

Non nitrate antimony aided refining

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Artikeln beskriver ett projekt med målsättningen att hitta alternativa luttringsmedel till antimonoxid oxiderad med nitrat. Sönderfallet av nitraten medför att olika kväveinnehållande gaser bildas. Genom att undvika nitrater vid glasframställning kan NO_x-emissionerna kraftigt reduceras.

Ersättare till nitraterna har undersökts. Två oorganiska peroxider har granskats: natriumperoxid (Na₂O₂) samt bariumperoxid (BaO₂). Luttringsresultatet blev fullt likvärdigt med eller eventuellt något bättre än den idag använda kombinationen antimonoxid oxiderad med nitrat.

Det har också gjorts försök att tillsätta antimoninnehållande föreningar, antimonater, där antimon förekommer i oxiderad form. Av de två undersökta antimonaterna, natrium-meta-antimonat (NaSbO₃) samt kaliumhexahydroxoantimonat (KSb(OH)₆) som båda fungerar väl ur luttringssynpunkt, har främst den första undersökts pga dess industriellt rimliga pris.

Även sulfiders luttrande förmåga i form av MoS₂ och Sb₂S₅ har kartlagts. I kombination med reduktionsmedel för MoS₂ samt oxidationsmedel för Sb₂S₅ ger dessa ett gott luttringsresultat, men färgar smältan något och kan därmed inte användas vid smältning av klarglas. Det här utesluter inte dessa vid tillverkning av manuellt glas emedan en viss del av smältorna ofta är färgade och en ytterligare svag färgning knappast påverkar det slutliga färgintrycket.

Introduction

Environmental aspects

Glass melting has a number of more or less pronounced environmental impacts. A common classification of those would be to look at emission products arising from the dusting of batch, evaporation of volatile glass components and emissions from the combustion of fuel, respectively.

The major actions to reduce the emissions of elements of special environmental impact would be either to substitute these elements in the batch or arrange various cleaning or conversion of the flue gases.

The elements of the present concern for the crystal/handmade in-

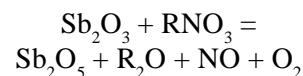
dustry are those coming from the batch. Particular attention has been paid to the reduction of lead or fluorine emissions, either by filter installations or by converting to alternative formulas.

Smaller melting furnaces, as those used by most of the crystal/handmade industry, are for the moment not subject of any regulations in terms of the amount of acidic gases that might result from the combustion of oil or gas, i.e. NO_x or SO_x. However the emission of such compounds is likely to be less tolerated in the future.

The role of nitrate and antimony

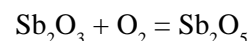
One should note that the emissions of NO_x are as well caused by the fact that nitrates, in quantities of 2-

3 %, are added to the batch in order to facilitate the refining process. The nitrates act according to the reactions:



where R commonly corresponds to Na or K.

The reason to introduce nitrate is thus to oxidise antimony(III)oxide to pentavalent oxide. In the melt, the tri- and pentavalent oxides of antimony are in equilibrium:



The equilibrium is shifted to the left at higher melt temperatures [1] and

oxygen released in the melt and diffuses into bubbles that will grow and thus rise faster to the melt surface. The temperature dependence on the ratio between antimony (III) and antimony (V) must be strongly dependent on the glass composition.

Approaches to substitute nitrate

The decomposition of nitrate, as described above, generates nitrous gases. In fact, in all-electric melters the nitrate addition would be the major source of NO_x . To try to avoid these emissions and try to understand more of the refining process, a project has been carried out at Glafo. The project has been directed to the areas:

- 1) Recording of reference data
- 2) Investigation of the role of sodium nitrate and potassium nitrate
- 3) Studies on alternative oxidation agents
- 4) Studies on adding pentavalent antimony compounds to the batch
- 5) Refining action of other compounds.

Experimental

All chemicals used were of industrial grade. The refining experiments were made by adding the refining agents to the host glass shown in table 1, or by adding various combinations to a commercial unleaded crystalline composition as described elsewhere [2].

The calculated viscosity is of the host glass is $\log \eta 2 = 1414^\circ\text{C}$ and the crystalline composition has the same viscosity at a temperature of 1420°C .

Refining agents were added in amounts shown in table 2. The amounts are given in the traditional unit kg per 100 kg of sand.

