

CORROSION OF METALS OF ORGAN PIPES IN VOLATILE ORGANIC COMPOUNDS ENVIRONMENT

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Abstract

The organ cabinet represents a specific corrosion environment with a high concentration of organic compounds that are released into the environment during the degradation of wood, glues and varnishes used in the production of the organ cabinet. Moreover, most of the metals from which organ pipes are made are highly sensitive to organic substances. In this study, the effect of relative humidity (54% and 75%) and concentration of organic compounds (formaldehyde, formic acid, acetic acid and propionic acid) on the corrosion of metals (lead, lead-tin alloy, tin and zinc) from which organ pipes are usually made was monitored. Corrosion rates were determined using gravimetric data (mass gain) and the composition of corrosion products was analysed by XRD.

Keywords: Indoor corrosivity, volatile organic acids, lead corrosion, preventive conservation

1. INTRODUCTION

Organ pipes are stored in a specific environment - a closed organ cabinet, which is made of wood and also contains other wooden pipes [1]. This microclimate is characterized by an increased concentration of organic substances, especially formaldehyde, acetic and formic acid, which are released into the environment during the hydrolysis of wood hemicelluloses [1-3]. The most important source of volatile organic substances is hardwood, especially oak [2]. The metals (lead, solder, tin and zinc) used for the production of organ pipes are known for their good corrosion resistance in normal atmospheric conditions due to the formation of a passive layer, especially based on oxides or carbonates [4-7]. However, in an environment polluted with organic substances, the dissolution and formation of other modifications of the original corrosion products occurs, the new corrosion products are unstable and soluble and no longer have a protective character [1, 2, 4-7]. It has already been described in the literature that the presence of acetic acid in the environment will significantly increase the corrosion rate of lead even at a very low concentration (0.1 - 1 ppm) [1]. In the case of formic acid, more stable corrosion products are formed, yet the corrosion rate of lead increases [8, 9]. Furthermore, there are reports of the use of higher carboxylic acids (capric, lauric acid) to protect lead with a barrier effect [10]. The aim of this study was to compare the influence of relative humidity and the concentration of organic pollutants (formic, acetic, propionic acids and formaldehyde) on the composition and protective properties of the layer of corrosion products of the aforementioned metals.

2. EXPERIMENTAL PART

2.1 Samples

Lead (Pb 99.97 %), lead-tin alloy (Sn63Pb37), tin (Sn 99.5 %) and zinc (Zn 99.5 %) samples in dimensions 15x50x1 mm were used in this work. The pure surface of samples was obtained with pickling in 1 %

hydrochloric acid, subsequent rinsing with deionized water and after grinding of the surface with abrasive wadding (3M Scotch-Brite CF-MF), subsequent rinsing with ethanol and then air drying.

2.2 Exposure conditions

Samples were exposed in a glass box with plastic cover (box volume 1 liter) with a beaker with a saturated salt solution that maintains a constant value of relative humidity (RH) and with the addition of formaldehyde/organic acid, which are a source of the pollutant. Two values of relative humidity were monitored as part of the experiment, approximately 54 % RH maintained using a saturated sodium bromide solution and 75 % RH maintained using saturated sodium chloride solution. The addition of formaldehyde/organic acids was chosen so that the final concentration of the solution was $0.001 \text{ mol}\cdot\text{l}^{-1}$ (lower concentration of formaldehyde/organic acids vapours) or $0.01 \text{ mol}\cdot\text{l}^{-1}$ (higher concentration of formaldehyde/organic acids vapours).

Eighteen different exposure conditions were tested in this work:

- no pollutant and RH approx. 54 %
- lower concentration of formaldehyde and RH approx. 54 % (0.001 F)
- higher concentration of formaldehyde and RH approx. 54 % (0.01 F)
- lower concentration of formic acid and RH approx. 54 % (0.001 FA)
- higher concentration of formic acid and RH approx. 54 % (0.01 FA)
- lower concentration of acetic acid and RH approx. 54 % (0.001 AA)
- higher concentration of acetic acid and RH approx. 54 % (0.01 AA)
- lower concentration of propionic acid and RH approx. 54 % (0.001 PA)
- higher concentration of propionic acid and RH approx. 54 % (0.01 PA)
- no pollutant and RH approx. 75 %
- lower concentration of formaldehyde and RH approx. 75 % (0.001 F)
- higher concentration of formaldehyde and RH approx. 75 % (0.01 F)
- lower concentration of formic acid and RH approx. 75 % (0.001 FA)
- higher concentration of formic acid and RH approx. 75 % (0.01 FA)
- lower concentration of acetic acid and RH approx. 75 % (0.001 AA)
- higher concentration of acetic acid and RH approx. 75 % (0.01 AA)
- lower concentration of propionic acid and RH approx. 75 % (0.001 PA)
- higher concentration of propionic acid and RH approx. 75 % (0.01 PA)

All exposures were done at laboratory temperature. Exposure conditions were monitored using Testo 174 H relative humidity loggers. The acetic acid concentration in air was verified using passive dosimeter tubes (PDTs) from GASTEC Corp. (model 81D). Duration of the exposures was 32 days. Three samples of each metal were exposed in each different conditions. One sample of each metal was characterized by X-ray diffraction (XRD) using the X'Pert PRO diffractometer and High Score Plus software (Malvern Panalytical Ltd).

