

Real time spectroelectrochemical growth and corrosion resistance monitoring of lead carboxylate coatings in an environmental cell (eCell)

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Abstract

Heritage lead is subject to attack from organic acids emitted from wood and other sources in its environment. Coating the lead is a possible solution if the source cannot be eliminated. We present a study of the growth and corrosion resistance of a lead carboxylate coating, $(\text{CH}_3(\text{CH}_2)_8\text{COO})_2\text{Pb}$, deposited using an environmentally friendly process. Using a combination of synchrotron X-ray diffraction and electrochemical impedance spectroscopy we demonstrate the monitoring of the growth of the coating in real-time in an environmental cell configured for electrochemistry. Then, using the same cell, we show the dynamics of exposing the coating to 6.3% (by mass) acetic acid vapour in air at 75% relative humidity. Whereas unprotected lead shows significant corrosion in under 2 h, a $\sim 1.5 \mu\text{m}$ coating can withstand the acid vapour for up to 7 h. However, some coatings fail much sooner but nevertheless still show some residual inhibition. Data are correlated with ex-situ techniques including mass gain measurements.

Keywords: heritage lead, spectroelectrochemistry, environmental cell, lead carboxylate, coating

Introduction

The combination of lead and hardwoods such as oak in close proximity is quite common. Unfortunately, the wood exudes organic acids which can attack the lead forming, for example, acetates and formates, causing serious damage, or even total loss. This problem can be exacerbated, as in the case of pipe organs, by relatively recent changes in human habits which result in warmer surroundings, large variations in relative humidity, and empty unserviced buildings. In some cases it is relatively simple to seek out and remove the source of the problem (e.g. the display or storage cabinet). In others the source may be furniture or technology (e.g. the wind chest of an organ) which form an intrinsic part of the display or artefact. In such cases, one might seek an aesthetically and ethically acceptable protective coating for the lead component.

Following the work of Rocca and co-workers (Rocca and Steinmetz 2001; Rocca et al. 2004), there has been considerable interest in the corrosion inhibition of the lead carboxylate coating $(\text{CH}_3(\text{CH}_2)_8\text{COO})_2\text{Pb}$ (otherwise $\text{Pb}(\text{C}_{10})_2$ for short) produced by soaking the lead in 0.05 M sodium decanoate solution. We have followed the growth of the coating in real-time using synchrotron X-ray diffraction (SR-XRD) in parallel with electrochemical impedance spectroscopy (EIS). This work was carried out in an environmental cell (eCell) which is configurable for

electrochemistry, gaseous/vapour exposure and other types of experiment. Carboxylate layers were then exposed to high levels of acetic acid vapour (6.6% by weight in air) and high relative humidity (75%) to promote attack within the time span of a single synchrotron beam-time allocation (typically 3-4 days). These preliminary experiments were carried out to meet the following objectives: to establish a general methodology for using eCell in this context to lay the groundwork for longer-term experiments, to discover the crystallographic relationship of the coating to the underlying lead (if any), to investigate possible indicators of coating quality, and to observe breakdown modes, albeit at unrealistically high concentrations of the corrosive agent.

Previously, we have shown that 1-D diffraction spectra are inadequate for this type of time-resolved spectroscopy (Adriaens et al. 2007). This is partly because time-dependent changes in orientation cannot be distinguished from changes in surface chemistry, but also because the out of plane diffraction is a rich source of information on substrate and coating orientation(s) and morphology. The SR-XRD data are therefore collected as 2-D images in pseudo-powder reflection mode.

Experimental

The experiments were carried out at the European Synchrotron Radiation Facility (ESRF) at Grenoble using beam line BM28

(XMaS). XMaS is equipped with a Mar CCD 165 camera (Mar USA) which was used to collect the X-ray images. The time resolution (repetition rate) available is limited by the read-out time of the camera/data system to around 12 seconds, and typical image capture times for our work lie in the range 1-60 seconds, so the parameters are well matched to the evaluation of processes taking minutes to days. The beamline features an 11-axis Huber goniometer with a large central ring so that the mounting of eCell or artefacts with dimensions of up to a few cm is straightforward.

Lead discs 12 mm in diameter and 2 mm thick were cut from 99.95% pure lead rod (Goodfellow Metals Ltd.). All but the top surface was encapsulated in epoxy resin to form the working electrode in eCell. Final surface preparation consisted of abrasive polishing using 1200 grit SiC paper, rinsing with laboratory grade propan-2-ol, and wiping with a soft lint-free wipe. Because the lead is so soft, the latter process provides a final burnish to the surface.