Table 1 Host glass used in refining studies, oxide content given in wt-%

SiO_2	70
Na_2O	10
K_2O	9
CaO	10
B_2O_3	1

Table 2 Amount of refining agents added (kg per 100 kg of sand).

Compound	Amounts
Sb_2O_3 (and equivalents)	0,6 - 2,2
Nitrates	3 - 7
Other oxidation agents	1 - 7
Other refining agents	0,2 - 1,2
Reducing agent	0 - 0,7

Batch corresponding to 230 g glass was charged in two charges. The second charge was done exactly 8

minutes after the first. The furnace used is electrically heated by Super Kanthal elements. The furnace temperature corresponded to a melt viscosity of $\log \eta = 2$. The melting time after the second charge was 50 minutes for the host glass and 40 minutes for the commercial glass. The glass melt was poured out to form a disc and the number of bubbles counted by use of an image processing system. The results will be presented as bubbles per 100 g glass.

Results and discussion

In this section, the results will be presented as number of bubbles per 100 g glass versus amount of antimony oxide (or other compound)

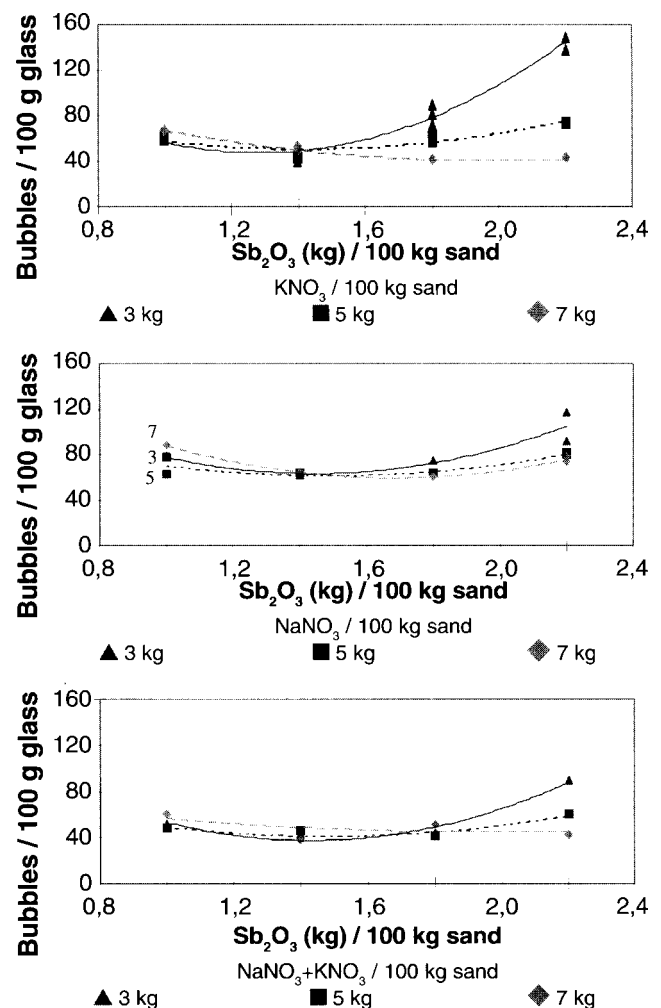


Figure 1 Bubble count for the refining agent combinations Sb_2O_3 oxidised by a) KNO_3 , b) NaNO_3 , c) 50/50 mix of KNO_3 and NaNO_3 .

added per 100 kg of sand in the batch.

Refining by use of antimony oxide and nitrate addition

The results of the refining studies by use of nitrate as an oxidation agent are shown in figure 1.

Figure 1 shows that all combinations behave in a similar way. A minimum around 1,4 kg Sb_2O_3 , however not especially pronounced, can be found for the various nitrate combinations. The refining becomes less efficient for low nitrate additions to batches containing higher Sb_2O_3 contents. It seems like the effects of sodium and potassium nitrate are very similar, it should thus not be of importance which of the

materials one choose.

Refining by use of antimony oxide and peroxide addition

When looking for alternative inorganic oxidation agents, the selection of industrial realistic compounds showed to be quite limited. The choice was to investigate the action of peroxides. Sodium and barium peroxide were chosen for the experiments. The results are shown in figure 2.

