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Replicas of Letters from the Museum Plantin-Moretus,
Antwerp**

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Micro Raman Investigation on corrosion of Pb-Based Alloy Replicas of Letters from the Museum Plantin-Moretus, Antwerp

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ABSTRACT

To better understand corrosion behaviour of lead-based (Pb) alloys exposed to volatile organic compounds (VOCs) – specifically acetic and formic acid – a preliminary research has been carried out on laboratory-made samples replicating such alloys. Replicas have been manufactured by simulating specific types of Pb-based alloys, with antimony (Sb) and tin (Sn) as alloying elements, in order to characterise corrosion products and evaluate the influence of each alloying element. Replicas were cast in a refractory mould and later placed in size-specific desiccators and exposed to concentrated acetic and formic acid vapours for 15 days. Each specimen was also subjected to gravimetric measurements and periodically monitored in order to understand the corrosion behaviour. Micro Raman Spectroscopy (μRS) and Scanning Electron Microscopy (SEM) together with energy Dispersive X-Ray Spectroscopy (EDS) were used for the characterisation of Pb-based replicas. Results showed the presence of typical corrosion products – more or less hydrated forms of Pb and Sn acetates and formates – but also a sudden increase in the volume and brittleness of some Sb rich specimens as well as the presence of seldom-detected metallic antimony peaks with μRS. In this perspective, the influence of Sb as an alloying element on the corrosion of Pb-based artefacts may generate serious problems when such objects have to be restored and particular attention should be given to conservation/stabilisation procedures.

KEYWORDS: Lead alloys, Micro Raman, corrosion, acetates, formates

INTRODUCTION

A study conducted by our research group from the *Universities of Genoa and Bologna* in collaboration with the *Conservation Studies Department of the University of Antwerp* on original printing letters from the *Plantin-Moretus Museum Collection* – consisting of specific types of Pb-based alloys (with Sb and Sn as alloying elements) seldom studied in the past – has brought to light new results on the characterisation of Pb-based artefacts under Volatile Organic Compound (VOC) vapours¹. During this research, different Pb based alloy replicas have been produced in order to:

- 1. morphologically and chemically characterise corrosion products and relative mechanisms;

2. evaluate the influence of alloying elements (Sn, Sb) on corrosion.

Pb alloys – in which Sn and Sb contents were conveniently modified on the basis of research conducted by one of the authors¹ and yet to be published – were reproduced in the laboratory and later subjected to specific tests simulating corrosion processes inside wooden boxes emitting organic pollutants. In order to investigate the corrosion behaviour, samples were exposed to accelerated corrosion tests (by using sealed desiccators with saturated organic acid atmospheres). The experimentation consisted of monitoring Pb based alloys exposed to specific organic acids – such as formic and acetic acid vapours – over a few days, characterising corrosion products step by step. The corrosion behaviour was periodically evaluated as the specimens showed remarkable changes in morphology, volume and weight: i.e. embrittlement and increase in volume with the formation of black and white oxidised compounds.

On such materials, Micro Raman Spectroscopy performed in both the Genoa and Bologna laboratories has given a crucial contribution to the ongoing research, proving itself a powerful technique not only for the uniqueness of its results and its high detection limits but also for its sensitivity to inorganic and organic compounds forming on the specimen surface – not identifiable with traditional metallographic analyses or electrochemical techniques. In fact, this sometimes-underestimated tool not only helped us detect all the corrosion products but allowed us to characterise general corrosion mechanisms affecting this type of alloy, giving a wide variety of information which will help evaluate other conservation procedures. Complementary techniques were also used such as Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS) so as to get a better overview of the corrosion mechanism.

The tendency of a metal to react with the surrounding environment in standard conditions leads to the formation of several corrosion products. Pb is a metal that has been common to many cultures since the 3rd millennium BC as it is easily cast and shaped. Consequently, Pb and its alloys have been used for many applications over the centuries such as water pipes (during the Roman period), decorative plates on the surface of houses, organ pipes and so on²⁻⁵. Lead was also once used to produce coins alloyed with copper or copper and tin^{6,7}.

