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Study on the Effect of Boric Oxide on the Titania Opacified Glass

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I. Abstract

Viscosity coefficients were measured, by Lillie's method, of titania opacified glasses of more than ten compositions, some containing B_2O_3 and some not containing it, at several temperatures between 560° and 700° C., with the object of explaining the strong opacifying power, that is the facility of depositing small titania particles by heat treatment, of the glasses containing B_2O_3. Comparing inner bond energies and softening points, calculated from these measurements, it is proved that this strong opacifying power is attributed to the lowering of inner bond energy, and addition of B_2O_3 must be of fairly large quantity.

II. Introduction

Titania opacified glass contains TiO_2 in the homogeneous states of the base glass and deposits the crystals of TiO_2 after heat treatment at 600°～700°C. The deposit of crystal is limited to the glass basses of certain compositions. B_2O_3 is known to be effective to opacification, but the mechanism of this effect does not seem to be explained. The adequate temperature of heat treatment is near the softening point (the temperature at which viscosity coefficient becomes 4.5×10^7 poises), so the decrease of viscosity seems to be a predominant factor, but the bond energy, with which TiO_4 tetrahedron is bound to the irregular net-work of glass, also seems to be an important factor. So we measured the viscosity coefficients at several temperatures near the softening point by Lillie's method, and calculated the inner bond energies of glasses of various compositions.

III. Experimental methods

About 20 gms of glass batches were melted in platinum crucible at 1400°～1500°C. for 2～3 hrs., using siliconit electric furnace.

The glass samples were drawn to the fibers of 0.5～1.0 mm. diameter by the flame of gas burner. Two nicrom rods were put to both ends of about 30 mm. glass sample and hanged in the vertical furnace, placing the sample in the upper part of the constant temperature range. The temperature difference of this part of about 10 cm. of the furnace tube was ±5°C. The elongation velocity was measured by the cathetometer with the accuracy of 1/20 mm., suspending adequate weight

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at several constant temperatures of 560°~700°C.

H.R.Lillie[1] proposed the following equation to determine viscosity coefficient from the measurement of the elongation velocity of glass fiber, and J.T.Littleton[2] and A.H.Falter confirmed the possibility of using this equation up to the softening point.

$$\eta = \frac{80\,L\,M\,g}{\pi\,D^2\,k_v} \tag{1}$$

L : fiber length, cm
M : hanged weight, g
g : gravity constant, dyne
D : fiber diameter, cm
k_v : velocity of elongation, cm/min
η : viscosity coefficient, poises

Near the softening point the elongation becomes large and increases rapidly with the changes of L and D, and k_v is not constant during measurement. If m and ρ are taken as the weight and the density of glass fiber sample,

$$m = \rho\pi\frac{D^2}{4}L$$

Introducing this relation to the equation (1), we obtain

$$k_v = \frac{20\,\rho M g\,L^2}{m\eta} = CL^2 \tag{2}$$

C is the constant during the measurement of constant condition. So the linear relation between elongation and time can be obtained, if the observed elongation is calibrated to the initial length according to equation (2).

IV. Experimental data

The ground composition of the glass samples used is as follows:

SiO_2, 70%
Na_2O, 20%
CaO, 4%
Al_2O_3, 4%
ZnO, 2%

In the 1st series 6%, 9%, 12%, and 15% of TiO_2 were added in place of SiO_2, and in the 2nd series 4%, 7%, 10%, 13% and 16% of B_2O_3 were added in place of Na_2O, keeping TiO_2 content to 12%, and in the 3rd series, percentage of TiO_2 was changed as in the 1st series, keeping B_2O_3 content to 13%.

Sample numbers of various compositions are listed in Table 1.

Samples, E5 and D6, were opacified completely by few minutes' heat treatment at 660° C. Samples, El and D5, were opacified a little by one hour's heat treatment at 660° C. Samples, Dl, C5 and D4, were opacified a little after heat treatment

1) Jour. Amer. Ceram. Soc. **16** (1933) 612.
2) Jour. Soc. Glass Techn. **24** (1940) 176.

Table 1. Sample number of glasses of various compositions

$\%B_2O_3$ / $\%TiO_2$	0	4	7	10	13	16
0	A 1				A 5	
6	B 1				B 5	
9	C 1				C 5	
12	D 1	D 2	D 3	D 4	D 5	D 6
15	E 1				E 5	

above 720° C. The other samples were not opacified. It was also observed from our results that the opacifying power increases much as B_2O_3 content increases.