Time resolved studies of the deposition of the $Pb(C_{10})_2$ coating on the lead took place in eCell during simultaneous X-ray and EIS measurements. Details of eCell can be found elsewhere in these proceedings, and in other literature (Dowsett and Adriaens 2006). The electrode remains immersed in fluid at all times and is moved by computer controlled stepper motor from an "X-ray" position with a fluid pocket of 125 μm thick between the surface and an 8 μm thick Kapton® X-ray window, to an "electrochemical" position with 3-5 mm of fluid above the surface. The cell was filled with ~35 ml of 0.05 M sodium decanoate solution produced by neutralizing 43.068 g of 99% decanoic acid (Fluka) with 0.1 M 98% pure NaOH (VEL) and diluting with deionized water to a volume of 5 L (see conclusions).

X-ray diffraction was done using an 8 keV beam of $\sim 10^{12}$ photons s^{-1} in multibunch mode. The beam was incident at 10° to

the surface (to give the optimum compromise between path-length in the fluid and surface specificity), and had a footprint of 6 mm \times 1 mm. The axis of the Mar Camera was placed at 35° to the beam with the camera objective plane at 130 mm from the diffraction centre. This gives a useful 2θ range of $\sim 10^\circ$ to 65° degrees and places the most significant lines across the centre of the field of view. In other experiments we used camera angles of 40° and 45° to extend the range of 2θ somewhat. Under these conditions, the diffraction cones are projected on the camera plane as eccentric ellipses. No available software could deal with this configuration, so we wrote a comprehensive image and spectrum batch processing package, esaProject (© Mark Dowsett 2006, 2007) which can transform (*reproject*) the images into a space where the rings are straight lines for easy display and spectrum extraction.

EIS data were obtained with an Autolab PGSTAT20 (Eco Chemie BV) controlled using the manufacturer's software FRA. A frequency range of 0.1 Hz to 1000 Hz was used. Data were taken in parallel with the SR-XRD measurements and also ex-situ for comparison.

For the acetic acid exposure, eCell was used with few cc of saturated NaCl solution in the bottom to control the RH at 75%. A droplet of glacial acetic acid of 2.5 μL was placed on the inside of the X-ray window with a micropipette, and the cell was sealed. This procedure produces a 6.3% mixture (m/m) of acetic acid in the air in the cell. Both untreated and treated lead were exposed in this way, and SR-XRD images taken over a period of several hours. The untreated lead surface was prepared as described earlier. The treated lead was soaked in sodium decanoate solution for 6 hours. Mass gain estimates show that this produces an average coating thickness between 1.5 and 5 μm depending on the exact neutralization procedure. These coatings were at the lower end of the range.

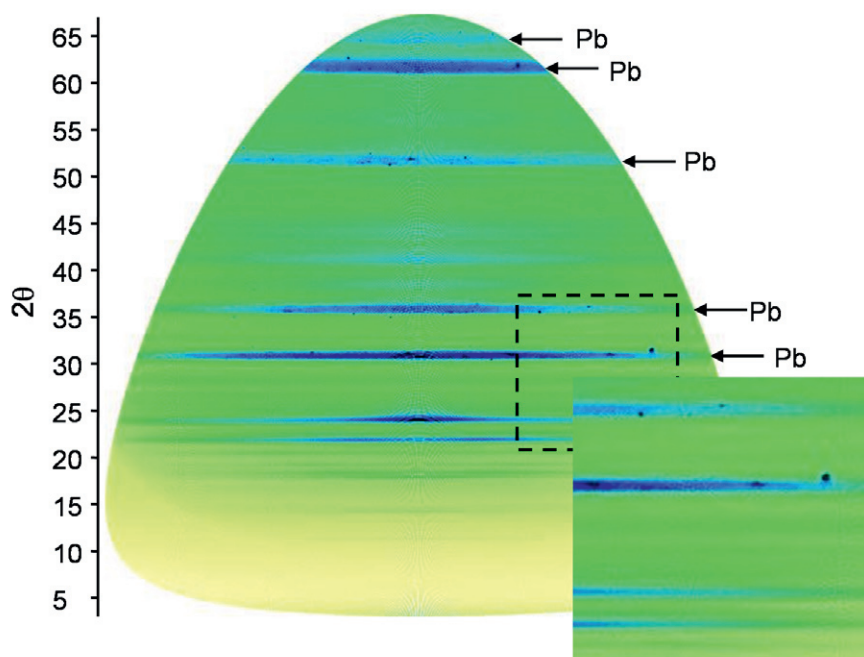


Figure 1: Reprojected X-ray diffractogram of the $Pb(C_{10})_2$ coating after 6 hours of growth. Unlabelled lines are due to carboxylate