2.3 Mass gain

According to the ISO standard 11844-2 [11] growth rate of the layer of corrosion products were calculated from the obtained mass gain values. Each sample was weighed twice (UYA 2.4Y Ultra-Microbalance) in relation to a reference balance standard of stainless steel with a similar mass to the sample.

3. RESULTS AND DISCUSSION

3.1 Exposure conditions

As part of the exposure, values of relative humidity and concentration of formaldehyde/organic acids in the box environment were measured. The relative humidity values in the individual boxes were constant during

the exposure. In boxes with a saturated sodium chloride solution, the RH values ranged from 75-80%, in boxes with a saturated sodium bromide solution, the RH values ranged from 56-60%.

The concentration of formaldehyde/organic acids in the box environment was measured after 5 and 30 days of exposure, the measured values are recorded in **Table 1**.

Table 1 The concentration of formaldehyde/organic acids in the box environment during the exposition

Concentration of the source solution (mol·l ⁻¹)	Concentration in the box environment (ppm)			
	54 % RH		75 % RH	
	after 5 days	after 30 days	after 5 days	after 30 days
0.001 F	0.2	0.7	0.1	0.3
0.01 F	0.1	2.8	0.4	4.3
0.001 FA	0.1	0.5	0.1	1.0
0.01 FA	4.5	6.2	0.8	1.4
0.001 AA	0.1	0.5	0.1	1.0
0.01 AA	3.8	5.5	1.2	1.5
0.001 PA	0.1	0.5	0.1	1.0
0.01 PA	4.2	6.0	1.1	1.5

3.2 Mass gain

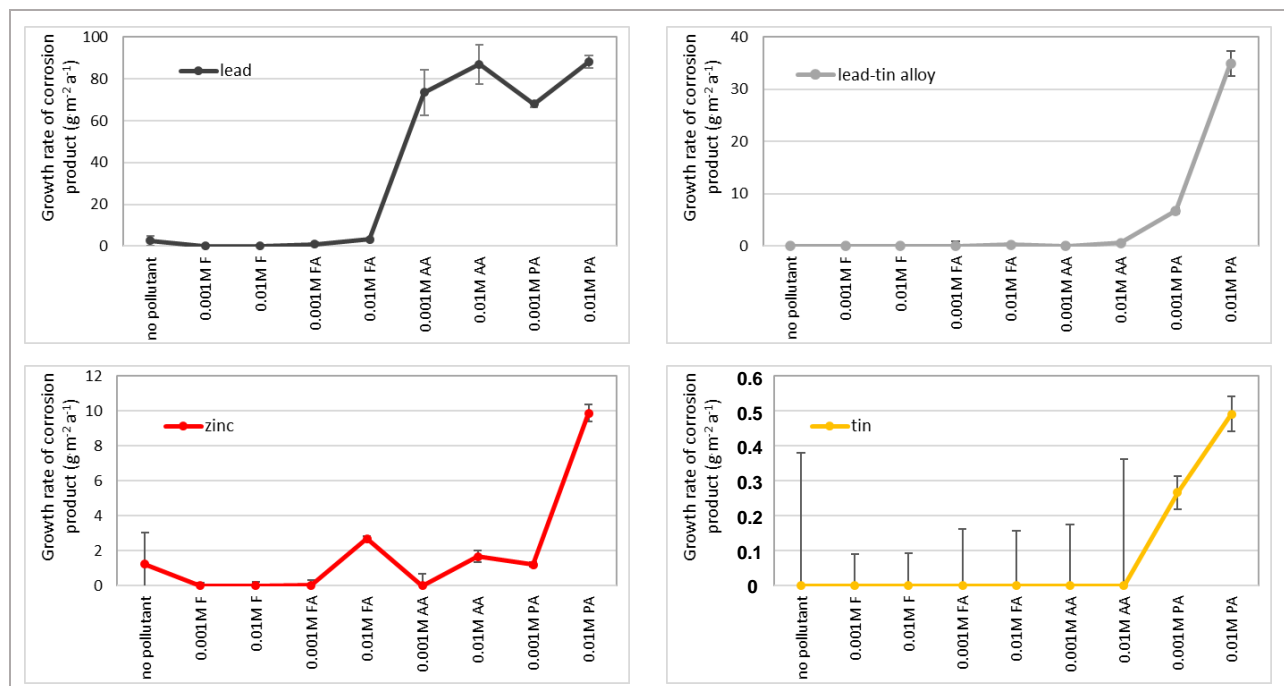


Figure 1 Growth rates of the layer of corrosion products of lead, lead-tin alloy, zinc and tin samples during exposure in humid environment (54 % RH) polluted with formaldehyde (F), formic acid (FA), acetic acid (AA) and propionic acid (PA) vapours calculated from mass gain