The curves in figure 2 show that the refining process using sodium and barium peroxides as oxidation agents is at least as efficient as the nitrate route. The functionality of peroxides in industrial raw material handling can be questioned, especi-

ally when introducing the materials into a pelletising process. Peroxides react with water to the products oxide + oxygen, so we had doubts about whether any oxidation power would remain after pelletising. The work continued by attempts to identify other possible solutions to achieve a non nitrate refining process.

Refining by addition of pentavalent antimony compounds

Since the reason for adding an oxidation agent is to oxidise antimony (III) oxide to antimony (V) oxide, one can ask the question: what happens when pentavalent antimony compounds are added without subsequent addition of oxidation agents?

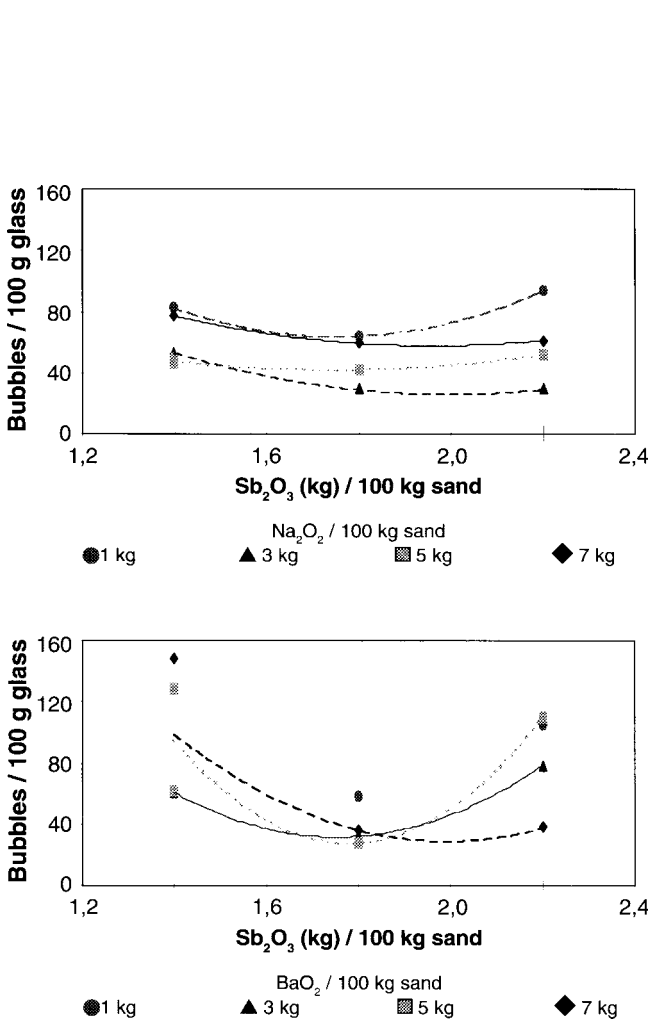


Figure 2 Bubble count for combinations between Sb_2O_3 and a) Na_2O_2 b) BaO_2 .

