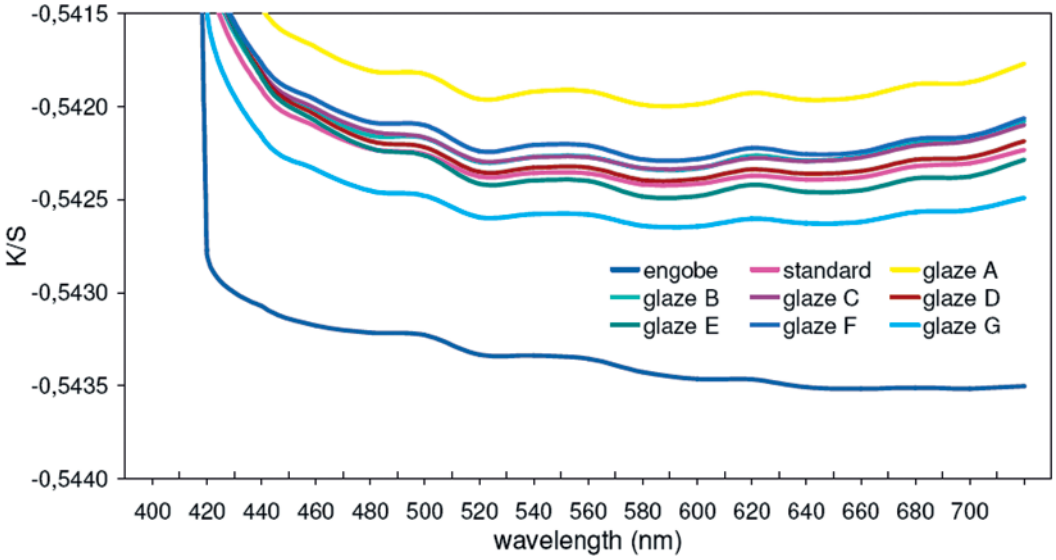

Figure 2. K/S ratio spectra for engobe, standard glaze and test glazes

Except glazes E and G all glazes have presented a lower covering effect than the standard glaze, being more transparent than the standard, therefore proving the fining effect on ceramic glazes. There is a maximum addition of fining elements to promote degasification: the fining effect is more intense when using sodium sulfate by itself, but the use of potassium nitrate by itself has caused lack of transparency in the glaze. Also, the combination of Na_2SO_4 and KNO_3 (glaze A) promoted the best results. Glaze G, with the maximum amount of KNO_3, and glaze E, with the maximum amount of both fining elements, resulted in the worst results, showing there is a limit in the use of fining elements.

The formulations with the maximum amount of sodium sulfate, glaze F, and the formulation with the lower amount of sodium sulfate but the maximum amount of potassium nitrate, glaze A, have presented the best results.

Finally, there was not a great change in the thermal behaviour of the glazes with the addition of fining elements, table 2. The major difference occurred for the glaze F due the addition of 0.5% of sodium sulfate, causing a small diminution in the glaze melting temperature. So, the fining agents can be added to a specific glaze composition without great changes in the glaze final characteristics.

GLAZE	Tg (ºC)	Tm (ºC)
standard	658	731
A	656	729
B	660	732
C	652	726
D	659	740
E	655	727
F	654	717
G	658	732

Table 2. Glass transition temperature (Tg) and melting temperature (Tm) for the studied glazes in comparison with the standard glaze

4. CONCLUSION

The fining process is efficient in the production of ceramic frits. When used adequately the fining agents produce glazes with higher transparency due the elimination of pores formed by degasification of gases saturated in the processed frits. The final characteristics of the glazes formed by frits processed with fining agents are similar to the standard glaze.

Finally, the use of fining agents depends on the glaze (frit) composition. The objective is to use a fining agent that reduces the gas content of a determined glass, so, the fining agent must decomposes in a gaseous system that enhances the removal of saturated gases in the glass system of interest.

REFERENCES

[1] Doremus, R.H. Glass Science. 2nd ed. New York: Wiley-Interscience, 1994.

[2] Pearce, M.L. J. Am. Ceram. Soc. 47 (1964) 342.

[3] Kroger, C.; Lummerzheim, D. Glastech. Ber. 38 (1965) 229.

[4] Strnad, Z. Phys. Chem. Glasses 12 (1971) 152.

[5] Preston, E.; Turner, W.E.S. J. Soc. Glass Technol. 18 (1934) 143.

[6] Fincham, C.J.B.; Richardson, F.D. Proc. Roy. Soc. A223 (1954) 40.

[7] Turkdogan, E.T.; Pearce, M.L Trans. AIME 227 (1963) 940.

[8] Douglas, R.W.; Isard, J.O. J. Soc. Glass Technol. 33 (1949) 289T.

[9] Greene, C.H.; Gaffney, R.F. J. Am. Ceram. Soc. 42 (1959) 271.

[10] Greene, C.H.; Kitano, J. Glastech. Ber. 32K (1959) 44.

[11] Greene, C.H.; Lee, H.A. J. Am. Ceram. Soc. 48 (1965) 528.

[12] Slavyanskii, V.T. Gases in Glass. Moscow, 1957.

[13] Cable, M.; Harron, M.A. Glass Technol. 11 (1970) 48.

[14] Lyle, A.K. In: Travaux du IV Congres Int. du Verre. Paris: Imprimerie Chaix (1957) 93.

[15] Greene, C.H; Platts, D.R. J. Am. Ceram. Soc. 52 (1969) 106.

[16] Harding, F.L.; Ryder, R.J. Glass Technol. 11 (1970) 54.