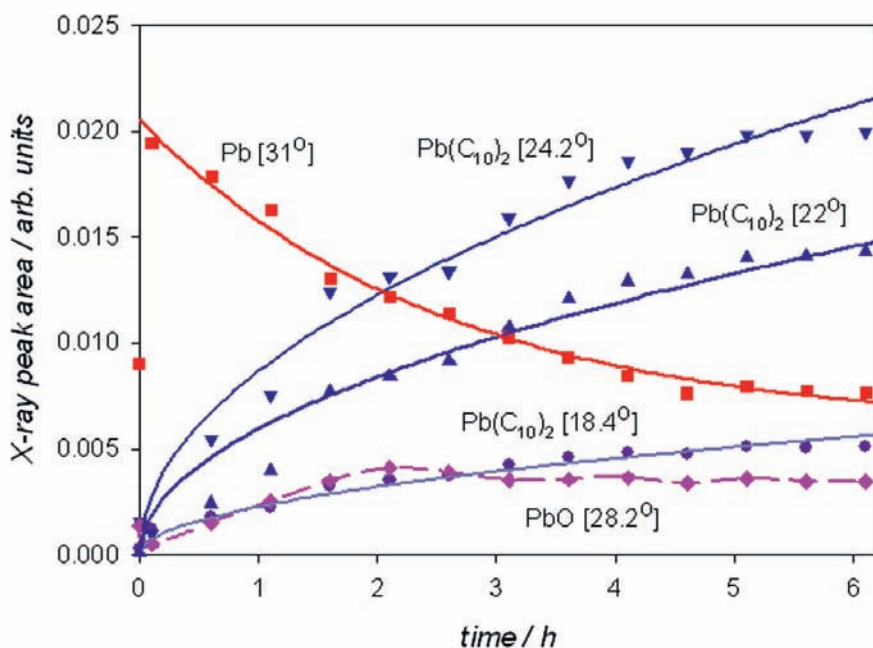


Figure 2: Time dependence of peak areas extracted from a sequence of images like that in figure 1

Separately, mass gain measurements were made ex-situ using the same sodium decanoate solution.

Results

Figure 1 shows a typical reprojected X-ray image from the carboxylate coating. The arrowed features are due to the lead substrate. All the others come from the coating. The inset shows a detail of both lead and carboxylate rings. The lead ring contains spots and streaks indicative of preferred orientations in the polycrystalline surface. Conversely, all the features associated with the coating are free from internal structure showing that there is no tendency to epitaxy, and that the coating consists of small randomly oriented crystallites. This type of information is only available from an image as opposed to a 1-D diffraction spectrum.

Figure 2 shows the behaviour of key peaks in the spectra extracted from the time sequence of images of which figure 1 is the last. The images cover a period of 6 h at intervals of 30 min. Reprojected images were integrated to spectra, normalized to the monitor count, and selected peak areas were tabulated automatically using esaProject. The data are (deliberately) not corrected for X-ray absorption in the growing layer. The peaks were selected to reflect four types of behaviour observed in the 35 or so peaks in the spectrum.

The lead area A_{pb} shows a decrease which is well described by

$$A_{pb} = A_o - ae^{-bt}$$

where A_o , a and b are fitting parameters and t is time. This is approximately what one would expect from absorption of the lead orders in the growing carboxylate layer. The carboxylate peaks are fitted by parabolas

$$A_{Pb(C_{10})_2} = A\sqrt{t}$$

In the case of the peak at 18.4° , used by Rocca (Rocca and Steinmetz 2001; Rocca et al. 2004) as one of the structurally determining peaks for the carboxylate planes the parabolic growth is an extremely good fit, except towards the end where self absorption in the layer starts to be significant (and the X-ray area tends to a constant value). For the other carboxylate peaks selected at 22° and 24.2° , one might argue for an initially linear behaviour in the first 4 hours. One peak out of 35 observed in the spectrum, that at 28.2° , shows a completely different trend – a linear increase in the first 2 hours, followed by a slight decrease in the next 4. This peak is tentatively identified as the largest diffraction from PbO. This seems to grow in parallel with the carboxylate initially, and then stops as the lead becomes fully covered. The EIS data measured simultaneously at intervals of 1 hour, starting 10 min after the growth commenced are shown in the Nyquist plot of figure 3.