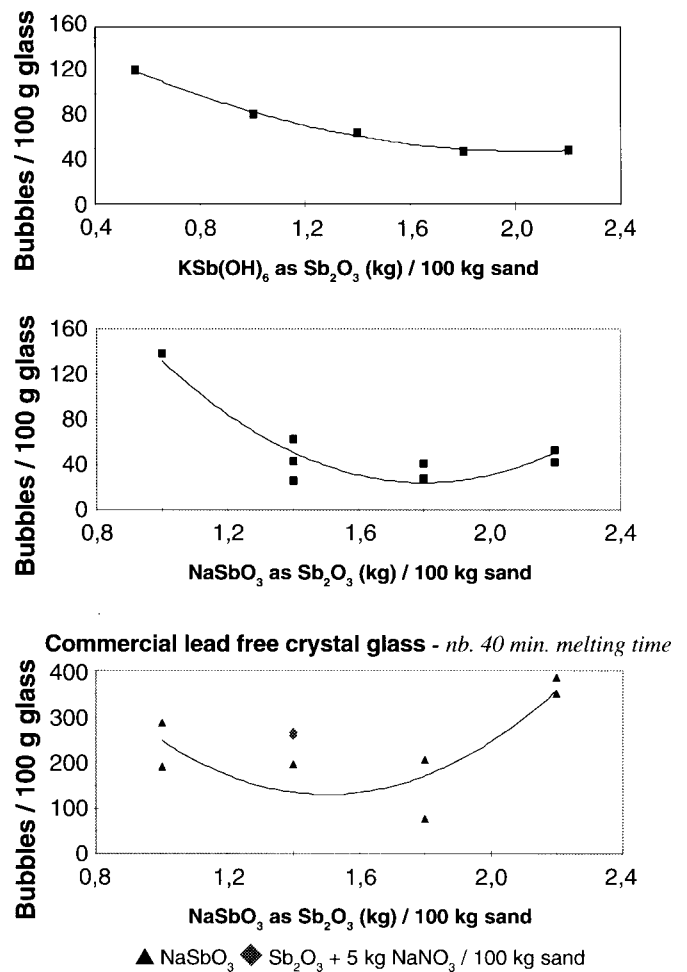


Figure 3 Bubble count after addition to the host batch of a) $KSb(OH)_6$ b) $NaSbO_3$ and c) addition of $NaSbO_3$ to a commercial composition. The added amount has been recalculated to Sb_2O_3 to facilitate the comparison with the other figures.

We found that two types of penta-valent antimony compounds were available for industrial use: so called alkali antimonates, $\text{KSb}(\text{OH})_6$ and NaSbO_3 . The results of studies on the refining action of these compounds are shown in figure 3.

One can observe from figures 3a) and b) that the refining action of antimonates seems to be as efficient as those observed for the combination Sb_2O_3 and nitrates. The observation led to the experiments shown in figure 3c), studies on the refining action of sodium antimonate added to a commercial composition. Sodium antimonate was chosen instead of potassium antimonate due to the raw material cost.

Figure 3c) shows a similar pattern as the one observed for the selected host glass, the refining seems to be as efficient as the Sb_2O_3 + nitrate combination. The bubble count for this standard refining agent combination is also indicated in fig 3c). Note that the melting time for the commercial composition is shorter than for the host glass. The bubble counts for the two different compositions can therefore not be compared directly.

The latter results led to industrial trials with non nitrate antimonate refining, as will be described below.

Refining by use of alternative compounds

During the work to find substitutes for cadmium compounds as yellow glass pigments, we have noticed that some of these substitutes resulted in seed free glass samples, de-

spite that no refining agent in the conventional sense (As_2O_3 , Sb_2O_3 , CeO_2 , Na_2SO_4) was added to the batch. The compound which showed this effect is molybdenum disulphide, MoS_2 .

During the course of this project, we took the opportunity to investigate the previous observations more systematically. The action of MoS_2 was investigated together with another sulphide, Sb_2S_5 , as well as the action of molybden di- and tri-oxides. All those were investigated under conditions of oxidation, neutral and reduction. The general pattern of refining can be summarised as shown in table 3.

Table 3 indicates the character of the refining reactions. In the case of MoS_2 , refining can be observed

for the neutral and reducing conditions. Oxidising conditions give no refining at all. Taking into account that no refining action was observed for molybdenum oxides, this indicates that the reduced state of molybdenum sulphide is the active component.

Sb_2S_5 on the other hand, is only an active refining agent under oxidising conditions. This indicates that the character of this compound rather is that the sulphide reacts to oxide, which is the active compound.

A quantitative evaluation of the refining efficiency of molybdenum and antimony sulphide is shown in figure 4.

Figure 4a) shows that the bubble count decreases when rather low amounts of MoS_2 are combined with