Like other metals, lead is subjected to corrosion yet its effects are less visible due to the formation of several passivation layers on the metal surface, which depends on the environment. The corrosion behaviour of Pb has been well studied in the past because of its industrial use. Its reactivity to atmospheric gases usually leads to the formation of different corrosion products such as *Cerussite* (PbCO_3), *Hydrocerussite* ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) or *Plumbonacrite* ($\text{Pb}_{10}(\text{CO}_3)_6\text{O}(\text{OH})_6$) which create a very weak protective layer^{8,9}. Generally, a first patina composed of Pb oxide and covered with an outer layer of pure or basic Pb carbonates is visible on Pb artefacts. This layer is usually protective enough to create a passivation patina (if the environment does not contain VOCs). Nevertheless, for certain environments, Pb acts differently and undergoes a high corrosion rate. Accordingly, protective treatments have recently been studied by many research teams – above all Rocca et al¹⁰ who tested sodium decanoate efficiency – in order to inhibit corrosion mechanisms of Pb under specific atmospheric conditions. However, more research is needed due to lack of knowledge.

Even though the corrosive behaviour of pure Pb has been extensively studied under standard conditions – such as wet environments – there is little research that deals with Pb and Pb alloy behaviour under specific conditions, such as its presence in the atmosphere of VOCs¹¹⁻¹⁴. The high reactivity of Pb alloys to VOCs has been widely recognised in studies of modern art objects in closed spaces characterised by VOC-rich atmospheres¹⁵. However, this research has not taken into consideration the role played by alloying elements, in our specific case antimony (Sb), in the corrosion process¹⁶. Research generally deals with pure Pb corrosion and does not focus on the corrosion characterisation of Pb alloys, which are usually studied to a lesser degree in the field of cultural heritage^{17,18}.

Furthermore, the use of Micro Raman Spectroscopy is generally well known for corrosion products of many kinds of materials^{8,19,20}. Nevertheless, this technique is often replaced by analysis with other well-established techniques, such as qualitative and quantitative elemental analysis (e.g. Energy Dispersive X-Ray Spectroscopy) or electrochemical analysis (e.g. Open Circuit Potential or potentiodynamic polarisation)^{5,21,22}. It is also true that sometimes all the possible information collected by those non-invasive techniques needs the confirmation that only a specific type of analysis can give, such as that of Micro Raman Spectroscopy.

EXPERIMENTAL

Experimental setup

Following the previously cited work of Storme et al.¹, in which some lead-based printing letters showed different corrosion behaviour according to the nature of the alloy, replicas of known composition were produced (table 1) in order to verify the influence of alloying elements and of specific types of environment. Pb-based alloys in which Sb and Sn act as alloying elements were selected for the investigation (see table 2-3). In addition, pure Pb specimens were used for the analysis in order to correlate corrosion behaviour to alloying elements influence

Table 1. Composition of the alloys selected for the investigation in wt%. All compositions were verified with SEM after production.

Table 2. Description of Pb- based alloys exposed to acetic acid.

Table 3. Description of Pb- based alloys exposed to formic acid.

Each specimen (1 x 1 cm² with a variable thickness (0.25 – 0.40 cm)) was specifically cast in a refractory mould, accurately shaped and later polished using metallographic emery paper up to 1000 grit. Specimens were rinsed gently with distilled water and washed in ethanol in order to eliminate corrosion and polishing residues. Samples were then placed in size-specific desiccators and exposed to concentrated acetic or formic acid vapours, maintaining a controlled environment for 15 days exposure time (see figure 1).

Figure 1. Experimental setup for pure Pb and binary Pb alloys specimens exposed to VOCs. Each specimen was weighted using an analytical scale. 2nd row: a) Type 1 b) Type 2 c) Type 3 corrosion as described in table 4.

