Decreasing lead exposure from lead crystal by sol–gel coating

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Investigations to develop sol–gel coatings on lead crystal glasses were carried out to reduce the migration of lead into beverages. Therefore three compositions (SiO_2, $Na_2O/B_2O_3/SiO_2$ and B_2O_3/SiO_2) were tested as coating materials. The best result was obtained from the B_2O_3/SiO_2 system. The coatings were densified to clear, transparent layers about 0·2 μm thick, not influencing the appearance of the lead crystal glass surface. For the coating of the inner walls of lead crystal containers, a special process has been developed. The coating reduces the leaching of lead to some percent of the value of uncoated surfaces and does not lose its effectiveness after 20 cycles in a heavy duty laboratory dishwasher.

Tableware from lead crystal is appreciated because of its brilliance and colouring effects due to a high dispersion of light. The lead content is also responsible for a relatively low transformation temperature and for a low dependence of viscosity on temperature (favourable for glass blowing). Lead crystal glass can easily be ground and polished either mechanically or by acids.

The high lead content however can cause problems by the leaching of lead from the glass surface during use. Recent studies in the USA[1] have shown that alcoholic beverages may leach Pb from lead crystal wine decanters and glasses in concentrations high enough to become hazardous for human health under certain circumstances. So Pb concentrations of about 7 mg/l in wine and spirits stored in crystal decanters for 8 months were measured.

According to German standards[2] the leaching of ≤ 4 mg/l from small containers (bottles, decanters etc.) into acetic acid at room temperature within 24 h is permitted. Although the study cited above on Pb loss has left some questions open, it is of interest to look for technically achievable measures to decrease the lead exposure from such glasses. One way is to leach out the network modifying components such as Pb^{2+} from the surface before using the glass, but the leaching of lead continues after a short time of exposure to liquids.

Dumas[3] describes a process to cover the inner walls of lead crystal bottles with a lead free glass layer by a special glass-blowing technique. Since both the refractive index and coefficient of thermal expansion have to be matched to those of the lead crystal glass, it will be very difficult to do this in practice. Therefore an approach to use sol–gel techniques was developed; this method is well known for coating glass surfaces for different purposes[4,5] and especially for building up diffusion barriers for alkaline ions.[6]

Very thin sol–gel layers can be prepared (a few hundreds of nanometres), so that a transparent layer will not affect the brilliance of the lead crystal even though its refractive index is different. Also, it is known that mechanical stress caused by a mismatch of the thermal expansion coefficient between substrate and layer can be relaxed more easily in thin than in thick coatings.[7]

So the question rose whether a sol–gel coating, which densified at T_g of lead crystal glass (only about 480°C), could be developed to act as a diffusion barrier against the leaching of lead.

Experimental

Materials

The experiments were carried out on commercial decanters with a PbO content of 24%. Samples were prepared by sawing decanters into strips about 20 × 100 mm with thicknesses varying according to the thickness of the walls of the decanters; they were not polished. For long term exposure tests two actual decanters of equal size, one coated and one uncoated, were used.

Three coating compositions (pure SiO_2 (A), $20B_2O_3.80SiO_2$ (B) and $5Na_2O.20B_2O_3.75SiO_2$ (C)) were synthesised from tetraethoxysilane, trimethylborate and sodium acetate as precursors diluted in ethanol and hydrolysed with water. For solution A the components were mixed and stirred for one hour at room temperature and for solutions B and C the components were mixed and stirred for 15 h at 50°C.

Blanks and samples to be coated (strips and decanters) were cleaned in a laboratory dishwasher. Before coating the strips were dip coated at a drawing speed of 3 cm/min; the viscosity of the coating solution was therefore adjusted to 4·8 mPa s by ageing it (stirring at room temperature) and diluting it with

ethanol. The decanters were coated by filling them with the coating liquid and emptying them at a controlled flow rate, but only with solution B; for this the viscosity of the solution was adjusted to 2·9 mPa s. The coatings were then dried for 10 min at 110°C in air, fired at 475°C for 30 min at a heating rate of 1 K/min, and cooled to room temperature within about 10 h.

