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Indoor corrosion of Pb: Effect of formaldehyde concentration and relative humidity investigated by Raman microscopy

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ABSTRACT

In this work the effect of relative humidity (RH) and formaldehyde (H_2CO) concentration on Pb corrosion was investigated; a possible synergism between the aldehyde and CO_2 effects was also considered. Triphasic aqueous salt solutions were used to produce 54% and 75% RH that, together with the 100% RH condition, were combined with 0, 0.62, 55 and 2.0 10^2 mg m^{-3} formaldehyde concentrations to compose the wanted environments.

The results pointed to the conclusion that even at low RH (54%) formates are produced at the metal surface as a consequence of formaldehyde adsorption, indicating that the aldehyde has an active role in Pb corrosion; formates were also observed at relatively low H_2CO concentration (0.62 mg m^{-3}). No synergism between formaldehyde and carbon dioxide were observed as demonstrated by the Raman images from a corroded Pb coupon, showing that formate and carbonate contributions to the corrosion products were not spatially related.

When compared to other volatile organic compounds (VOCs), formaldehyde harmful effect towards metals is frequently underestimated and the results here reported clearly indicate that, even at low RH, its concentration in indoor environments, where it tends to be produced and accumulated, has to be carefully controlled.

1. Introduction

Over the last two decades, that is, at least since Brimblecombe's pioneer review published in 1990 [1], there has been a steady increase of the awareness of the potential degradation impacts associated with the presence of gaseous harmful chemical species in museums and storage areas in general [2]. This has led to investigations on the actual sources, presence and dynamics of several pollutants in indoor environments as well as more in-depth studies of their effects on collection materials [3–5]. Meanwhile, tools for assessing the associated overall environmental damage risk are receiving more and more attention, in approaches which tend to value the role of gaseous pollutants, especially in synergism with other environmental factors [6–9].

Airborne pollutants in indoor areas can have an external or an internal source. External sources have become important in highly polluted contexts (although not necessarily), such as urban environments and require suitable and generally costly segregation measures. Sulfur dioxide, nitrogen oxides and particulate matter, as well as secondary oxidant pollutants such as ozone, have been pointed out as key dangerous species that demand special attention [1,2,5].

In the case of indoor emissions, the concern is normally with the accumulation of volatile organic compounds (VOCs). Cleaning products, wood and plastic pieces of furniture, construction materials are the main sources of a class of pollutants which mainly encompasses carbonyl compounds, but also hydrocarbons of all different sorts (e.g., terpenic substances) [2]. It is, in many ways, a perfidious sort of pollution because it often comes from the degradation of materials that are part of the collections or of the apparatus used to protect them; a threat, therefore, that might easily go underestimated or even undetected.

VOCs play a particularly important role in metal corrosion. In the specific case of carbonyl compounds, the well-known effect of formic and acetic acids formed as by-products of wood degradation (i.e., hemicellulose hydrolysis) has been addressed in a considerable number of investigations [10–14], resulting in effective actions aimed at reducing the exposure of metals and other materials to such compounds, e.g., by replacing wooden display cabinets with showcases made of more inert materials. Now, whereas the role played by volatile organic acids on metal oxidation is somewhat unanimously recognized, the effect of formaldehyde (methanal, H_2CO) is more controversial. Formaldehyde is also released during wood degradation, however, its main sources are anthropogenic:

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resins, paints and adhesives are mostly responsible for the H_2CO emissions in indoor environments. Formaldehyde can be oxidized to formic acid in the gaseous phase and this route has been proposed to explain its action on metals [15]. A search in the literature reveals that the studies about the effect of formaldehyde on Pb corrosion can be divided in three groups, being considered either harmless [14,16], at least as aggressive as organic acids [17] or only harmful when in the presence of oxidizing agents, such as hydrogen peroxide [15]. In a previous investigation, Raman microscopy was successfully used to show that Pb formates are produced when the metal is exposed to a humid environment (100% RH) containing formaldehyde at concentrations of 55 and 2.0×10^2 mg m^{-3} [18]. The reaction does not depend on the presence of an oxidizing agent (hydrogen peroxide or ozone, for instance), contrarily to the literature [15], but several products were formed depending on H_2CO and CO_2 concentrations and exposure time. Concentration and relative humidity (RH) also plays an important role on the formaldehyde aggressiveness towards Pb [16] but the composition of the corrosion layer, the mechanism of H_2CO action and the hole played by water are still open issues.

Considering that the understanding of the degradation agents and mechanisms are essential to guide the choice of the best preventive conservation strategy, in this work an extensive Raman investigation was carried out, in order to assess the effect of RH and formaldehyde concentration on Pb corrosion by H_2CO, as well as to investigate the existence of synergism between CO_2 and formaldehyde actions.

