

# SURFACE TREATMENT OF LEAD GLASSES FOR REDUCING THE LEACHING OF LEAD

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*Lead crystal glass was studied in order to establish the effect of preliminary treating the surface on concentration profiles of lead in the surface and on lead leaching into acetic acid solutions. The surface was treated in two ways: 1) by exposure in solutions of acids (acetic acid, hydrochloric acid), 2) exposing the surface to decomposition products of ammonium chloride at the elevated temperature. Both treatments resulted in reducing the leaching of lead from the surface while the effect of decomposition products of ammonium chloride was more efficient. The latter treatment also succeeded in extracting lead from deeper layers of glass.*

## INTRODUCTION

Leaching of lead from lead crystal glass ware during use may be reduced by suitable surface treatment. Basically, the following two types of treatment are possible:

1. Extracting of lead from the surface layers of glass prior to its use.
2. Applying a protective coating of an additional material.

The first type of treatment consists of treating the surfaces with solutions of acids. Apart from alkalies, also lead is eluted. Another modification of this type of treatment is based on the effect of reactive gases ( $\text{SO}_2$ ,  $\text{HCl}$ , etc.) on the surface of glass at elevated temperatures, which also leads to extraction of alkalies and other elements including lead from surface layers of glass [1 - 4]. It is based on interaction of these elements in the glass surface with reactive gaseous substances ( $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{HCl}$ ). The reaction products (chlorides or sulfates) either volatilize at the treatment temperature or form a soluble deposit on the surface of glass, which can be removed by rinsing. This surface treatment leads to an effective suppression of surface corrosion of glass by aqueous solutions as well as by air humidity as a result of changes in the chemical composition and structure of the glass surface layer. Study of the surface layers of glass treated by this method shows that a thin compact layer rich in  $\text{SiO}_2$ , similar in its structure to silica glass, is formed on the surface [1].

In our previous paper [5], results were given of measuring the concentration profiles of lead in the surface layer of lead crystal glass before and after

treatment with decomposition products of ammonium chloride at 280 °C and 450 °C respectively. The experiments showed that the lead concentrations in the surface layers of treated glass were significantly reduced compared to non-treated surface. The present study is a follow-up of the respective results, being concerned with examining the effects of this type of treatment in comparison with preliminary exposure the glass surface to solutions of acids, on the leaching of lead from the surface of lead crystal glass.

Suppression of the amount of lead leached from glass is practically desirable particularly in the case of ware whose use may be assumed to include long-term contact of their surface with liquids, especially beverages, for example glass carafes of lead crystal. For this reason, the effect of the respective surface treatments was studied on just this type of products.

## EXPERIMENTAL PART

### Samples and their treatment

The experiments were carried out on commercial lead crystal glass (24 wt.%  $\text{PbO}$ ) carafes of about 1000 ml capacity. The internal surfaces were treated in two ways:

1. Surface treatment by decomposition products of ammonium chloride. Weighed amounts of the reagent in powder form were introduced into the hot product prior to its entry into the annealing lehr. Two different doses of the substances were employed (0.3 g and 2 g). A part of carafes treated in this way were subsequently chemically polished

with a mixture of HF and H<sub>2</sub>SO<sub>4</sub>, which removes a thin surface layer by dissolution.

2. Preliminary extraction of lead from the internal surfaces of samples by exposure to a solution of acetic acid (4 vol.%) or hydrochloric acid (0.1 and 1 mol l<sup>-1</sup>) at room temperature for 24 hours.

#### Determination of lead extracted from the sample surface

The preliminary treated and non-treated internal surfaces were leached at room temperature with standard acetic acid solution (4 vol.%) [6] for periods of 24 hours to 280 days. Lead concentration in the extracts was determined by the AAS method with the use of flame atomisation (Pb determination limit: about 0.08 mg l<sup>-1</sup>).

#### Measurement of lead concentration profiles

The concentration profiles of lead in the surface of glass were measured in a separate series of experiments on samples prepared by cutting from commercial products. The surfaces were mechanically ground and polished and then treated by decomposition products of ammonium chloride at 450 °C or by extraction in acetic acid solution (4 vol.%) for 24 hours.

The concentration profiles were measured by X-ray photoelectron spectroscopy in combination with the ion sputtering by high-energy ions. Before sputtering and after each sputtering step photoelectron lines of Pb 4f and the other elements (Si 2p, O 1s, K 2s and Na 1s) were measured. The concentrations of elements in the samples were calculated according to [7] by means of intensity lines of the individual elements measured. The sputtering was effected by the ionic gun, the rate of sputtering the surface layers of glass was about 0.6 nm/min.