Determination of lead loss

The loss was determined after exposure for 24 h at room temperature to acetic acid,[2] whisky, sherry and white wine by determining the Pb content of the liquids by atomic absorption spectroscopy (Perkin Elmer 1100 B AAS with HGA 700 graphite tube furnace and AS 70 autosampler): $(NH_4)_2HPO_4$ in a concentration of 4 g/l was used to stabilise the Pb in the test solution. The Pb content of the liquids before leaching was determined by the extrapolating standard addition method. Calibration was carried out for each liquid using four standards (0, 20, 40 and 60 ppb lead). 50 ml liquid was used for each experiment. Decanters filled with whisky were used for the long term experiment and the Pb concentration in the whisky was determined after 24 h and then after 1, 4, 6, 11, 15, 18, and 20 weeks at room temperature.

Dishwasher test

These were carried out with coated and uncoated glass rods (solution B) with a laboratory dishwasher, running for 30 min at 80°C with a potassium hydroxide solution (pH 11 to 12) and citric acid. Samples were treated up to 20 times. After the test the samples were exposed to whisky and the Pb loss was determined as described above.

Results and discussion

Properties of coatings

After coating the glass rods and the decanters with the sol and drying at 110°C the gel layers were clear and transparent and showed coloured interferences. The thickness of the layers could therefore be estimated to be about 200 to 300 nm. After firing, the layers were still clear and transparent but without any interference, so that their thickness was believed to have been reduced to 100 to 200 nm. Crack-free coatings were obtained on the samples but cracks formed in coatings on the decanters (preferentially in corners) and this could be prevented by a concentrated solvent atmosphere in the decanter at the end of the emptying step. To do this, the decanter was placed on a sponge soaked with ethanol immediately after the sol had flowed out. No differences in the performance of the coatings due to composition were observed.

The three coatings were tested to investigate the influence of densification and chemical durability on their barrier function. The Pb loss from coated samples exposed to whisky is listed in Table 1: the average error of these values was estimated to be

Table 1. Pb loss from strips coated with sol–gel layers of different chemical composition after 24 h in whisky at room temperature

Layer composition	Pb loss ($\mu g/cm^2$)
SiO_2	0·037
$20B_2O_3.80SiO_2$	0·015
$5Na_2O.20B_2O_3.75SiO_2$	0·030
Uncoated glass rod	0·4

20%. All the coatings markedly reduce the Pb loss from the lead crystal, the lowest losses being obtained with the boron silicate system, possibly due to its relatively low T_g (about 650°C) combinated with the absence of alkali.

Pb loss in different liquids

Further experiments were carried out with the B_2O_3/SiO_2 system. According to the present standard[2] for testing the Pb loss from lead crystal only acetic acid (4%) is used: as a rule, Pb loss from glasses and glazes increases with decreasing pH and acetic acid is considered to be representative of acid solutions.[9] However, it is also necessary to test the behaviour of beverages since factors other than pH (e.g. complex formation) may influence the leaching process.

Figure 1 shows the Pb loss from coated and uncoated samples in wine, whisky, sherry and acetic acid after 24 h exposure at room temperature. It can be seen that the loss tends to increase with decreasing pH, but the highest value was obtained with dry white wine. This is attributed to the ability of some organic components to form complexes such as tartaric acid, leading to an increased attack on the glass network.[10] The coated samples show substantially lower losses than the uncoated ones and the loss from the coated samples increases only slightly with decreasing pH. Whisky (pH 3.9) causes the lowest loss, about 0·015 µg/cm², and acetic acid (pH 2·5) the highest, about 0·060 µg/cm².