Methodologies of Investigation

Each specimen was subjected to gravimetric measurements and periodically monitored in order to evaluate the corrosion rate. Observations were carried out using a Light Optical Microscope (LOM) in order to better differentiate the corrosion products by their morphology and colour. Micro-Raman analyses (Genoa lab) were performed with a Renishaw System 2000 spectrometer with Leica Optical microscope using 20x long focal and 50x objectives and equipped with a Peltier-cooled CCD detector. A Red He-Ne laser (632.8 nm wavelength, full power 4 mW) was used as an excitation source, with laser power reduced to 50% transmission filter in order to avoid sample damages. A Renishaw Raman Invia coupled with a Leica DMLM microscope (objectives used 50x, 50x l.f.) was used in the Bologna lab. The excitation source was a near IR diode laser ($\lambda = 785.0$ nm, full power 300 mW, reduced with different filters to avoid sample degradation). Spectra were recorded from 4000 to 100 cm⁻¹ – 1 cm⁻¹ spectral resolution. The integration time was 10 seconds and accumulations varied from 1 to 9 depending on the sample. Measurements were repeated on different points. Experimental spectra were compared to data published in literature. Analyses on cross sections were performed using a Scanning Electron Microscope (SEM) ZEISS EP EVO 50 with Secondary (SE) and Backscattered Electron Detectors (BSE) in low vacuum variable pressure mode (100 Pa) using an accelerating voltage of 20 KV. The microanalysis was

carried out with an EDS Oxford Instrument INCA ENERGY 350 including a Si(Li) detector equipped with an ultrathin window ($Z > 4$ (Be)).

RESULTS AND DISCUSSION

Monitoring of corrosion patina and mass variation tests

The corrosion behaviour of each sample was monitored for 15 days, both by optical observations and by gravimetric measurements, in order to identify changes in morphology and weight. Mass variation measurements as a function of time are shown in **graphs 1-2**.

Graph 1. Mass variation as a function of exposure time for samples exposed to acetic acid: weight loss was observed.

Graph 2. Mass variation as a function of exposure time for samples exposed to formic acid: weight gain was observed, especially for Sb-rich alloys.

In agreement with LOM observations, it was possible to identify different corrosion patinas on each specimen according to the alloying element influencing corrosion behaviour. Generally, each sample exposed to acetic acid showed a preliminary 'wet' patina, which increases the severity of the corrosion process, also making the dissolution of the corrosion products easier. After 15 days, a white corrosion layer was observed on each specimen and general weight loss was observed due to the leaching effect of the acetic acid caused by severe condensation.

On the other hand, formic acid determined the formation of several patinas, with different morphologies and colours as a function of alloying element content. PbSb10 and PbSb15 specimens show a sudden increase in volume and brittleness due to macroscopic expansion of the samples but no white patina is visible. Conversely, PbSb5, PbSn5 and PbSn2 seem to exhibit a similar behaviour which is coherent with previously performed analyses^{1,23}: a white patina was observed and whitish powders appeared on the surface of all samples.

The patina of pure Pb specimens for both acetic and formic acid vapours seem to have the same trend in colour and morphologies as PbSb5 and PbSn alloys.

Table 4 summarises patina morphologies after exposure tests.

Table 4. Patina morphologies on specimens exposed to acetic and formic acid.

Characterisation of corrosion patinas

In this study, a multi-analytical approach was employed in order to completely characterise the corrosion behaviour of VOC-exposed specimens.

Raman analyses were carried out on representative samples, selected on the basis of morphological observations and gravimetric results. Subsequently, SEM-EDS was performed on cross sections in order to investigate the chemical composition and to better understand the influence of alloying elements.

Acetic acid results

Molecular identification was performed by μ RS and different compounds were identified, related to the main alloying constituents of each sample.

On the basis of gravimetric measurements (**graph 1**), a comparable behaviour is expected for all specimens exposed to this environment. The results shown in **figure 2** confirm this assumption.

Figure 2. Raman spectra collected with 632.8 nm laser on a) pure Pb b) PbSb5 c) PbSb15 d) PbSn5 replicas after exposure to acetic acid. Parameters of the analysis: acquisition time: 10 sec.; number of accumulations: 4; power: 25% transmittance. Lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) and Tin (II) acetate ($\text{Sn}(\text{CH}_3\text{COO})_2$) were identified.

Lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) was identified on pure Pb and Sb-rich specimens (215, 482, 614, 651, 938, 1345, 1423, 1533, 1614, 1645, 2931 cm^{-1}) whilst Tin (II) acetate ($\text{Sn}(\text{CH}_3\text{COO})_2$) was detected on Sn-rich specimens (209, 283, 335, 535, 670, 935, 1343, 1425, 1560, 1642, 2930 cm^{-1}). **Table 5** summarises the detected compounds for each specimen and also reports the band positions of the detected compounds. Slight variations of vibrational bands are observable probably due to the influence of the alloying elements, which tend to modify the molecular structure of the Pb based compounds.