The data were recorded with frequency scanned from high to low, so time runs from left to right across the plot. Because the layer grows appreciably in the time taken to make the EIS measurement (10 min) the layer capacitance and resistance must be seen as variable (inset model circuit). Rather than the expected half circles, one sees, especially at the low frequencies to the right of the graph, points which are members of different half circles of progressively increasing radius. Nevertheless, one can estimate that the layer resistance is $\sim 20 \text{ k}\Omega \text{ cm}^2$ after 6 hours, rather low for a protective coating. Figure 4 shows EIS data measured ex-situ using a differently prepared sodium decanoate solution where conductivity was used as the measure of solution quality rather than pH (publication in preparation). In this case, although one must still remember that the model values are changing, the growth rate is 3-4 times lower than in our simultaneous measurement and depressed half circles are observed. The effect of growth during measurement is to stretch the half circles along the real axis and distort them slightly, making the centres appear to

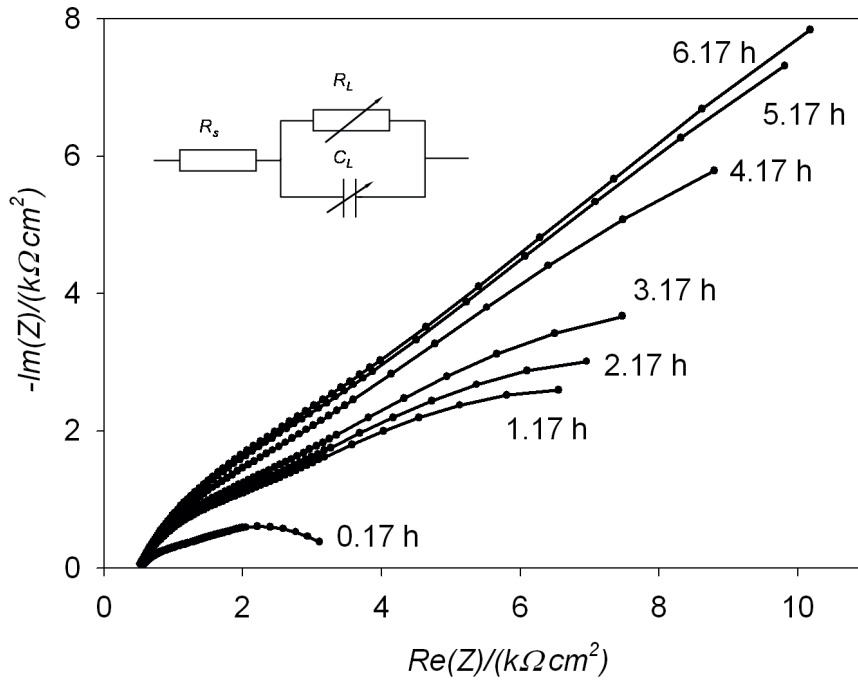


Figure 3: Nyquist plot of the EIS data measured simultaneously with the SR-XRD sequence with impedances for 0.79 cm² of coating. Inset shows effective model with variable impedances

