Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 30, No. 5, May 1987

BEHAVIOUR OF ARSENIC AND ANTIMONY OXIDES AS GLASS REFINING AGENTS

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(Received September 4, 1986; revised April 4, 1987)

The refining action of arsenic and antimony oxide under commercial glass melting conditions has been investigated in Soda-lime-silica glasses. It has been shown experimentally by the bubble count method that arsenic oxide at 1450° is a better refining agent than antimony oxide. The investigations have further shown that the refining behaviour of both antimony oxide and arsenic oxide is enhanced considerably in the presence of the oxidising agent, sodium nitrate. The slopes of log N against concentration of the two refining agents also confirm the above statement.

Key words: Glass refining agents; Glass; Fining.

INTRODUCTION

Good melting of glass batch followed by a rapid removal of gas bubbles is a prerequisite for an economical production of glass containers and window glasses. A good deal of bubbles produced as a result of distintegration of raw materials are automatically removed during the early stages of melting but there still remain gaseous inclusions, visible as bubbles (blisters or seeds) which affect the saleable quality and properties of the final product. The main sources of these bubbles are: (i) gases evolved during melting, (ii) air entrapped in the batch, (iii) gases from porous refractories, and (iv) gases dissolved in the melt from the flue gases.

The gaseous contents of the occluded gas bubbles have been analysed by different researchers [1]. The prominent gases present in the bubbles are CO, CO_2, N_2, SO_2, O_2 and water vapours. The process of eliminating the above mentioned gaseous inclusions from the melt is called fining (refining). In refining two mechanisms are involved the evolution of bubbles by buoyancy forces and the solution of small residual bubbles. Fining rates can be increased both by physical and chemical means. Physical methods are expensive or impracticable for one reason or the other. Refining can be improved by increasing the temperature of the furnance but this would cause the dissolution of expensive imported refractories and additional fuel cost. Therefore, the only choice left with the glass technologist is to make use of the chemical agents for refining and homogenising glass melts. The use of refining agents has been found economical.

The chemical refining agents are either sulphates or redox oxides (AS_2O_3, Sb_2O_3). Fining agents react chemically and enhance fining by increasing the size of the existing bubbles. This requires the evolution of gas, a characteristic feature of all fining agents. The redox oxide during the early stages of melting acquires a higher valence state by absorbing oxygen and generates it at later stages and this flattens the existing seeds by increasing their internal pressure. By doing so a good deal of bubbles are removed from the melt.

The refining behaviour of arsenic has been studied by a number of investigators [2, 3, 4]. But the refining behaviour of antimony oxide and its comparison with arsenic oxide as glass refining agent has been a bone of contention. In the present study comparison of two redox oxides, Sb_2O_3 and AS_2O_3, as glass refining agents has been studied experimentally.

EXPERIMENTAL

1. *Melting of glasses.* Chemical analysis of the water washed sand was carried out by the conventional methods of silicate analysis. The SiO_2 content of the sand was 99.89 % while Fe_2O_3 was 0.03 %. The rest of the materials were pure chemicals. The composition of the glass used in the present investigation was (Wt. %) SiO_2 (73.5 %), CaO (10 %), and Na_2O (16.5 %). This is the appropriate composition of the soda-lime glasses being used in the commercial production of container glasses. Each melt was founded at 1450 ± 10° for 3 hr. The time and temperature of melting have been established by earlier workers [2,3] as optimum for bubble removal and refining of soda-lime glass compositions. These meltings were carried out in molachite pots

2. *Bubble count method.* At the end of the chosen founding time, the melts were poured on iron plates and were at once put in a small annealing furnace. After annealing at 535°, the samples were polished and washed

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with xylene. The number of seeds per cm. cube was determined by counting the total number of seeds in a sample and dividing by volume of the sample which was calculated from its weight and the known density of the glass. The average of three melts for each founding time was taken as the number of seeds per cm. cube. The results are depicted as log N of seeds/cm^3 versus percent of redox oxide. The slopes of these curves have been determined (Table 1).

Table 1

Sr. No.	Refining agent	Slope of plots	Figure No.
1.	AS_2O_3 only	2.33	1
2.	AS_2O_3 + $NaNO_3$	3.2	1
3.	Sb_2O_3 only	1.27	2
4.	Sb_2O_{93} + $NaNO_3$	2.25	2
5.	AS_2O_3 + $NaNO_3$	3.25	3
6.	Sb_2O_9 + $NaNO_3$	2.30	3

RESULTS AND DISCUSSION

Fig. 1 shows a logarithmic plot of seeds remaining in per cm^3 of glass sample against the different additions of AS_2O_3. The lower and upper plots show the refining behaviour of arsenic with and without the addition of sodium nitrate. It is evident from the lower curve (Fig. 1) that the seeds decrease considerably when arsenic is used in the presence of an oxidising agent $NaNO_3$. The point log N = 2.5 of Fig. 1 is characteristic of the base glass composition without any refining aid. This poor refining behaviour of the melt is due to the supersaturation of the melt with CO_2, N_2 etc. bubbles. After the expiry of the melting reactions, the melt in the absence of refining aids, does not acquire the oxygen bubbles which because of their higher diffusibility rates flatten and enlarge the existing CO_2 and N_2 bubbles and help their removal by buoyancy and absorption in the melt.