## RESULTS AND DISCUSSION

The results of leaching on samples treated by decomposition products of ammonium chloride are summarized in figure 1 as time dependence of lead concentration in extracts into standard solution of acetic acid. The results are given for two different doses of ammonium chloride (0.3 g and 2 g) and for surfaces treated in the same way but subsequently polished chemically, i.e. from which the surface layer was dissolved by a mixture of hydrofluoric and sulphuric acids. Results of extraction from samples with original non-treated surface are also given.

A comparison of results for samples with non-treated surface and those for samples treated with decomposition products of ammonium chloride shows that the treatment leads to a significant reduction of the amount of lead extracted from the surface of glass. The lead concentration values established in leachates even after long-term extraction (280 days) were generally

about 0.1 mg/l, which is a value frequently requested (particularly in some countries) as a limit one for ware intended for long-term contact with beverages.

Lead concentrations in extracts from sample surfaces treated with ammonium chloride but subsequently chemically polished were significantly higher compared to those treated in the same way but unpolished, and comparable to values established for original untreated samples. The subsequent polishing of treated samples with HF and H<sub>2</sub>SO<sub>4</sub> mixture (which is a common operation in the production of lead crystal glass) obviously leads to complete removal of the treated surface layer. The surface treatment should therefore be used only after chemical polishing of the ware, or the polishing bath should be prevented from coming into contact with the treated internal surface.

The amount of the reagent (ammonium chloride) had no discernible effect on the efficiency of the treatment (figure 1). The results indicate that it is possible to use relatively small doses of the reagent, which is desirable in particular with respect to the amount of decomposition products generated and their effects on environment.

Apart from ammonium chloride, also ammonium sulphate was used as reagent for the treatment. The results obtained from samples treated with ammonium sulphate were very similar to those from samples treated with ammonium chloride.

Evaluation of leachates from samples treated by preliminary exposure in solutions of acids is summarized in figure 2. Use is again made of long-term time dependence of lead concentration in acetic acid leachates for samples with surfaces non-treated and preliminary treated in the following ways:

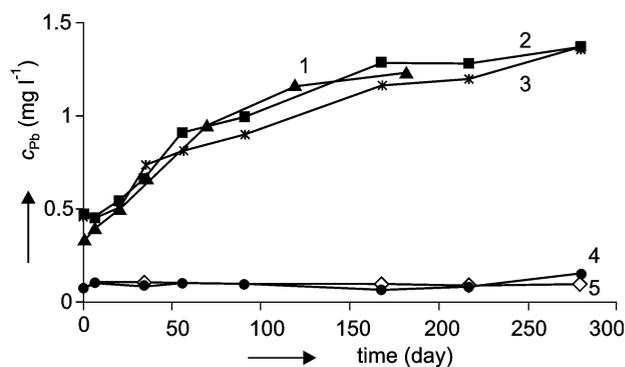


Figure 1. Concentration of lead in leachates into acetic acid (4 vol.%, room temperature) vs. time of leaching.

▲ - non-treated surface; ■ - surface treated with ammonium chloride (0.3 g), subsequently chemically polished; \* - surface treated with ammonium chloride (2 g), subsequently chemically polished; ● - surface treated with ammonium chloride (2 g), subsequently not chemically polished; ◆ - surface treated with ammonium chloride (0.3 g), subsequently not chemically polished.

- exposure in acetic acid (4 vol.%) for 24 hours.
- exposure in HCl at concentrations of 0.1 and 1 mol l<sup>-1</sup> for 24 hours.

The results given in figure 2 show that preliminary extraction of lead by exposure to solutions of the acids leads to reduced concentration of lead in leachates during even long-term leaching. However, unlike the case of surfaces treated by reactive gases at elevated temperatures (cf. figure 1), the lead concentration in leachates tends to increase in terms of time of leaching, even when the difference between the original non-treated and preliminary treated surfaces remains retained after long-term leaching.

Apart from acetic acid, also solutions of hydrochloric acid of two concentrations were used in the preliminary extraction. The results shown in figure 2 indicate that there was no substantial difference between the effects of the individual solutions of the acids employed.

The results show that preliminary extraction in solutions of acids can be used for reducing the amount of lead subsequently leached from the surface of lead crystal glass. During short-term subsequent contact of the treated glass with acidic solutions (approx. 24 hours), also this treatment provides lead concentration values in leachates close to the limit of 0.1 mg Pb/l. However, longer subsequent contact with acidic solutions yields Pb concentration values exceeding this limit and gradually increasing beyond it.