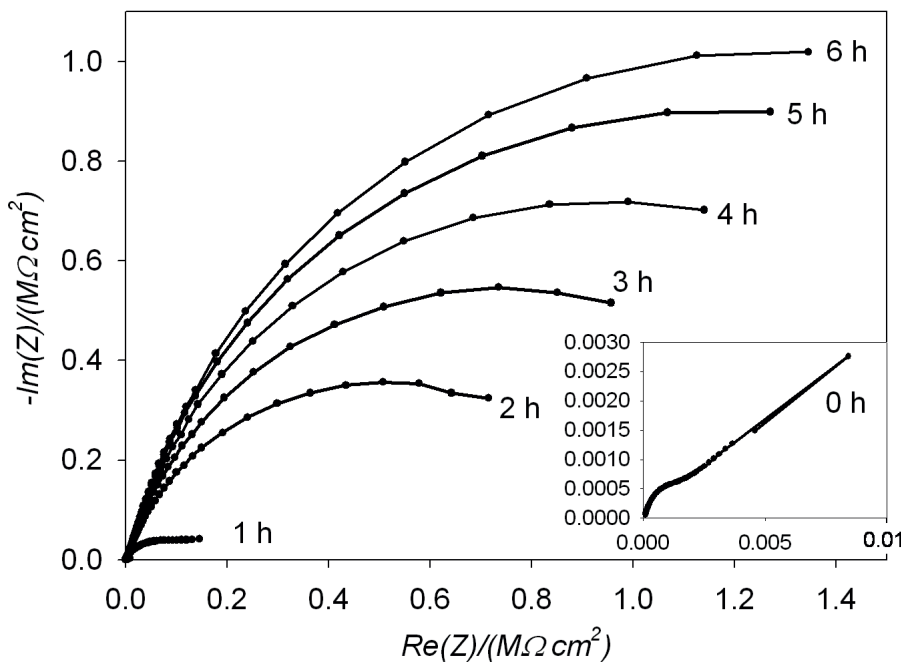


Figure 4: EIS data measured ex-situ after growth in a solution neutralized using a more sophisticated protocol (impedances for 1 cm² of coating)

be more depressed than they should be to the modelling programme. If a constant phase element with admittance Y_0 such that

$$Z = \frac{1}{Y_0(j\omega)^n}$$

is used in place of C_L values of n and C_L recovered from a fitting programme will be inaccurate. We are currently working on a simple dynamic model to improve this situation. However, the layer resistances are much higher $\sim 2.6 \text{ M}\Omega \text{ cm}^2$, indicating much improved coverage of the lead.

Figure 5 shows mass gain and thickness data for the solution

used in figures 1 and 2.

Average layer thickness is calculated using a density of 1.89 g cm^{-3} (and may be slightly underestimated). The data show an initially more rapid growth rate, in good agreement with both the XRD and EIS data. The mass cm^{-2} m is well fitted by behaviour of the type

$$m = 0.625t + 0.091\sqrt{t}$$

(a combination of linear and parabolic) which probably reflects an initial 2-D crystallite spread across the surface followed by 1-D vertical growth with decreased lead availability once the sur-

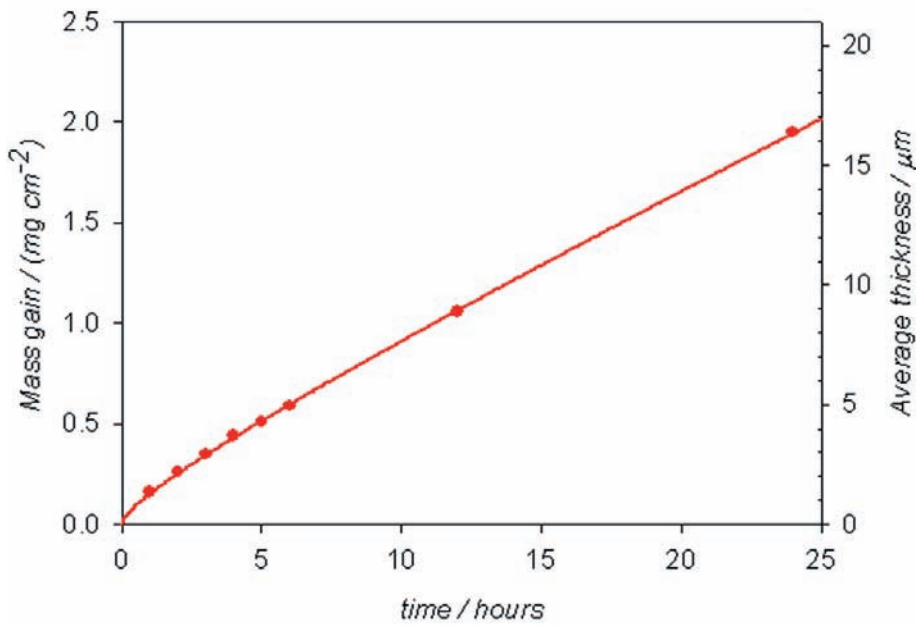


Figure 5: Mass gain data (points) and parabolic+linear fit (solid line) for coating deposited as in figures 1-3