Table 5. Vibrational bands of corrosion products, compared to data from the literature (cm^{-1}).

The replicas were subsequently analysed with SEM-EDS in order to investigate their morphological and chemical peculiarities and to correlate corrosion behaviour to alloying element influence. SEM observations carried out on cross sections allowed us to determine the thickness of the patinas, which ranges from 80 to 90 μm for the PbSb5 alloy. Elemental mapping at the microstructural level is shown in **figure 3**.

Figure 3. Elemental mapping by EDS (X-Ray maps) of cross sections after exposure to acetic acid. Top row: PbSb5 specimen, from left to right: SEM-BSE micrograph, C, O, Pb, Sb distribution in the analysed area. Bottom row: PbSn5 specimen, from left to right: SEM-BSE micrograph, C, O, Pb, Sn distribution in the analysed area.

It was noted that alloying elements tend to influence corrosion behaviour and in particular corrosion product formation and growth. In the case of Sn-containing specimens, a thinner patina layer (about 60 μm) is formed on the surface. From the analysed sample (PbSn5), it was possible to see that Sn tends to concentrate on the outer part of the corrosion layer, directly reacting with the surrounding environment. Accordingly, tin acetates were identified.

On the other hand, a thicker corrosion layer tends to form on Sb rich specimens. Since no Sb-rich compounds were identified by μRS , elemental analyses on cross sections were carried out. It was observed that Sb tends to concentrate in specific areas of the corrosion layers under a first superficial layer of Pb based compounds in contact with the atmosphere. In fact, Pb acetates were detected.

A different behaviour of Sn and Sb was observed. Sn tends to concentrate in the outer zone of the patina: the Sn acetate layer seems to be able to limit the interaction of Pb with the environment, thus leading to a lower total thickness of the patina. On the other hand, Sb tends to create aggregates inside the inner corrosion layer, which do not hinder the interaction between Pb and acetic acid, thus forming Pb acetates (see also **figure 9**).

Formic acid results

Micro Raman analyses of selected samples confirm the trend observed during the monitoring phase. Despite the low crystallisation degree of some of the corrosion products on the exposed surfaces – as in the case of the pure Pb specimen – which caused some noise problems, it was possible to recognise the main compounds in each corrosion layer. Representative spectra are reported in **figure 4**.

Figure 4. Raman spectra collected with a 632.8 laser on a) pure Pb b) PbSb5 c) PbSb15 d) PbSn5 replicas after exposure to formic acid. Parameters of the analysis: acquisition time: 10 sec.; number of accumulations: from 1 to 4; power: 25% transmittance. Lead formate ($\text{Pb}(\text{HCOO})_2$) was identified on all replicas. On Sb-rich replicas, Raman vibrational bands of metallic antimony are also visible.

Two different behaviours were observed. In each specimen exposed to formic acid, lead formate ($\text{Pb}(\text{HCOO})_2$) was detected. This result indicates that alloying elements do not contribute to

differentiate corrosion products. Nevertheless, in the case of Sb rich alloys, also other seldom-detected peaks are visible ($139, 276, 331 \text{ cm}^{-1}$), indicating the presence of metallic antimony inside the corrosion layers related to the presence of eutectic phases in the samples (see **figure 5**).

Figure 5. SEM BSE 250x micrograph on a cross section of PbSb5 sample. Eutectic phases (grey and black lamellae) surrounding the Pb matrix (grey areas) are observed.

Table 5 reports the main Pb formate and metallic Sb vibrational bands of samples, compared to data from the literature. Minor contributions at low wavenumbers were observed in the case of the PbSn5 alloy (**figure 4d**), where the peaks at 144 cm^{-1} could be attributed to PbO, Litharge²⁴.

Figure 6 shows a comparison between the two laser excitation sources on the same sample (PbSb5 alloy). Two different corrosion products (are detected using the 785 nm laser on the spots analysed).

Figure 6. Comparison of Raman spectra on PbSb5 specimen after exposure to formic acid: a) 632.8 nm laser b) 785 nm laser c) 785 nm laser on a different spot. Parameters of the analysis: acquisition time: 10 sec.; number of accumulations: 4; power: 25%.

