THE VOLATILIZATION OF LEAD OXIDE FROM LEAD SILICATE MELTS.

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The experiments described below were undertaken in the course of the Geophysical Laboratory's work on optical glass during the war, in order to determine the order of magnitude of the loss due to volatilization of lead oxide from lead silicate melts under certain conditions. An exact determination of such data, with perfect control of all determining factors, would involve a very comprehensive set of experiments, but approximate results may be obtained with simple means.

The material for the experiments consisted of homogeneous glasses containing, apart from incidental impurities, only lead oxide and silica in various proportions. The heatings were done in the same electric furnace in which the experimental glasses had been made, with the opening covered but not tightly closed. The broken glass was filled into a platinum crucible, which had been previously tested for approximate constancy of weight under the conditions of the subsequent experiment. The crucible with charge was heated until the glass formed a melt with level surface, then cooled and weighed. The furnace was then regulated to the temperature desired for the experiment and the crucible was introduced and held for a certain time, taken out, cooled, and weighed again. The difference between the two weighings gives the loss in the melt and as the only volatile constituent in every case was lead oxide, the total loss may be safely calculated as PbO . The area of the surface was then measured.

A few tests showed that the actual loss from the same melt at the same temperature was proportional to the area of the exposed surface and independent of the weight of the melt. The factor determined was therefore the rate of loss per unit of the exposed surface of the melt. The units used were 1 hour, 1 square centimeter, and 1 milligram.

It was found that the rate of loss decreased with a prolonged heating when the melt was left without stirring, but remained constant when stirring was applied. The explanation of this is that diffusion alone works very slowly and will only partly offset the change in composition due to volatilization of lead oxide from a thin film next to the surface of the melt. This film will therefore become gradually richer in silica, at the same time growing lighter than the underlying melt so that it will remain at the top as a protecting film and thereby diminish the rate of volatilization. If, on the other hand, the melt is stirred the rate of volatilization will remain practically constant for a long time because the total loss of lead oxide will be distributed throughout the melt and the actual change in composition of the whole melt, and consequently also of the surface film, will be small. To obtain the exact rate of loss for a certain melt it should therefore be necessary to stir it during the entire period of heating.

This, however, would involve a rather complicated arrangement of experiments and would consume much time. Tests were therefore made to find out whether the rate of loss computed from a short heating without stirring would not be materially the same as the one obtained through a prolonged heating with stirring. The experiments in Table I were carried out with a melt of the composition: 70 per cent (by weight) PbO , 30 per cent SiO_2 , at a temperature of 1300° .

TABLE I.
Volatilization of PbO under Different Conditions.

Time of heating.	Condition.	Rate of loss mg./hr./sq. cm.
20 hours	No stirring	8
15 min.	No stirring	23
1 hour	With stirring	22

These tests show that the rate obtained on the basis of a short heating without stirring is practically identical with the one obtained by a somewhat longer heating with continual stirring.

It is also seen that a prolonged heating without stirring gives a much lower rate of loss than either of the other methods.

In view of these facts the computed rates of loss were based on a short heating without stirring of the melt. A period of 15 minutes was found convenient.

The results are tabulated in Table 2 and plotted in Fig. 1.

TABLE 2.
Volatilization of PbO from Pure Lead Silicate Glasses.
(Loss in mg./hr./sq. cm.)

Percentage of PbO in glass.....	85	78.7	75	70	65	60
Temperature °C.						
1400	318	131	91	60	46	33
1300	100	40	30	23	16	13
1200	37	11	8	7	5	4
1100	13	4	2	2	1	1
1000	8	2	1	1	..	..
900	1	1	..	..	..	..

Fig. 1.

In several cases the refractive indices at various depths of the melt were determined after certain heatings. It was invariably found that a thin layer near the surface, and sometimes a film creeping up along the inside of the crucible, showed a considerably lower refractive index than the underlying glass. Table 3 contains a few examples of this relation.

TABLE 3.
Volatilization of PbO from Surface of Glass Melt.

