

temperatures and rapidly cooled down in air to room temperature. As examples, the changes in density with time are shown in Table 1-a, b and c.

Table 1. Change in Density (g./cm³.) at Room Temperature with Time of Heat Treatment.

(a) 540°C			(b) 530°C			(c) 460°C		
Time (min.)	Density Increase	Density Decrease	Time (min.)	Density Increase	Density Decrease	Time (hr.)	Density Increase	Density Decrease
0	2.4887 (1)	2.4975 (2)	0	2.4887 (1)	2.4975 (2)	0	2.4887 (1)	2.5003 (3)
2.5	2.4918	2.4958	2.5	2.4916	2.4966	2.5	2.4961	2.5003
5	2.4924	2.4949	5	2.4926	2.4964	5	2.4971	2.5004
10	2.4927	2.4936	10	2.4935	2.4957	10	2.4983	2.5005
20	2.4928	2.4928	20	2.4938	2.4951	20	2.4992	2.5006
			40	2.4939	2.4948	40	2.5000	2.5013
			80	2.4941	2.4944	80	2.5010	2.5017
			120	2.4942	2.4942	280	2.5023	2.5020

(1): Density of rod-as-drawn, 4mm. in diameter. (2) and (3): Density of samples treated at 480°C for 4hrs. and 10 days respectively.

From the above figures, it is shown that the change in density, D , with time, t , can not be represented by the relaxation equation of Maxwell type: $d(D_r - D)/dt = k_1 \cdot (D_r - D)$, where D_r is equilibrium density at temperature $T^\circ\text{C}$, nor of Adams-Williamson type: $d(D_r - D)/dt = k_2 \cdot (D_r - D)^2$, as the rate of change in density is extremely rapid while the difference, $(D_r - D)$, is large and the rate decreases rapidly as D approaches to D_r . To interpret these figures, it seems important to take account of the change in viscosity of glass with time at constant temperatures in the annealing range.

11. Factors Affecting Diffusion Velocity of Oxygen through Heat-Resistant Enamel Coatings

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At high temperatures, oxygen in air diffuses through an enamel layer and reacts with the base metal. Therefore, the property to prevent the diffusion of oxygen is most essential for the heat-resistant enamel. In order to acquire fundamental knowledge about factors which affect the diffusion velocity of oxygen, the authors measured successively the volume of oxygen, which diffuses through an enamel layer during heating at 800°C. The method used for the measurement is the same as reported by one of the authors (Jap. Ceram. Assoc. 1949, 57, 96). With a few exception, the frits now generally applied as the heat-resistant coatings

were used for the present experiments. Their compositions, mill additions and fusibilities are shown in Table 1. The fusibility is represented by the ratio of the area of the enamel flowed down at the button-test. The application weight of enamel on low carbon steel plates was in all cases 4 gr. per sq. dm.

The diffusion velocities of oxygen for the various enamels determined from the experiments are shown at the end of Table 1.

Table 1

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
SiO ₂	55.0	66.0	69.0	71.0	73.0	75.0	63.0	56.4	49.7	51.1
Al ₂ O ₃	5.0	5.0	5.0	5.0	5.0	5.0	5.0	7.2	7.4	7.6
Na ₂ O	15.0	15.0	14.0	13.0	11.0	9.0	13.0	10.5	10.6	10.9
K ₂ O	5.0	5.0	5.0	5.0	5.0	5.0	5.0	6.6	4.5	4.7
CaO	5.0	5.0	3.0	2.0	2.0	2.0	5.0	3.0	—	—
B ₂ O ₃	15.0	4.0	4.0	4.0	4.0	4.0	—	9.9	9.3	9.6
CaF ₂	—	—	—	—	—	—	—	4.2	3.9	4.1
TiO	—	—	—	—	—	—	—	—	—	12.3
ZrO ₂	—	—	—	—	—	—	9.0	—	—	—
BeO	—	—	—	—	—	—	—	—	12.0	—
CoO	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.5	0.5	—
NiO	—	—	—	—	—	—	—	0.5	0.5	—
MnO ₂	—	—	—	—	—	—	—	1.7	1.6	—
Total	100.3	100.3	100.3	100.3	100.3	100.3	100.3	100.5	100.0	100.3
Frit 100, Clay 5.5, MgSO ₄ 0.2										
Fusibility	1.00	0.65	0.59	0.45	0.37	0.27	0.44	0.70	0.37	0.24
Diffusion Velocity of Oxygen (cc/min.cm ²)	8.50	6.46	5.74	5.12	2.80	2.23	4.94	4.57	1.86	1.45 × 10 ⁻³

From these results the authors have reached to the following conclusions:

- (1) The diffusion velocity of oxygen is mainly controlled by the fusibility of enamel. Their relationship is in linearly inversproportional.
- (2) The composition of the enamel does not affect the diffusion velocity of oxygen, if the fusibility of enamels are the same.