Metallic antimony peaks are much more defined on spectra collected with the 785 diode laser where no other corrosion product is detected (**figure 6**). In that case, a resonance effect can be assumed given the fact that elemental Sb was detected as the only 'corrosion product' on selected areas of the sample. The presence of elemental Sb has already been stated in recent studies, however its presence has never been correlated to corrosion products of alloys of known composition but to the solid state transition of its body centred cubic lattice^{25,26}. However further research needs to be carried out in this area. In **figure 7**, it is possible to see Raman bands of elemental Sb on the PbSb15 replica. It is worth noting that this sample displays a narrow band at 139 and a broader one at 276 cm^{-1} (**table 4**), whilst the reference for ambient pressure Raman spectra of metallic Sb²⁷ reports two Raman peaks at 114 cm^{-1} (E_g mode) and 151 cm^{-1} (A_{1g} mode), as well as a broad feature between 235 and 320 cm^{-1} , attributed to second-order scattering by optical phonon modes. In our samples, the peak at 114 cm^{-1} is not visible due to the cut of notch. The peak at 139 cm^{-1} is red-shifted of about 12 cm^{-1} by comparison to the literature value of 151 cm^{-1} , probably due to solid solution effects related to the presence of Pb in the alloy (the solubility of Pb in Sb is low but not negligible). Also morphological and chemical assessments were made during the analysis which lead us to exclude the possibility of thermal degradation.

Figure 7. Raman vibrational bands of metallic Sb using a near IR diode laser (785 nm excitation source) and spot of analysis.

Cross sections were obtained from PbSn5, PbSb5 and PbSb15 specimens and elemental mapping was carried out on the corrosion layers. SEM results were similar to those performed on replicas exposed to acetic acid for PbSn5 and PbSb5, in which a variation in corrosion products is determined by the presence of different alloying elements. On the other hand, for the PbSb15 specimen, different assumptions have to be made. In fact, it is possible to observe aggregates of metallic Sb, which tend to concentrate inside the corrosion layers in large quantities (see **figure 8**).

Figure 8. Elemental mapping of PbSb15 specimen (cross-section, after exposure to formic acid), from left to right: SEM-BSE micrograph, C, O, Pb, Sb distribution in the analysed area.

On Sb-rich, Pb-based alloys, the presence of metallic Sb in specific areas of the sample seems to be correlated to the sudden expansion and increase of volume and brittleness. It is therefore assumed

that metallic Sb has an influence on the corrosion mechanism of Sb-rich alloys, probably due to selective lead corrosion.

Generally, the corrosion behaviour of all samples seems to be correlated to the well-known process of atmospheric corrosion of lead, where a protective layer of Pb(II) oxide (mainly *litharge* or PbO) is formed²⁸. In presence of acetic and/or formic acid, a chemical reaction occurs with the formation of acetates or formates, which disrupt the original protective layer. In our specific case, only traces of Pb oxides were detected, indicating that the aggressive environment constituted by VOCs lead to extensive formation of acetates and formates, increasing the dissolution rate of the specimens as well as the sudden increase of volume and relative brittleness (**figure 9**).

Figure 9. Schematic representation of the corrosion process for all specimens. First line, from left to right pure Pb, PbSn5, PbSb5 sample exposed to acetic acid. Second line, from left to right pure Pb, PbSn5, PbSb5, PbSb15 sample exposed to formic acid.

CONCLUSIONS

Corrosion behaviour of samples exposed to VOCs vapours (acetic and formic acid) simulating the effect of wooden boxes was characterised. After 15 days, exposed samples showed remarkable changes in morphology, volume and weight: for some of them, the increase in volume lead to sudden expansion in all directions, accompanied by extensive cracking. Alloys with low Sn or Sb content showed low corrosion rates; on the contrary, alloys with a high Sb content (PbSb10, PbSb15) corroded much more quickly and severely, with a noticeable increase in thickness and volume. The use of a multi-analytical approach – μ RS combined with SEM- EDS – allowed us to identify the main corrosion products forming on the surface of the replicas. More or less hydrated forms of Pb and Sn acetates and formates were detected as well as metallic antimony on Sb-rich specimens.

Accordingly, the corrosion behaviour is strictly dependent upon alloying elements, which may contribute to accelerate corrosion. In particular, Sb as an alloying element was the main cause of increased reactivity, determining the embrittlement and increase of volume on samples exposed to formic acid. Since no Sb-based corrosion products are formed in these processes, it is still unclear as to what the exact role of Sb is in generating such an extensive Pb-corrosion. This topic needs further study.