Figure 1 and **Figure 2** represent growth rates of the layer of corrosion products obtained using the mass gain. As expected, the corrosion rates of the monitored metals in a pollution-free environment are almost zero, even at a humidity of 75%. Furthermore, it can be seen that the presence of formaldehyde alone in the environment

does not increase the corrosion rate of any of the metals. Even in the case of exposure, where the concentration of formaldehyde in the air was three times higher than that of organic acids (according to **Table 1**). The corrosion rate of tin in all exposures is negligible. At lower environmental humidity, corrosion rates are lower. In the monitored environments, lead was the most sensitive metal, in most exposures 3-8 times higher corrosion rate values were calculated for lead than for other metals in the same conditions. The significant influence of acetic acid can be seen on the graph for lead, especially in an environment with 75% RH and a higher concentration of acetic acid, the value of the growth rate of the layer of corrosion products is significantly higher than for other exposures. With zinc and lead-tin alloy, the aggressive effect of more concentrated acetic acid can also be seen in environments with higher humidity. The lead-tin alloy reacts significantly to the presence of a higher concentration of propionic acid in the environment. Zinc in an environment with a lower RH (54%) shows a low growth rate of the layer of corrosion products, with a higher environmental humidity (75% RH), the sensitivity of zinc to organic acids, especially formic and acetic acid, is also higher.

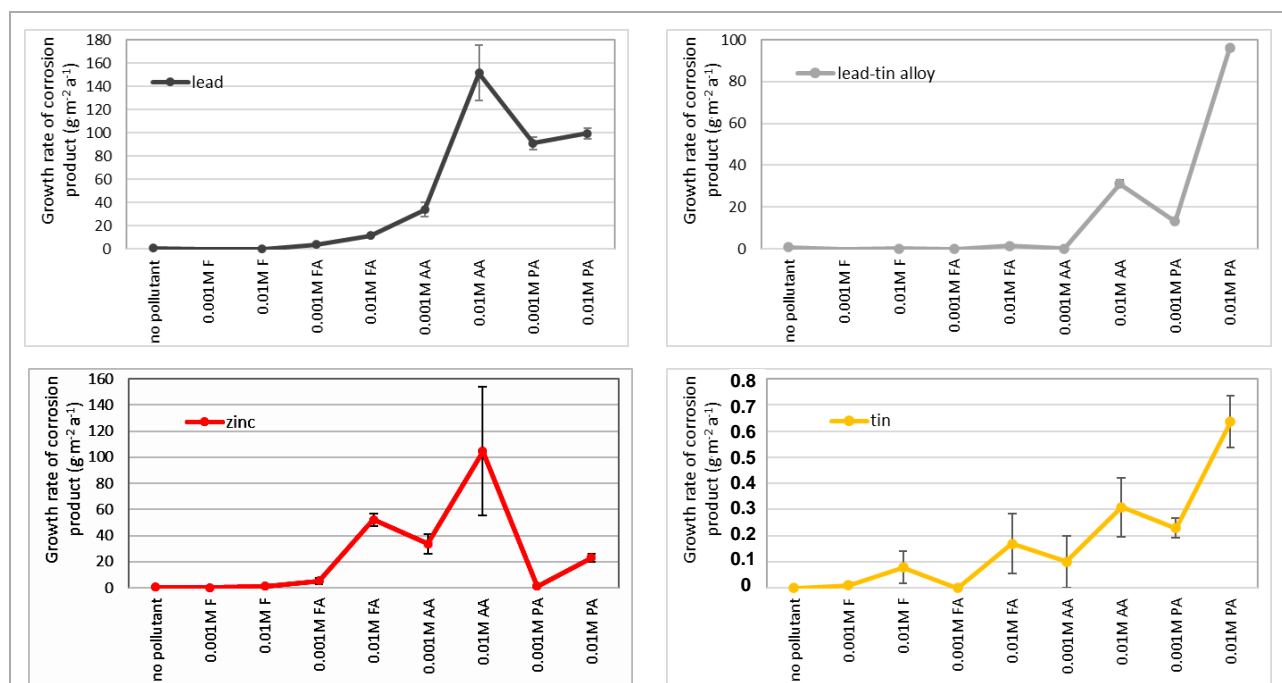


Figure 2 Growth rates of the layer of corrosion products of lead, lead-tin alloy, zinc and tin samples during exposure in humid environment (75 % RH) polluted with formaldehyde (F), formic acid (FA), acetic acid (AA) and propionic acid (PA) vapours calculated from mass gain