The addition of arsenic to the base glass improves the refining considerably. The oxygen bubbles increase the internal pressure of CO_2 and N_2 bubbles which are removed under the byoyancy effect. The remaining bubbles in the form of seeds being rich in oxygen disappear as a result of their greater solubility in the melt and the glass gets refined. The addition of $NaNO_3$ with AS_2O_3 improves the situation still further because $NaNO_3$ provides oxygen which helps to dissolve the existing bubbles.

The results of the different additions of antimony oxide against the logarithmic plot of bubbles remaining per

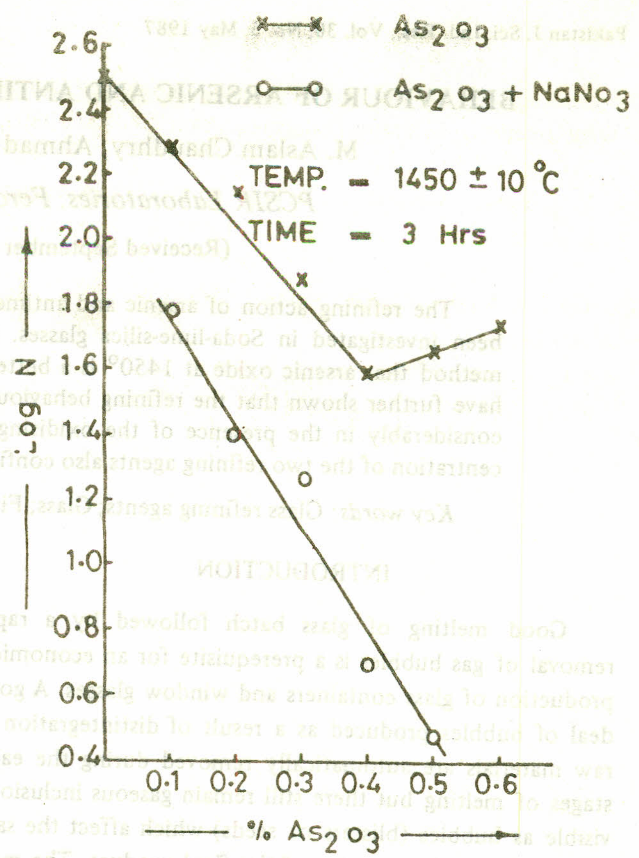

Fig. 1. Effect of arsenic as refining aid with or without $NaNO_3$.

cm^3 of glass can be seen from Fig. 2. The upper curve and the lower plots in Fig. 2 represent the refining behaviour of Sb_2O_3 and Sb_2O_3 + $NaNO_3$ respectively. The pattern of refining in this case is the same as that in the arsenic containing glass. The effectiveness of refining (Fig. 3) for the equal addition of the arsenic and antimony oxides goes in favour of arsenic. This might be due to the fact that Sb_2O_3 is a lower melting oxide than arsenic and most of it escapes into the atmosphere before it is entrapped in the melt. This reduces its effectiveness at higher temperatures. As the temperature of melting lowers down, its relative refining action may improve considerably as has been stated by A.A. Naqvi [5] and S.R. Scholes [6] (Fig. 4).

The effectiveness of refining agents in the presence of oxidizing agent ($NaNO_3$) has also been confirmed by the slopes of the curves (Table 1). The refining action of redox oxides decreases considerably in the absence of oxidants. It is evident from Table 1 and relevant figures that the slopes of the curves with an oxidizing agent are of higher values than those without an oxidizing agent.

The refining action of Sb_2O_3 follows the pattern of AS_2O_3. However, the slopes of the plots (Fig. 2 and