SEM investigations of the coating do not show any pores, suggesting that the coatings are dense but, because the densification temperature used was lower than the T_g of the coating, the presence of some micropores has to be taken into consideration. This would explain the still detectable leaching and the remaining influence of pH for the coated samples: the
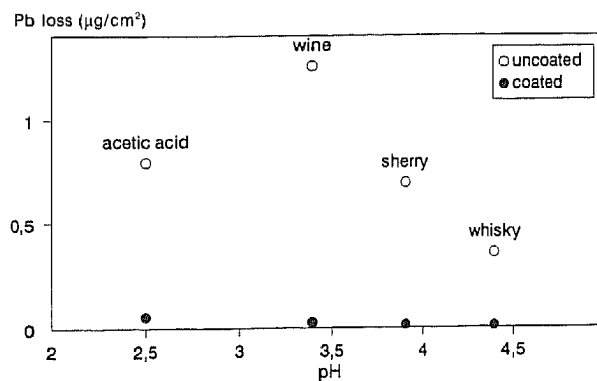

Figure 1. Pb loss from coated and uncoated samples in different liquids after 24 h at room temperature

diffusion of organic molecules can be excluded. Summarising, one can say that the protecting effect of the B_2O_3/SiO_2 coating is remarkable in the short term experiments. This is surprising especially in the case of the strips, since the surfaces produced by sawing are very rough and have sharp edges. The coating demonstrates its ability to cover even this type of damaged surface perfectly.

Long term experiment

In order to test the long term protection of the sol–gel layers, the Pb losses from a coated and an uncoated decanter containing whisky were compared for 20 weeks at room temperature.

It was expected that the loss from the uncoated decanter would follow an exponential increase with time, t^x,[11] where the value of x is dependent on glass composition. To determine x, time versus leaching rate curves were plotted and various values for x were used to fit the time law to the curves: Figure 2 shows the cross correlation coefficient r^2 as a function of x. The best fit was obtained for an exponent of 0·35 ($r^2 \approx 0.97$ for the coated samples and ≈ 0.98 for the uncoated samples). The conclusion can therefore be drawn that, to a first approximation, the time dependence of the Pb loss is the same for both cases.

This result supports the hypothesis that the loss from the coated sample is caused by micropores in the coating because the time law indicates that in both cases the Pb is leached from the bulk glass surface and not from the coating with Pb having migrated into it during densification.

Figure 3 shows the linearised Pb loss curves ($t^{0.35}$ time dependence) and it can be seen that the rise of the loss from the coated decanter (about 0·023 µg/cm² per day) is much lower than for the uncoated one (about 0·095 µg/cm² per day), so that the coated decanter needs more than 100 days to reach the same Pb loss as an uncoated one after one day.

Comparison of the losses from strips (Figure 1) with losses from the uncoated decanter after 24 h shows a lower loss in the case of the decanter (0·13 compared to 0·37 µm/cm²), but the values for the coated strips and decanter are nearly the same (0·017 and 0·018 µg/cm²). This means that the high loss from

Pb loss (µg/cm²)

Figure 3. *Pb loss from a coated and an uncoated decanter*

the rough surfaces of the strips is reduced down to the level of a coated decanter surface by the coating.

Dishwasher tests

The tests were carried out to investigate first the resistivity of the coating to the alkaline attack of the washing liquid and second to find out whether protective layers are built up on the surface of uncoated samples through loss of Pb and K, which may form a silica rich protective layer. A laboratory dishwashing machine was used, since the alkaline attack is more aggressive than in commercially available household machines. 20 washing cycles were performed and after each cycle the Pb loss was tested in whisky (24 hours standard leaching test).

Figure 4 shows the Pb loss from coated and uncoated strips as a function of the number of cycles and the results demonstrate that the effect of the coating remains unchanged. This proves the excellent chemical resistivity of the coating, especially taking into account the fact it is only about 0·2 µm thick; on the other hand, one does not observe a decay in the Pb loss with uncoated samples. This can be explained by the fact that the coated surface does not lose significant amounts of lead and acts as an untouched reservoir even after 20 cycles. In comparison with this, the uncoated sample shows a marked decrease of the leaching rate as the number of cycles increases, and this can be attributed to the formation of a silica rich leached layer of increasing thickness which reduces the permeation rate of Pb.