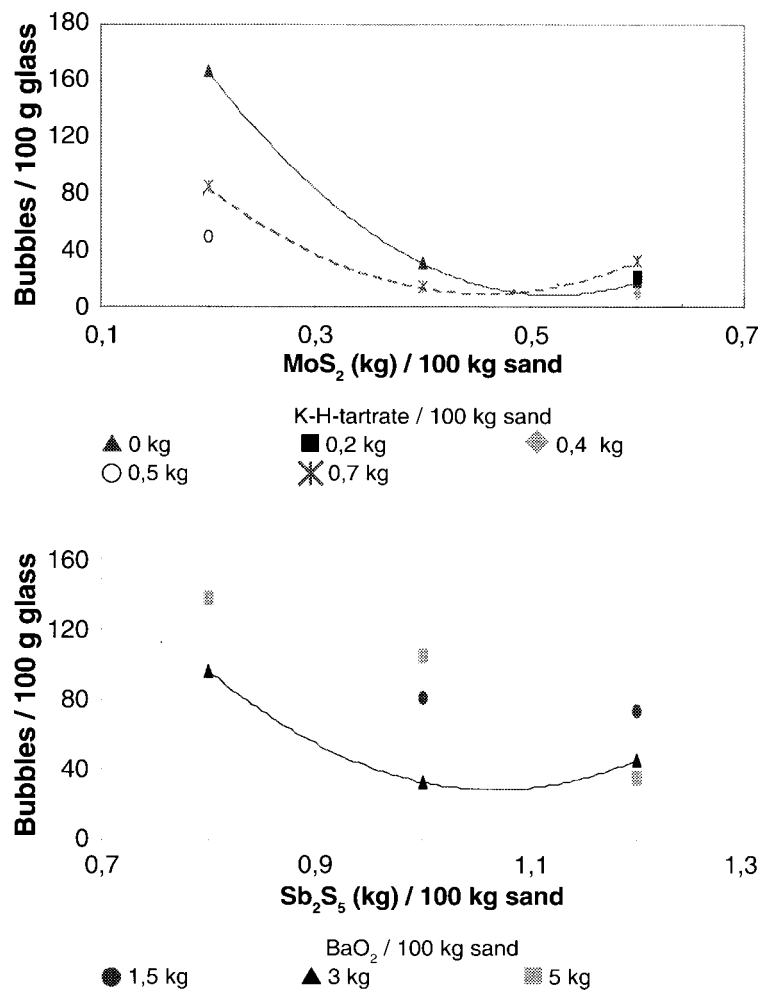


Figure 4 Bubble count for host glass refined with a) MoS_2 under neutral and reducing conditions b) Sb_2S_5 under oxidising conditions.

Table 3 Observations of refining action for alternative compounds:

	Oxidation	Neutral	Reduction
MoS_2	no	YES	YES
$\text{MoO}_2/\text{MoO}_3$	no	no	no
Sb_2S_5	YES	no	no

a reducing agent (potassium hydrogen tartrate). Higher additions of MoS₂ give a low bubble count under neutral conditions.

Figure 4b) shows similar numbers of bubbles as those observed in experiments with antimony oxide and antimonates.

One should keep in mind that the effect of MoS₂ is not only a refining one. Even low additions give a fully visible yellow coloration of the glass, which unfortunately makes this route less suited for clear colourless crystal. When the demands for colourlessness are lower or used in coloured glasses, MoS₂ could be an interesting alternative refining agent.

Industrial trials

The laboratory studies summarised above in figure 3c), refining by addition of sodium antimonate instead of antimony oxide and nitrate, were judged to be interesting by the industry and one factory in Sweden wished to try the alternative refining agent.

The commercial batch was modified to give minimum alteration of the oxide chemical composition. Pelletised batch was melted in pot furnaces having open pots carrying roughly 550 kg of glass. Melting took place over night and the production covered most of the products.

The experiences after melting roughly 50 tons of batch can be summarised as :

- Batch costs increased by roughly 4 %
- A slight reduction of the melting time was observed, otherwise a similar melting behaviour was noted
- The bubble count was reduced by roughly 10 %

- The blister count was reduced by roughly 70 %!

An improvement of the glass quality, in addition to the fact that no nitrous gases of batch origin were generated, could thus be noted after the first trial period. This is of course a strong incitement to continue to evaluate the long time performance of a non nitrate crystal batch.

Conclusions

The laboratory studies of this work showed that an antimony aided non nitrate refining of typical handmade/crystal batches can be performed by:

- 1) Peroxide substitution of nitrates
- 2) Substituting antimony oxide + nitrate by antimonates

Molybdenum sulphide, especially under reducing conditions, works as a refining agent but also as a colouring agent.

The industrial trials indicate that sodium antimonate may substitute the refining agent combination antimony oxide + nitrate and even improve the glass quality.

Acknowledgement

The author is grateful to Pontus Lindberg who performed all the experimental work and participated in the analysis and conclusion of the results.

References

- [1] **RA Cameron**, 67th Annual Meeting of the American Ceramic Society, 1965
- [2] **LG Johansson, B Jonson**, Glass Technology 34 (1993) 91