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Acrylate-based coatings to protect lead substrates

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ABSTRACT

This study investigates the surface protection treatment of hydrophobic acrylate-based polymers with built-in carboxylic acid groups produced using a controlled Reversible Addition Fragmentation chain Transfer (RAFT) polymerization. The synthesized polymers are dissolved in a water-organic solvent mixture and afterwards deposited on lead substrates by immersing them in the solution. The coatings produce a hydrophobic film, which slows down the lead corrosion processes. The protective properties of the coatings are analyzed using non-destructive odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS) in an acetic acid corrosive solution containing tertbutylammonium bromide (TBAB) supporting electrolyte. The impedance data and electron images of the coatings demonstrate that the coating thickness, pore formation, diffusion and electrolyte uptake profile depend on the polymer's acrylic acid content and the molecular weight. All these parameters have a clear impact on the inhibition of the corrosion process.

1. Introduction

Due to its softness, inert nature, malleability, ductility and easy access, lead metal was often used for the production of objects and compounds making the everyday life of our ancestors more comfortable [1]. As confirmed by Shotyk et al. [2], around 3000 B.C. the atmospheric release of lead increased over natural levels due to lead mining and smelting and production of lead items. Many of these lead containing artifacts, dug up during archeological excavations, have an important economical, sociological and cultural value nowadays [3].

At this moment, however, lead and lead alloyed artifacts are placed in uncontrolled environments, which make them vulnerable for atmospheric corrosion due to the presence of volatile inorganic and organic compounds [4]. One of the most aggressive is acetic acid produced by hydrolysis of acetylated hemicelluloses found in cell walls of wood [5,6]. The kinetics of this corrosion process depend on the relative humidity, temperature, wood type and treatment [7–10]. Unfortunately, the combination of wood and lead metal artifacts is very common in museums due to the lack of funding. Another example is the destruction of lead-tin organ pipes in churches [11], because of the high acetic acid concentrations in the pipe organ's wind chest (0.04 ppm–2.4 ppm) [12].

Because no better treatments are available today, waxes, varnishes or resins are used as coatings to protect lead artifacts [13–15]. Research towards new barrier protection methods is necessary in order to find a more stable, reversible, reproducible and corrosion protective coating that is also aesthetically justified [16]. Recent efforts have investigated the influence of organic compounds (such as surfactants) containing polar functional groups [17–20].

In previous communications of our group, hydrophobic linear long chain monocarboxylic acids [21–23] and dicarboxylic acids [24] were proposed as a protection treatment for lead objects. This new study investigates a surface protection treatment using polymers. The advantages of using polymers include (a) more active groups per chain producing a more stable layer, (b) the possibility to modulate functional groups to tune the coating properties and (c) the modulation of the molecular weight with respect to monomer compounds.

More specifically, this paper proposes the use of acrylate-based polymers as a coating for lead substrates. As Wicks et al. [25] postulates that "molecular weight is often a critical factor

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Nomenclature

List of symbols

A	Area, in [m^2]
C	Capacitance, in [F]
C_{eff}	Effective capacitance, in [F]
d	Thickness, in [m]
E_{corr}	Corrosion potential, in [V]
f	Frequency of the multisine excitation signal, in [Hz]
f_{max}	Maximum excited frequency of the multisine excitation signal, in [Hz]
j	The imaginary number $\sqrt{-1}$
k	Refers to the k^{th} frequency of the harmonic grid of the multisine excitation signal
N	Number of harmonic related sine waves in the multisine excitation signal
t	Absolute time, in [s]
$U(k)$	Amplitude of the sine waves in the multisine, in [V]
$u(t)$	Multisine excitation signal in the time domain, in [V]
Y_0	Parameter of the constant phase element, in [$s^n\Omega^{-1}$]
$\|Z\|$	Modulus of the complex impedance Z, in [Ω]
$Z_{re}(\omega)$	Real part of the complex impedance Z at the angular frequency ω, in [Ω]
$Z_{imag}(\omega)$	Imaginary part of the complex impedance Z at the angular frequency ω, in [Ω]