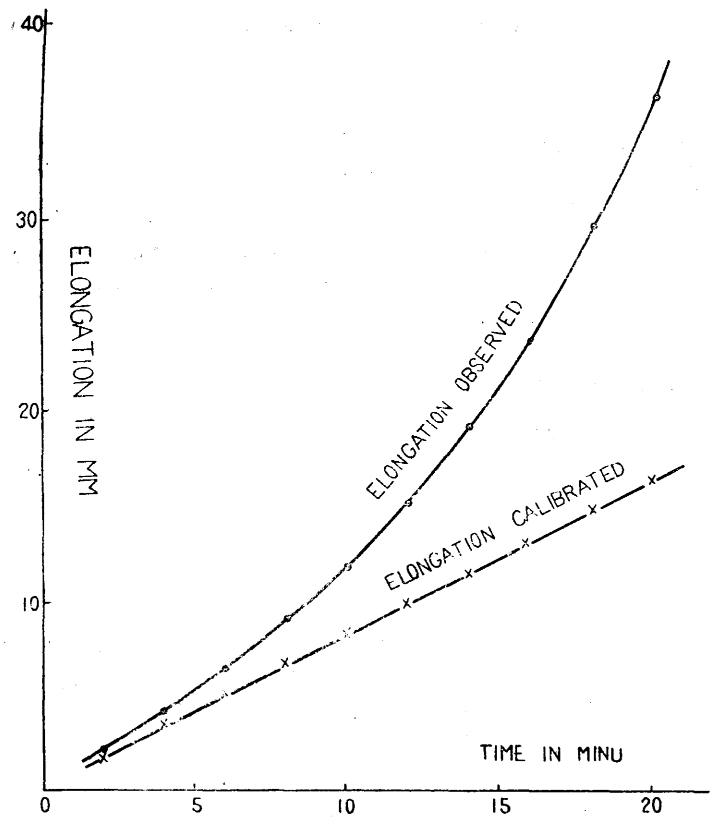

Fig 1. Relation between elongation and time of sample A1, at 580° C; D, 0.813mm; L, 31.5mm; W, 51.39gms.

The elongation observed and calibrated of sample Al at 580° C. is plotted against time, as shown in Fig. 1. The calibrated elongation velocity, k_v, can be immediately obtained from this inclination, and viscosity coefficient, η, from equation (1). The relation between logarithm of viscosity coefficient and the reciprocal of the absolute temperature, T, must be linear, if the following equation is satisfied as many authers reported,

$$\eta = Ae^{E/RT}$$

Here R, and E are respectively taken as gas contant and inner bond energy, which is approximately equivalent to average of bond energies in glass, kcal/mole., but strictly it means the average activation energy of viscosity.

A must be a function of temperature for the large temperature range, but, because our obserbation is limited to the neighbourhood of softening temperature, A should be regarded as constant for this small temperature range.

Fig. 2, 3, and 4 show that these linear relations are nearly completly satisfied for the glasses of the lst, 2nd and 3rd series.

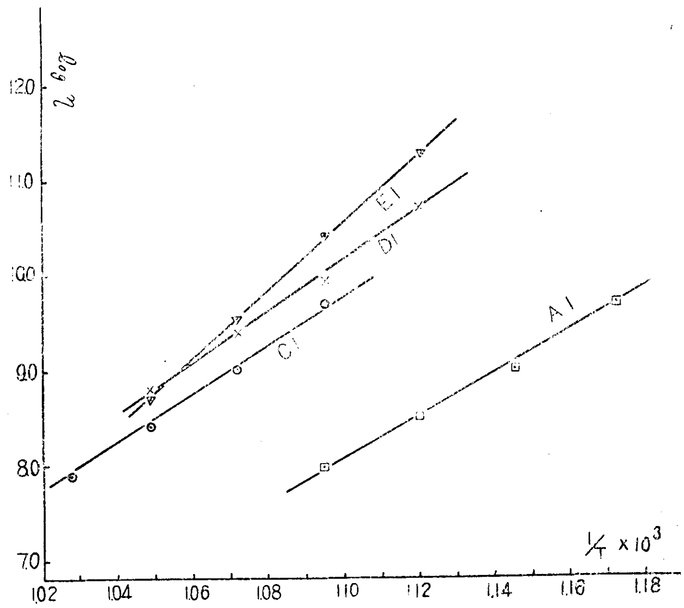

Fig. 2. Relation between logarithm of viscosity coefficient, η, and reciprocal of absloute temperature, T, in the 1st series

In Fig. 5, 6 and 7 the inner bond energies and softening temperatures are shown against each glass compositions for the 1st, 2nd and 3rd series.