3.3 Surface characterization

The results of XRD analysis showed that when samples are exposed in an environment without pollution or with formaldehyde, only a passive layer based on oxides forms on the surface of metals. **Table 2** and **Table 4** show that in an environment containing formic acid, lead formate-based corrosion products are formed on lead or lead-tin alloy. At a higher concentration of formic acid in the environment, the more aggressive lead formate is represented to a greater extent in lead corrosion products. Similarly, in an environment with acetic acid, a high corrosion rate can be observed in the presence of hydrated lead oxide acetate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO} \cdot \text{H}_2\text{O}$). Exposure of lead and lead-tin alloy to propionic acid vapors results in the formation of corrosion products consisting primarily of lead propionate. According to **Table 4** and **Figure 2**, it can be seen that the presence of acetate or peroxyformate in the corrosion products increases the corrosion rate of zinc.

Table 2 Summary of XRD analyses for lead samples after exposure in humid environment (54 % and 75 % RH) polluted with formaldehyde (F), formic acid (FA), acetic acid (AA) and propionic acid (PA) vapours

Semiquantitative representation of compounds in corrosion products (%)	Concentration of the source solution (mol·l ⁻¹)											
	54 % RH						75 % RH					
	0.001 FA	0.01 FA	0.001 AA	0.01 AA	0.001 PA	0.01 PA	0.001 FA	0.01 FA	0.001 AA	0.01 AA	0.001 PA	0.01 PA
PbO					15							
PbO ₂					5	*						
Pb(HCOO)(OH)	91	7					40	21				
Pb(HCOO) ₂	9	93						79				
PbCO ₃											13	
Pb ₃ (CO ₃) ₂ (OH) ₂			100	11	41					30	66	
Pb ₅ (CO ₃) ₃ O(OH) ₂				78	23	*	60		88	64	21	*
Pb(CH ₃ COO) ₂					7	*						
Pb(CH ₃ COO) ₂ ·2PbO·H ₂ O			*	11	9					6		*
Pb ₃ O ₂ (CH ₃ COO) ₂ (H ₂ O) _{0.5}									12			
Pb(CH ₂ COO) ₂						*					*	*
Pb(CH ₃ CH ₂ COO) ₂						100						100

* compound detected in corrosion products in trace amounts

Table 3 Summary of XRD analyses for zinc samples after exposure in humid environment (75 % RH) polluted with formaldehyde (F), formic acid (FA), acetic acid (AA) and propionic acid (PA) vapours

Semiquantitative representation of compounds in corrosion products (%)	Concentration of the source solution (mol·l ⁻¹)			
	54 % RH		75 % RH	
	0.01 PA	0.01 AA	0.001 PA	0.01 PA
PbO ₂			62	
SnO ₂			38	
Pb ₃ (CO ₃) ₂ (OH) ₂		62		
Pb(HCOO) ₂		25		
Sn(CH ₃ COO) ₂	10	13		9
Pb(CH ₃ CH ₂ COO) ₂	90			91

Table 4 Summary of XRD analyses for lead-tin alloy samples after exposure in humid environment (54 % and 75 % RH) polluted with formaldehyde (F), formic acid (FA), acetic acid (AA) and propionic acid (PA) vapours

Semiquantitative representation of compounds in corrosion products (%)	Concentration of the source solution (mol·l ⁻¹)				
	0.01 FA	0.001 AA	0.01 AA	0.001 PA	0.01 PA
Zn(HCOO) ₂ (H ₂ O) ₂	100				
Zn ₅ (OH) ₈ (CH ₃ COO) ₂ ·H ₂ O		7	100	100	50
Zn ₅ (CO ₃) ₂ (OH) ₆		93	*		
Zn(CH ₃ CH ₂ COO) ₂					50

* compound detected in corrosion products in trace amounts

4. CONCLUSION

Especially lead, but also the lead-tin alloy (in the presence of propionic acid) are metals sensitive to organic acids in an environment with normal humidity (54% RH). At lower humidity, it is for zinc and lead-tin alloy more aggressive propionic acid than acetic acid. Acetic acid is very aggressive for lead even at a relative humidity of 54%, at a humidity of 75% it proved to be dangerous for lead-tin alloy and zinc as well. The composition of corrosion products has a significant effect on the corrosion rate of the metal - the presence of acetates, succinates and propionates in corrosion products increases the corrosion rate of lead, zinc and lead-tin alloys.

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