The use of μ RS, which is generally well known for corrosion products of archaeological and artistic materials, not only gave a crucial contribution to the ongoing research, but helped us identify all the corrosion products inside the patina, with the final aim of characterising the corrosion mechanisms that affect this type of alloy.

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SAMPLE	Element (wt%)		
	Pb	Sn	Sb
Pb	100	-	-
PbSn2	98	2	-
PbSn5	95	5	-
PbSb5	95	-	5
PbSb10	90	-	10
PbSb15	85	-	15

Table 1. Composition of the alloys selected for the investigation in wt%. All compositions were verified with SEM after production.

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	SAMPLE	CORROSION PRODUCT	MAIN VIBRATIONAL BANDS	VIBRATIONAL BANDS FROM LITERATURE [18,19,24,27,28]
Acetic Acid Vapours	Pb	Lead Acetate trihydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	215(s); 482(vw); 614(vw); 651(w); 938(s); 1345(m); 1423(s); 1533(w); 1614(vw); 1645(vw); 2931(vs)	198(s); 466(w); 651(w); 815(vs); 930(s); 1414(m); 1428(w); 2926(vs)
	PbSn5	Tin (II) Acetate $\text{Sn}(\text{CH}_3\text{COO})_2$	209(m); 283(m); 335(w); 535(w); 670(w); 935(s); 1343(m); 1425(m); 1560(w); 1642(w); 2930(vs)	
	PbSb5	Lead Acetate trihydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	216(s); 479(vw); 616(vw); 649(w); 939(s); 1342(m); 1423(s); 1530(w); 1614(vw); 1646(vw); 2930(vs)	198(s); 466(w); 651(w); 815(vs); 930(s); 1414(m); 1428(w); 2926(vs)
	PbSb15	Lead Acetate trihydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	215(s); 477(vw); 613(vw); 650(w); 936(s); 1345(m); 1424(s); 1528(w); 1609(vw); 1642(vw); 2932(vs)	198(s); 466(w); 651(w); 815(vs); 930(s); 1414(m); 1428(w) 2926(vs)
Formic Acid Vapours	Pb	Lead Formate $\text{Pb}(\text{HCO}_2)_2$	202(w) 1342(vs); 1530(m); 2845(m)	193(s); 757(vw); 1065(vw); 1343(vs); 1374(w); 1531(m) 2850(s)
	PbSn5	Lead Formate $\text{Pb}(\text{HCO}_2)_2$	174(s); 197(s); 761(vw); 1075(vw); 1342(vs); 1375(w); 1530(m); 2843(m); 2872(w)	193(s); 757(vw); 1065(vw); 1343(vs); 1374(w); 1531(m); 2850(s)
		Litharge (PbO)	144(m)	82(m), 147(vs), 339(w)
	PbSb5	Elemental Sb	139(vs); 276(m); 331(m)	114(m); 151(vs); 235- 320(vw)
		Lead Formate $\text{Pb}(\text{HCO}_2)_2$	177(s); 193(s); 758(w); 1075(vw); 1343(vs); 1378(w); 1533(m); 2845(m); 2874(w)	193(s); 757(vw); 1065(vw); 1343(vs); 1374(w); 1531(m); 2850(s);
	PbSb15	Elemental Sb	139(vs); 278(m); 334(w)	114(m); 151(vs); 235- 320(vw)
		Lead Formate $\text{Pb}(\text{HCO}_2)_2$	174(s); 197(s); 761(vw); 1073(vw); 1342(vs); 1373(w); 1530(m); 2843(m); 2872(w)	193(s); 757(vw); 1065(vw); 1343(vs); 1374(w); 1531(m); 2850(s)

Table 5. Vibrational bands of corrosion products, compared to literature data (cm⁻¹).

Figure 1. Experimental setup for pure Pb and binary Pb alloys specimens exposed to VOCs. Each specimen was weighted using an analytical scale. 2nd row: a) Type 1 b) Type 2 c) Type 3 corrosion as described in table 4.