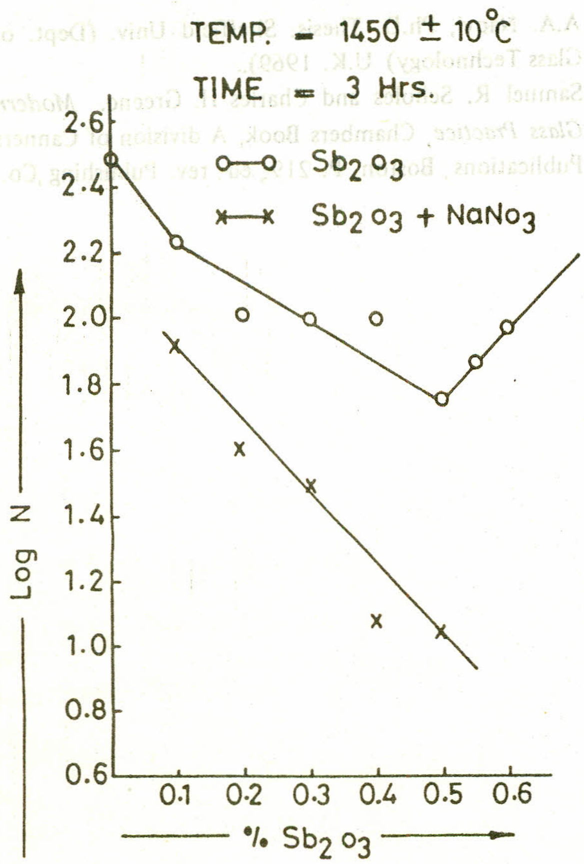

Fig. 2. Effect of Sb_2O_3 as refining aid with or without $NaNO_3$.

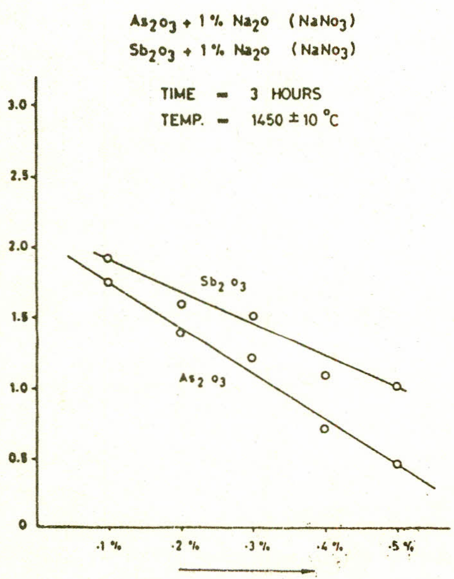

Fig. 3. Comparison of refining action between AS_2O_3 and Sb_2O_3.

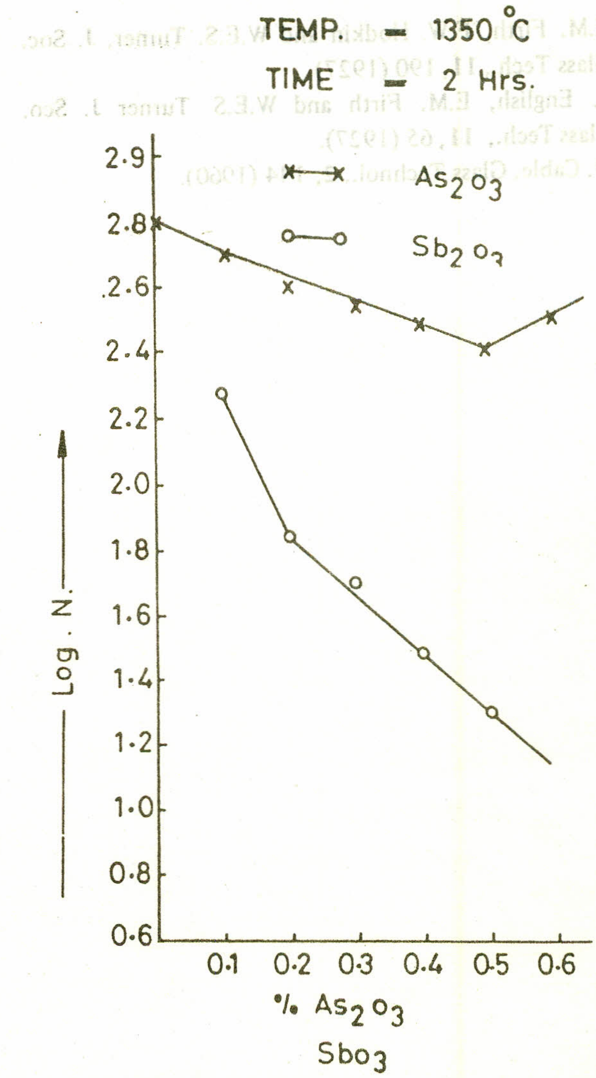

Fig. 4. Refining behaviour of Sb_2O_3 and AS_2O_3 (Cable & Naqvi)

Table 1) for Sb_2O_3 are lower in value than those of AS_2O_3. This clearly shows the superiority of AS_2O_3 over Sb_2O_3 as a glass refining agent. In commercial practice where gas or oil are preferred fuels, arsenic has been reported a better refining agent. It has also been observed in commercial production that container glasses containing Sb_2O_3 exhibit a greenish tinge which is not acceptable by the end users.

Acknowledgement. The authors wish to thank Mr. Mukhtar Ahmad, Senior Technician of Glass & Ceramics Division for his assistance in the experimental work.

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