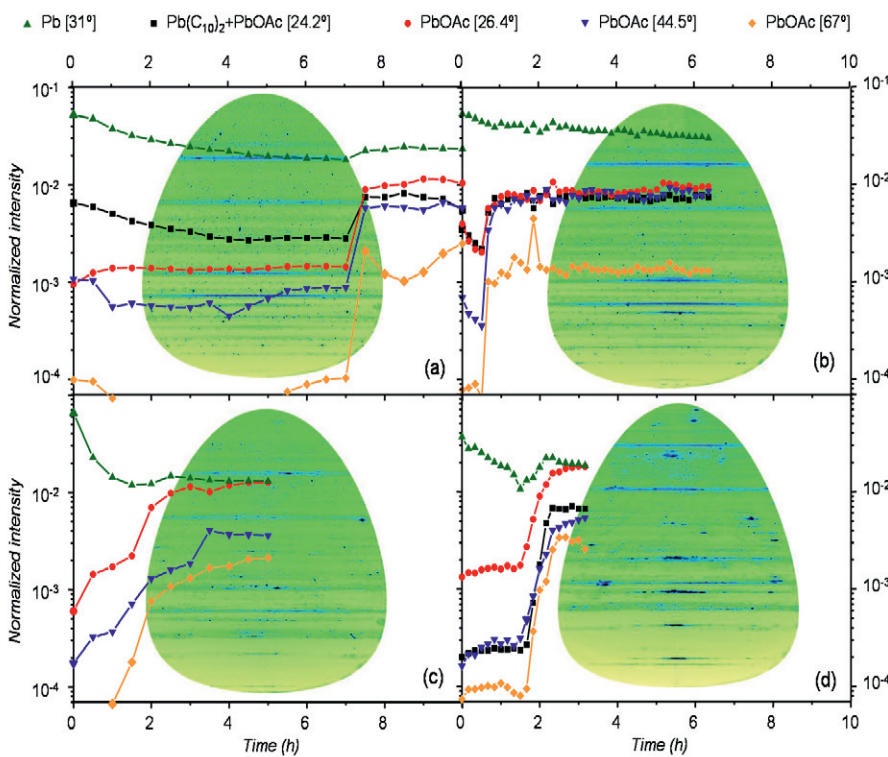


Figure 6: Real-time SR-XRD data for 6.3% acetic acid exposure at 75% RH (a) and (b) carboxylate coated surfaces, (c) and (d) unprotected lead. Inset images are diffractograms from end of sequences

face is covered. A combination of the parabolic dependence and X-ray absorption explains the approximately parabolic increase observed in the X-ray peak areas in the 6 hours of the measurement in figure 2.

The real time exposure to acetic acid vapour is summarized in figure 6, where 6(a) and 6(b) show peak areas representative of lead, $Pb(C_{10})_2$ and lead acetate $(CH_3COO)_2Pb$ in two separate exposures, whilst 6(c) and 6(d) show similar measurements for unprotected lead. The inset X-ray images correspond to the end

points in each case. The breakdown of the coating takes place very abruptly after 7 hours (a) or 40 min (b), but, thereafter, the surface still remains relatively stable and the images imply that the net corroded areas are too small to produce strong diffraction rings, but rather introduce spots due to localized orientational preferences. The corrosion of the unprotected lead may be either progressive (c) or abrupt (d), but in each case the coverage indicated by the XRD is more extensive after a shorter time than for the protected layers.

Conclusion

We show that time resolved SR-XRD in an environmental cell can be used to study the details of the growth and destructive testing of $\text{Pb}(\text{C}_{10})_2$ coatings on lead, with simultaneous electrochemical characterization during growth. It appears that the carboxylate coating offers both protection through coverage, and through inhibition. More detailed failure mode studies and high and low acetic acid concentrations are in progress, and our recent work (to be published elsewhere) has shown that the precise neutralization of the decanoic acid with NaOH is critical to obtaining effective and reproducible protection.

Materials list

- Sodium hydroxide (NaOH) >98%

VEL

VWR International

“Le Périgares”, bât. B, 201 rue Carnot - 94126 Fontenay sous Bois cedex

Tel. +33 (0) 1 45 14 85 00

- Decanoic acid $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ 99%

Fluka

Sigma-Aldrich Chemie GmbH, Industriestrasse 25, CH-9471 Buchs SG

Switzerland

Tel. +41(0) 81 755 25 11

- Acetic acid CH_3COOH >96%

Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany

Tel. +49 6151 72-0

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