



Development of solvent- and water-borne fluoropolymer protective coatings for patina-free bronze discs



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ABSTRACT

Solvent- (SB) and water-borne (WB) fluoropolymer coatings were produced for the outdoor protection of bronze. The coatings were prepared from commercially available resins with alternating fluoroethylene/vinylether copolymers. Because any application of protective coatings on works of art requires that they be removable in accordance with conservation ethics, various approaches to achieve removability of coatings were tested. The influence of modifications was verified through comparisons of hydrophobic, compact and irremovable protective coatings. Consequently, we prepared four types of coatings: two SB coatings and two WB coatings. The first SB coating was designed to have a hydrophobic compact structure (SB-c coating), and the second SB coating was modified with the addition of agents that impart strippability (SB-h coating). The same approach was used for the preparation of the two WB coatings: a compact (WB-c) coating vs. a hydrophilic (WB-h) coating, the latter being prepared through the addition of hydrophilic polyisocyanate.

The surface properties of the coatings were compared using scanning electron (SEM) and atomic force (AFM) microscopy. WB coatings were found to be more homogeneous in comparison with SB coatings and to have lower surface roughness. Contact angles confirmed the more hydrophobic nature of SB coatings. Potentiodynamic polarisation measurements and accelerated corrosion tests (exposure to acid vapours) revealed that protection efficiency not only increased with thickness but significantly depended on the coating structure. The structure of coatings depended on the rheological parameters of the formulations simulating their behaviour during storage, deposition, and formation of the dry coating. Combined electrochemical and vibrational spectroscopic experiments were used to simulate long-term outdoor exposure of the protective coatings. *Ex situ* IR RA spectroelectrochemical measurements showed that hydration was more prevalent with WB coatings, and oxidation of bronze at the interface eventually occurred (656 cm^{-1} band). WB coatings with more free C=O groups were more prone to degradation. *In situ* Raman spectroelectrochemistry confirmed the better protection efficiency of SB over WB coatings. The optical properties of the coatings on glass showed higher transmittance for WB coatings compared to SB coatings.

1. Introduction

One approach to achieve corrosion resistance for bronze works of art in outdoor environments is the use of protective coatings. The natural protective layer of patina that evolves during the exposure of bronze to air can protect the bronze [1]. Consequently, it is not surprising that patinas are also produced by artists for protective and colour effects [1,2]. However, in urban and industrial environments, the species in naturally formed patina may contribute to various corrosion processes [1]. For this reason, protective coatings can also be

deposited directly on the bronze surface. The preparative aspect (i) of this study is oriented towards the development of fluoropolymer protective coatings for patina-free bronze while considering the removability requirements of conservators (Fig. 1A). The preparative approaches were tested on solvent-borne (SB) and water-borne (WB) coatings. The second aim (ii) is the use of advanced analytical approaches that combine electrochemical techniques with spectroscopy (IR, Raman) to obtain insight into the degradation mechanisms of the coatings (Fig. 1B).