List of Greek symbols

ε_0	Permittivity of the vacuum [$8.85 \times 10^{-12}\,F\,m^{-1}$]
ε_r	Relative permittivity
ϕ	Angle which describes the phase shift, in [degrees]
ϕ_k	k^{th} random phase in the multisine excitation signal between [0,2π] such that $E[e^{j\phi k}] = 0$ with E[] the expected value
ω	Angular frequency (=2πf), in [rad/s]

controlling the strength of films that are not cross-linked.", we propose to use a form of reversible-deactivation radical polymerization to be able to control the molecular weight and dispersity of the polymer. The Reversible Addition Fragmentation chain Transfer (RAFT) polymerization procedure discovered by Rizzardo et al. [26] has proven to be one of the most versatile methods of controlled radical polymerizations [27]. The particular advantages of RAFT are the easy setup and the ability to control the polymerization for a wide range of monomers including acrylates [28]. In a RAFT process a typical thiocarbonylthio compound, in the form of a dithioester, dithiocarbamate, trithiocarbonate or xanthate, is used as chain transfer agent (CTA) to acquire a fast dynamic equilibrium between a dormant polymeric species containing a thiocarbonylthio end group (Pm-X) and a propagating free polymeric radical Pn• via an intermediate macroRAFT radical (Pm-(X•)-Pn), leading to the synthesis of well-defined polymers as seen in Fig. 1a.

Based on the RAFT polymerization, random hydrophobic acrylate macromolecules with built-in carboxylic groups are prepared using a hydrophobic monomer, 2-ethylhexyl acrylate (EHA), together with a protected acrylic acid monomer, 1-ethoxyethyl acrylate (EEA). Subsequently, the deprotected carboxylic copolymers are dissolved in a water-organic solvent mixture. Finally, the coating is deposited on lead substrates by immersing them in the inhibitor solution. The coating's protective properties are analyzed using non-destructive odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS) in an acetic acid corrosive solution containing tertbutylammonium bromide (TBAB)supporting electrolyte.

2. Experimental part

2.1. Materials

2-ethylhexyl acrylate (98%, Sigma Aldrich, USA) was purified by passing over a basic aluminum oxide filtration column to remove the stabilizers. 1-Ethoxyethyl acrylate was prepared (see Fig. 1b) in large quantities according to literature procedures, with a yield of 90% [29,30]. The monomer was stored at −18 °C and was characterized by ^{1}H NMR signals at 1.07 (3H, t, $-OCH_2CH_3$), 1.30 (3H, d, $-COOCH(CH_3)$), 3.40–3.63 (2H, m, $-OCH_2-$), 5.73 (1H, d, $CH_2=CH-$), 5.90 (1H, q, $-COOCH(CH_3)$), 6.00 (1H, dd, $CH_2=CH-$),

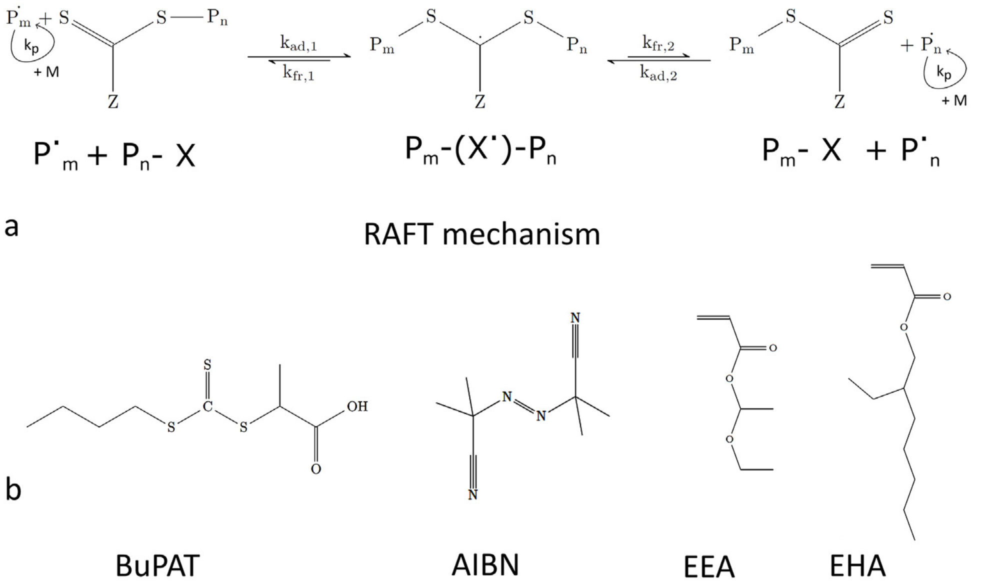

Fig. 1. (a) General mechanism (main equilibrium) of the RAFT polymerization and reagents (b) for the RAFT copolymerization of EEA and EHA with AIBN as initiator and BuPAT as RAFT reagent.