Time of heating.	Composition.		Refractive index after heating.		Remarks.
	SiO ₂ .	PbO.	Middle of glass.	Surface film.	
2 hours	21.3	78.7	1.888	1.860	{ Surface film creeping up inside of crucible
3 hours	11.9	88.1	2.09	1.63	
2 hours	35.0	65.0	1.724	1.70	

During the experiments it was often noticed that small isolated patches of thin glass film on the sides of the crucible very soon lost so much lead oxide that silica began to crystallize out, the glass becoming white. Under the microscope the crystals were found to be tridymite, which, according to Fenner,¹ is the stable form of silica between 870° and 1470°.

To apply the results to actual glass-melting one may take the following example: A glass containing 60 PbO and 40 SiO₂ is heated for 48 hours at 1300°. Suppose the area of the surface to be 7500 sq. cm. (approximately the area exposed in a pot of 39 inches inside diameter). The loss according to the diagram (Fig. 1) is $48 \times 7500 \times 13$ mg. or 4.68 kg. On a 1000 kg. charge this means a loss of about 0.5 per cent of the weight of the glass, or 0.8 per cent of the PbO. This will have an influence on the refractive index of about 2 in the third decimal place. Similarly, if this glass were fired at 1400°—the usual practice—the loss² by

¹ C. N. Fenner, *Am. J. Sci.*, 36, 331-384 (1913); *J. Soc. Glass Tech.*, 3, 116-125 (1919).

² With the shortened melting and firing schedules used more recently the losses would be approximately half those calculated.

volatility would be 12.2 kg. PbO which is equivalent to 1.22 per cent on the weight of the glass or 2.0 per cent on the weight of PbO. Since melts of a particular kind of glass are always given as nearly as possible the same kind of treatment, the loss will be subject to only small changes from melt to melt and any considerable variation in refractive index is probably not to be ascribed to a variation in the amount of lead oxide lost through volatilization from the surface of the melt. If, however, the heating schedule of the same melt has been considerably changed a noticeable variation in optical properties due to change in loss by volatilization must be expected in all melts rich in lead oxide. This factor is probably largely responsible for the considerable variations in optical properties found in melts, presumably of the same composition, made experimentally on a small scale to determine the relation of optical properties to composition in the lead glasses.¹

That volatilization is a factor of large magnitude is apparent to anyone who has observed the dense "smoke" issuing from the opening of a covered pot containing a lead glass melt which, on account of accident, has been taken from the furnace at the fining temperature. The vapors in this case consist not only of lead oxide but also of alkalis and boric oxide; the opacity and apparent magnitude of the cloud is increased by the condensation of these vapors to solid particles on striking the cold air, but even after allowing for this impression the amount of material evolved is surprisingly large.

The losses of PbO observed in large-scale operations have at times actually reached figures in excess of 5 per cent of the PbO content. These large losses were partly caused by volatilization as above described, but also, in addition, by litharge being mechanically carried out of the pot by gases such as O, CO₂, and oxides of nitrogen derived from the decomposition of batch materials. Such losses were particularly noticeable with the extremely finely-divided sublimed litharge used so extensively in the last year of the war. The rate of filling in the batch would be an important factor in determining such losses, and likewise

¹ Data to be presented in a subsequent paper.

also the practice in regard to stoppering the opening of covered pots, when such pots were used.

Summary.

Experiments were made on the amount of PbO volatilized from the surface of lead silicate glasses at temperatures from 900° to 1400° C. It was found that the volatilization from an unstirred glass in 15 minutes took place at practically the same rate as from a stirred glass heated for a longer period. The rate of volatilization falls off considerably during a long heating if the glass is not stirred, as a film considerably lower in PbO forms on the surface of the melt, into which PbO must diffuse from below before it can escape. The rate of volatilization of PbO at temperatures usually used in optical glass manufacture would seem from these experiments to be small enough so that variations in refractive index due to volatilization are not to be expected if the procedure is reasonably constant from melt to melt, but large enough to cause considerable variations in index if the melting schedule is changed.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
August, 1919.