With respect to reducing the leaching of lead from the surface of glass by long-term contact with liquids, the treatment using reactive gases at elevated temperatures is more efficient than the treatment by preliminary extraction with solutions of acids. This finding is in agreement with the results of measuring the concentration profiles of lead in the surface of glass treated by the two methods. Figure 3 shows the

concentration profiles of lead in the surface of glass treated by products of ammonium chloride decomposition (450 °C), and in the surface of a sample treated by exposure for 24 hours in acetic acid (4 vol.%) at room temperature. A comparison of the two treatments shows that both result in a significant reduction of lead content in the glass surface. The lead concentration in the thin surface layer of both samples is comparable. However, the treatment using decomposition products of ammonium chloride succeeded in removing lead from deeper layers of the glass. In this case the significant decrease of lead concentration reaches to substantially greater depth than with the sample extracted with acid.

The high efficiency of extraction of lead by reactive gases at elevated temperatures is obviously also due to the effect of the treatment on the character of the surface layer. According to [1], this treatment brings about formation of a high-silica surface layer similar to silica glass. This layer then improves the chemical durability of the glass surface. The surface layer formed on lead crystal glass by decomposition products of ammonium chloride at elevated temperatures obviously acts as a more effective barrier against transfer of lead from the inner layers of glass towards its surface during subsequent leaching, than the extracted gel-like layer resulting from preliminary exposure in acidic solutions.

## CONCLUSION

Preliminary extraction of lead from crystal glass surfaces in solutions of acetic or hydrochloric acid, and treatment of the surface by the effect of decomposition products of ammonium chloride at elevated temperature result in a significantly reduced concentrations of lead in leachates into standard solution of acetic acid. The treatment using ammonium chloride has proved more effective, as the amount of lead extracted by long-term leaching remained very low. The concentration profiles

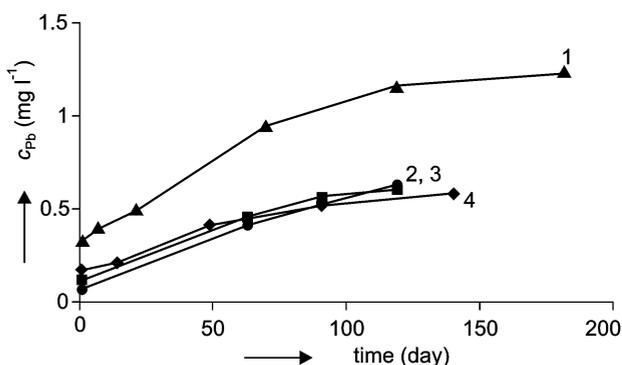


Figure 2. Concentration of lead in leachates into acetic acid (4 vol.%, room temperature) vs. time of leaching. ▲ - non-treated surface; ■ - surface exposed in advance for 24 hours in acetic acid (4 vol.%) ; ● - surface exposed in advance for 24 hours in hydrochloric acid (0.1 mol l<sup>-1</sup>) ; ◆ - surface exposed in advance for 24 hours in hydrochloric acid (1 mol l<sup>-1</sup>).

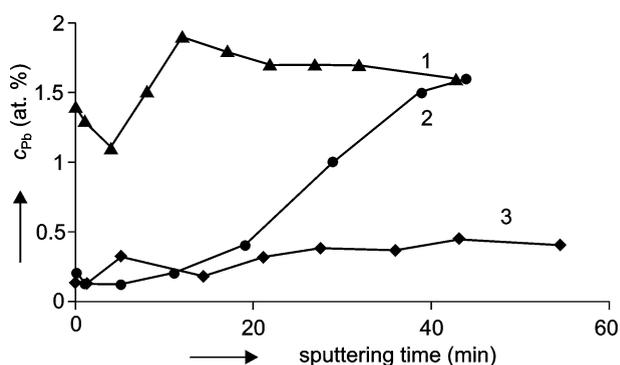


Figure 3. Concentration profiles of lead in the surface of samples (the depth of the removed layer is characterized by sputtering time). ▲ - initial surface; ● - exposure in acetic acid (4 vol.%, 24 hours, room temperature); ◆ - treatment with ammonium chloride (450 °C)

of lead in the surface of treated glass show that this treatment removes lead from deeper layers of glass than in the case of preliminary extraction with acetic acid solution.

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#### ÚPRAVY POVRCHU OLOVNATÝCH SKEL KE SNÍŽENÍ VÝLUHŮ OLOVA

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U olovnatého křišťálu byl sledován vliv úprav povrchu na koncentrační profily olova v povrchu skla a na výluhy olova při následném loužení v roztoku kyseliny octové. Povrchy byly upravovány dvěma postupy:

1. předběžným loužením v roztocích kyselin (kyselina octová, chlorovodíková).
2. působením produktů rozkladu chloridu amonného za vyšších teplot.

Obě úpravy vedly ke snížení výluhů olova z povrchu, účinnější byla úprava působením produktů rozkladu chloridu amonného. Při této úpravě také došlo k extrakci olova z hlubších vrstev skla, než při úpravě předběžným loužením.