V. Discussion

Inner bond energies increase as TiO_2 percentage increase in the 1st series which does not contain B_2O_3. This considered to be the reason why glasses in the 1st series are difficult to opacify. The increase of softening points also seems to be one reason of this difficulty, but the softening point of the glass, E1, contaning 15% TiO_2 falls considerably.

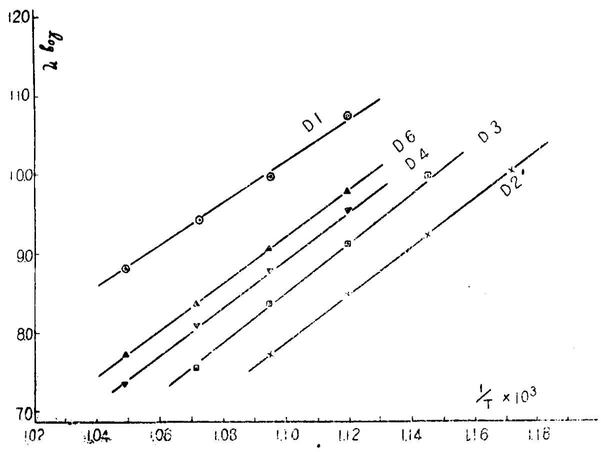

Fig 3. Relation between logarithm of viscosity coefficient, η, and reciproal of absolute temperature, T, in the 2nd series

In the 2nd and 3rd series inner bond energies of D6 and E5 fall suddenly, and these two glasses are easiest to opacify in this experiment. Softening points rise

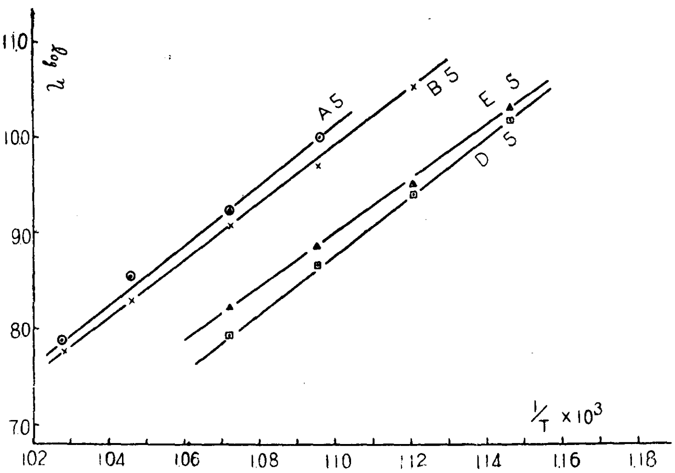

Fig. 4. Relation between logarithm of viscosity coeffcient, *η*, and reciprocal of absolute temperature in the 3rd series

a little in these parts of series ends.

These two facts are explained by assuming that the bond between SiO_4 and TiO_4 tetrahedrons in the glass irregular network structure is much stronger than the bond between TiO_4 and BO_4 tetrahedrons, or BO_3 triangles. So, latter bonds are easy to break, and TiO_2 molecules begin to be free and bind with one another and grow up into crystals by heat treatment. And the glass is opacified.