2. Material and methods

2.1. Material

For the investigation of the effect of RH and formaldehyde concentration in Pb corrosion by H_2CO, the Pb foil used (0.125 mm thick, 99.99+%, Goodfellow Cambridge Ltd.) was cut in 1 cm × 2 cm coupons and cleaned with a fiber glass brush before exposure to the controlled environments; in the study of synergism involving CO_2 and H_2CO the coupons were 5 mm × 5 mm. Formaldehyde 40% (Carlo Erba), stabilized with methanol (10%), was used to prepare aqueous solutions that generated 0.62, 1.5, 55 and 2.0×10^2 mg m^{-3} concentrations of formaldehyde in the gas phase (0.50, 1.2, 44 and 1.6×10^2 ppmv, respectively). Formaldehyde concentrations were calculated according to Dong and Dasgupta who also found that ionic strength has "no discernible salting out effect" [19], thus allowing the use of triphasic solutions with salt and formaldehyde, as described in Table 1 and below, to control relative humidity in the experiments. NaCl (Nuclear, 99.0+%) and $Mg(NO_3)_2 \cdot 6H_2O$ (Riedel-de Haën, 99.5+%) were employed to produce environments with 75% and 54% RH, respectively.

$Pb(HCO_2)_2$ was prepared by treating a saturated Pb carbonate solution with formic acid and reducing the solution volume by gentle heating (60 °C) and stirring. The crystals formed were filtrated, dried in a desiccator and characterized by Raman Microscopy.

The influence of methanol, used in commercial formaldehyde solution (formalin), was assessed by analyzing the lead corrosion products formed in an atmosphere generated by a methanol (Merck 99.9+%) aqueous solution (1% in volume).

Synergism between CO_2 and formaldehyde was investigated by exposing Pb coupons to formaldehyde at 2.0×10^2 mg m^{-3} in the gas phase (and at 100% RH) for 2, 5 and 16 days at room conditions (temperature and illumination). Pb coupons were also exposed to a carbon dioxide saturated environment prepared by extensively purging the flask with CO_2 (Air Products, Brazil).

2.2. Methods

Pb exposure was carried out in 50 mL Erlenmeyer flasks containing 5 mL of the solutions described in Table 1. The metal coupons were kept suspended by Parafilm (Pechiney Plastic Packaging Co.) threads; Parafilm was also used to seal the Erlenmeyer flasks that were kept on a laboratory bench at room temperature (ca. 23 ± 2 °C) and under ambient illumination until a visually detectable corrosion layer was formed. The coupons were then analyzed by Raman Microscopy and, to account for sample heterogeneity, 5 to 15 spectra were obtained from the same sample and eventually co-added to produce averaged spectra. XRD was used to characterize the corrosion products formed on a single coupon that was exposed for ca. 5 months to formaldehyde at 55 mg m^{-3}.

All the experiments were performed at least in duplicate and the results were in full agreement. Experimental details on the setup employed are shown in Table 1.

Raman spectra were obtained in a Renishaw inVia Reflex, fitted with a Peltier cooled CCD detector (Renishaw, 600 × 400 pixel) and coupled to a Leica Microscope; Raman images were obtained using the Streamline® configuration. The 632.8 and 785 nm laser lines from He–Ne and diode lasers, respectively, both from Renishaw, were focused onto the sample by a ×50 Leica objective (NA 0.75) and the laser power was kept below 1.5 mW at the sample to avoid degradation. Raman spectra were analyzed using the Grams package (Thermo Sci. Inc.).

In order to compare the relative contribution of carbonates and formates to the corrosion products, Raman images from a Pb coupon exposed for 16 days to H_2CO at 2.0×10^2 mg m^{-3} were obtained. The images were generated from 19239 spectra obtained from the metal surface (940 × 930 μm) in the 900 to 1400 cm^{-1} range, using a ×20 objective (NA 0.40) and 785 nm excitation. Carbonate distribution was imaged by integrating the signal between 1040 and 1060 cm^{-1} (symmetric C–O stretching vibration) whereas formates were detected using the integrated area of the bands in the 1320–1360 cm^{-1} range (symmetric carboxylate stretching vibration).

X-ray diffractograms were obtained with a Rigaku Miniflex equipment employing the Cu $K\alpha$ line (30 kV and 15 mA) and compounds identification was performed using the International Centre for Diffraction Data.

Ozone concentration in the laboratory atmosphere was measured with an Ozone Monitor, Dual Beam, 2B Technologies. O_3 concentration was monitored during a week to ensure that it was not affecting the corrosion experiments.

3. Results and discussion

A Raman microscopy analysis of a Pb surface exposed to a humid atmosphere containing H_2CO and CO_2 reveals the presence of several different compounds. Lead carbonates, mainly $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$ and $Pb_{10}(CO_3)_6O(OH)_6$ (which correspond to the minerals cerussite, hydrocerussite and plumbonacrite, respectively) are the most frequently detected species and formates are present at a much smaller concentration.

Fig. 1 reports the spectra obtained from some of the Pb formates generated at the metal surface. The band at ca. 1050 cm^{-1} clearly reveals the presence of carbonate ions and a careful data analysis of the low frequency region (below 400 cm^{-1}) points to the existence of new phases and not only the contribution of different amounts of lead carbonates (such as cerussite and hydrocerussite) and Pb formate.

Although the oxidation of formaldehyde to formic acid can take place in the gas phase in a well-known reaction [20], it was already shown [18] that H_2CO reacts directly with the Pb oxide layer. Fig. 2