222x152mm (299 x 299 DPI)

Figure 2. Raman spectra collected with 632.8 nm laser on a) pure Pb b) PbSb5 c) PbSb15 d) PbSn5 replicas after exposure to acetic acid. Parameters of the analysis: acquisition time: 10 sec.; number of accumulations: 4; power: 25% transmittance. lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) and Tin (II) acetate ($\text{Sn}(\text{CH}_3\text{COO})_2$) were identified.
297x209mm (300 x 300 DPI)

Figure 3. Elemental mapping by EDS (X-Ray maps) of cross sections after exposure to acetic acid. Top row: PbSb5 specimen, from left to right: SEM-BSE micrograph, C, O, Pb, Sb distribution in the analysed area. Bottom row: PbSn5 specimen, from left to right: SEM-BSE micrograph, C, O, Pb, Sn distribution in the analysed area.

437x146mm (299 x 299 DPI)

Figure 4. Raman spectra collected with 632.8 laser on a) pure Pb b) PbSb5 c) PbSb15 d) PbSn5 replicas after exposure to formic acid. Parameters of the analysis: acquisition time: 10 sec.; number of accumulations: from 1 to 4; power: 25% transmittance. Lead formate ($\text{Pb}(\text{HCOO})_2$) was identified on all replicas. On Sb-rich replicas, Raman vibrational bands of metallic antimony are also visible.

297x209mm (300 x 300 DPI)

Figure 5. SEM BSE 250x micrograph on a cross section of PbSb5 sample. Eutectic phases (grey and black lamellae) surrounding a Pb matrix (grey areas) are observed.

32x24mm (300 x 300 DPI)

Figure 6. Comparison of Raman spectra on PbSb5 specimen after exposure to formic acid: a) 632.8 nm laser b) 785 nm laser c) 785 nm laser. Parameters of the analysis: acquisition time: 10 sec.; number of accumulations: 4; power: 25%.

297x209mm (300 x 300 DPI)

Figure 7. Raman vibrational bands of metallic antimony using a near IR diode laser (785 nm excitation source) and spot of analysis.
297x209mm (300 x 300 DPI)

Figure 8. Elemental mapping of PbSb15 specimen (cross-section, after exposure to formic acid), from left to right: SEM-BSE micrograph, C, O, Pb, Sb distribution in the analysed area.

435x69mm (300 x 300 DPI)

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Figure 9. Schematic representation of the corrosion process for all specimens. First line, from left to right pure Pb, PbSn5, PbSb5 sample exposed to acetic acid. Second line, from left to right pure Pb, PbSn5, PbSb5, PbSb15 sample exposed to formic acid.
81x60mm (300 x 300 DPI)

Graph 1. Mass variation as a function of exposure time for samples exposed to acetic acid: a weight loss was observed.
85x48mm (300 x 300 DPI)

Graph 2. Mass variation as a function of exposure time for samples exposed to formic acid: a weight gain was observed, especially for Sb-rich alloys.

85x48mm (300 x 300 DPI)

ALLOY	COUPON		WEIGHT (g)	
	Original	After 15 days	Original	After 15 days
Pb			7.15	7.10
PbSn2			6.08	6.06
PbSn5			6.41	6.39
PbSb5			5.61	5.61
PbSb10			9.33	9.35
PbSb15			13.38	13.36

Table 2. Description of Pb- based alloys exposed to acetic acid.
175x164mm (300 x 300 DPI)

ALLOY	COUPON		WEIGHT (g)	
	Original	After 15 days	Original	After 15 days
Pb			5.53	5.54
PbSn2			11.21	11.22
PbSn5			10.12	10.19
PbSb5			9.69	9.72
PbSb10			15.29	16.51
PbSb15			10.66	12.96

Table 3. Description of Pb- based alloys exposed to formic acid.
175x142mm (300 x 300 DPI)

Corrosion morphology		Description
Type 1		A preliminary 'wet' patina is visible on each sample increasing the aggressiveness of the corrosion process also making the dissolution of the corrosion products easier. After a while, a white oxidised patina was observed.
Type 2		A white patina is observed and whitish powders appear on the surface of all samples.
Type 3		Specimens show a sudden increase of volume and brittleness due to macroscopic expansion of the samples but no white patina is visible.

Table 4. Patina morphologies on specimens exposed to acetic and formic acid.

135x117mm (300 x 300 DPI)