Cross correlation coefficient (%)

Exponent x
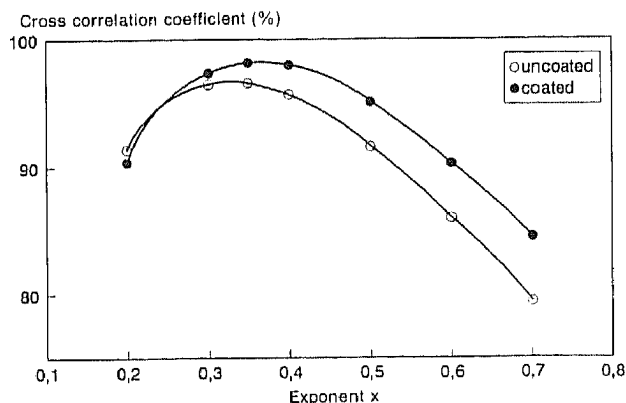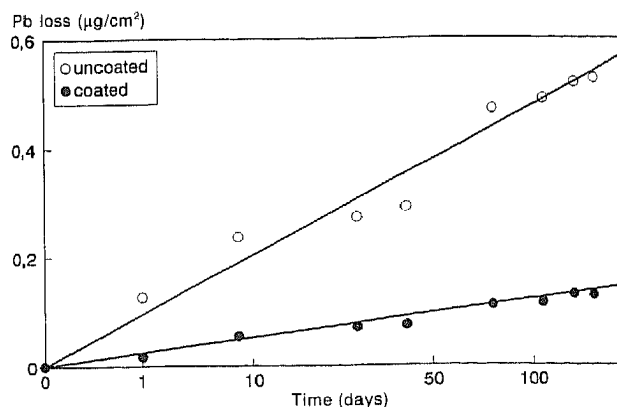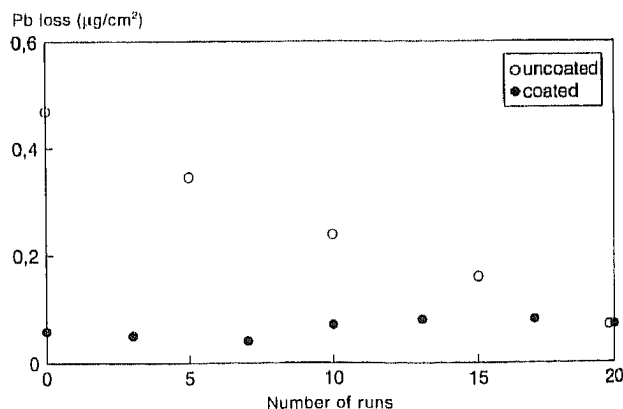
Figure 2. *Cross correlation coefficient versus exponent x to fit the time dependence of the Pb loss from coated and uncoated decanters*

Pb loss (µg/cm²)

Number of runs

Figure 4. *Pb loss from coated and uncoated glass strips after washing*

Conclusions

The results show that the B_2O_3/SiO_2 system is interesting for the formation of barrier coatings on glass surfaces. The stability against alkaline solutions is one of the most important properties of the composition investigated. The insensitivity of the coating to wine (compared to the lead crystal glass) excludes the formation of Si organic complexes, as may be the case with unprotected surfaces. The residual low Pb loss through the coating is attributed to micropores but this hypothesis needs further investigation and it does not seem unlikely that it will be possible to optimise the system to complete density.

The B_2O_3/SiO_2 system in general can be considered as a promising candidate for barrier coatings for glasses and glazes to reduce the leaching of Pb (and other components) in contact with food and beverages.

Acknowledgements

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