(i) *Preparative aspect.* Although waxes and Incralac™ are currently

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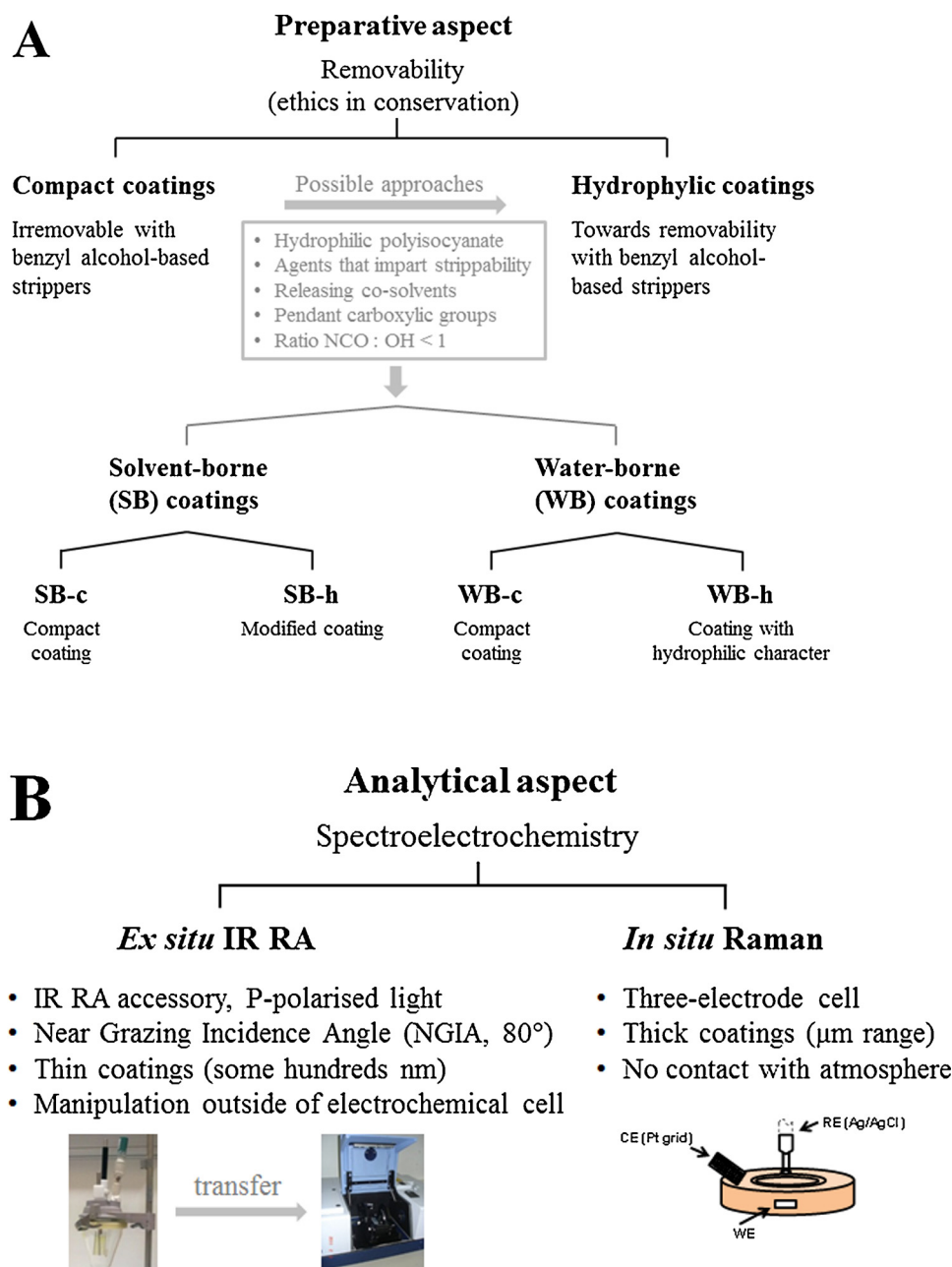


Fig. 1. Schematic representation of the preparative (A) and analytical (B) aspect of this work.

the most used artificial protection of bronze objects, research into other possible protections remains active. Reports range from the use of organic protective films with inhibiting properties [3,4] and chitosan [5] to various coatings made via sol-gel [6] or prepared from formulations of polymeric resins (methyl methacrylate [7], polyurethanes [8] and fluoropolymers based on polyvinylidene fluoride (PVDF) [4]).

PVDF coatings have been studied because they are known for their outstanding exterior durability and chemical and moisture resistance. Although fluorocarbons and hydrocarbons have different properties and express phase separation behaviour in some mixtures [9], the direct bonding of $-\text{CH}_2\text{-CF}_2-$ units to PVDF enables the formation of a semicrystalline polymer with an extended zigzag chain. When PVDF is used for the protection of bronze, the dispersion of pigments and adhesion is not sufficient [4]. Consequently, physical mixing with acrylic modifiers was attempted, but adhesion only increased from poor to average [4]. Another possible strategy is the introduction of acrylic moieties in the polymerisation stage of polymer production, which

significantly improves the properties in SB and WB formulations [10]. A similar approach, mixing various building blocks in the polymerisation process, was used for the production of fluoroethylene/vinyl ether (FEVE) alternating copolymers by AGC (Asahi Glass Company), Japan (Lumiflon products) [11]. Instead of $-\text{CH}_2\text{-CF}_2-$ building units of PVDF, in which two incompatible moieties are linked by a covalent bond, the fluoroethylene monomer in FEVE is composed of $-\text{CF}_2\text{-CFX}-$. A certain amount of covalently bonded chlorine is present in FEVE structures, but despite this limitation, highly protective coatings have been produced, even for extreme situations (e.g., bridges) [11]. The solubility of FEVE is afforded by the regularly repeating vinyl ether pattern and the $-\text{CF}_2\text{-CFX}-$ units. Crosslinking can be obtained via reaction with OH functionality in FEVE with polyisocyanates.

FEVE fluoropolymer resins can be distinguished based on their use in solvent-borne (SB) or water-borne (WB) formulations, which also influences the barrier properties of the coatings. Swartz et al. [7], for example, showed by electrical impedance spectroscopy (EIS) of methyl

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