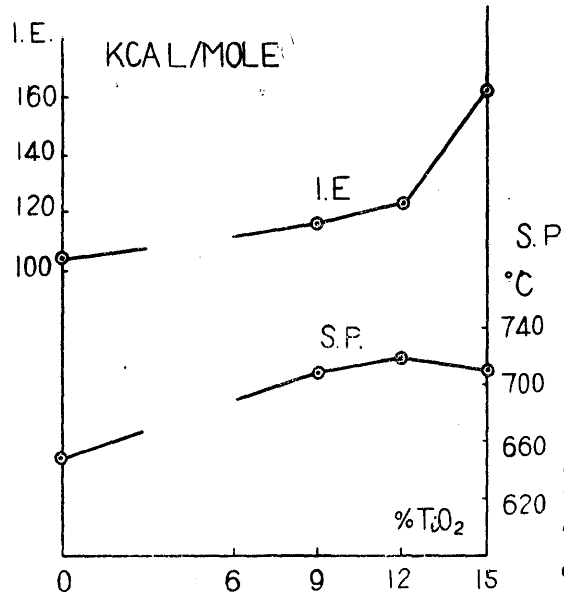

Fig. 5. Relation between inner bond energy, I.E. and softening point, S.P. and glass composition in the 1st series

Generally the addition of B_2O_3 to glass increases inner bond energy. It was also observed that in the second series inner bond energies increase once with the increase of B_2O_3 content. Their decrese at the series end shows that the bond between BO_3 or BO_4 and TiO_4 is weak enough to deduce this increase.

So B_2O_3 addition needs to be of conciderably large quantity if used for the opacification of the titania opacified glass, but its adequate addition is extremely effective.

Lowering of the softening point does not seem to be of so much important factor.

VI. Summary

1) The effect of B_2O_3 on the opacification of the titania opacified glass is explained by lowering of inner bond energy, calculated from measured viscosity coefficient. It is due to the weakness of bonds between TiO_4 and BO_4 tetrahedrons or BO_3 triangles, in the glass structure. This fact facilitates the breaking of these bonds and the depositing of TiO_2 particles by heat treatment.

2) The addition of B_2O_3 must be of considerably large quantity, but its adequate addition is very effective.

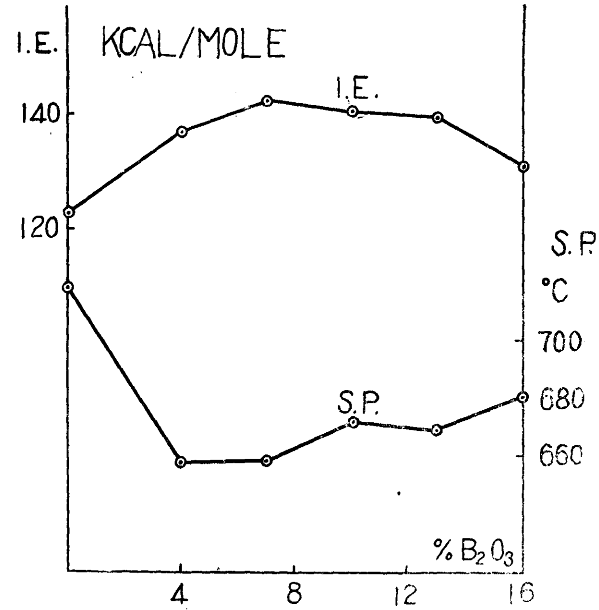

Fig. 6. Relation between inner bond energy, I.E. and softening point, S.P. and glass composition in the 2nd series

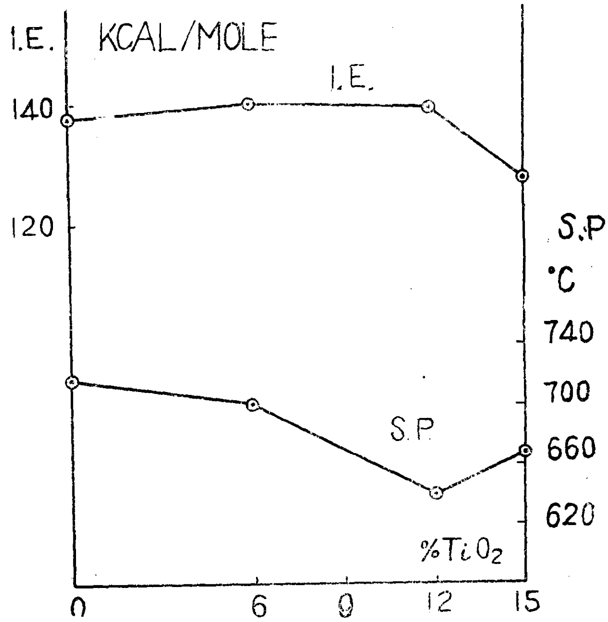

Fig. 7. Relation between inner bond energy, I.E., and softening point, S.P. and glass composition in the 3rd series