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B-IMPACT project: eco-friendly and non-hazardous coatings for the protection of outdoor bronzes

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Abstract. Application of protective coatings is the most widely used conservation treatment for outdoor bronzes. Eco-friendly and non-hazardous coatings are currently needed for conservation of outdoor bronze monuments. To fulfil this need, the M-ERA.NET European research project B-IMPACT (Bronze-IMproved non-hazardous PATina CoaTings) aimed at assessing the protectiveness of innovative coatings for historical and modern bronze monuments exposed outdoors.

In this project, two bronze substrates (historical Cu-Sn-Zn-Pb and modern Cu-Si-Mn alloys) were artificially patinated, by acid rain solution using dropping test and by “liver of sulphur” procedure (K₂S aqueous solution) to obtain black patina, respectively. Subsequently, the application of several newly developed protective coatings was carried out and their performance was investigated by preliminary electrochemical tests. In the following steps of the work, the assessment of the best-performing coatings was carried out and their performance was compared to Incralac, one of the most widely used protective coatings in conservation practice. A multi-analytical approach was adopted, considering artificial ageing (carried out in representative conditions, including exposure to rain runoff, stagnant rain and UV radiation) and metal release, as well as visual aspect (so as to include aesthetical impact among the coating selection parameters) and morphological and structural evolution of the coated surfaces due to simulated outdoor exposure. Lastly, also the health impact of selected coatings was assessed by occupational hazard tests. The removability and re-applicability of the best-performing coatings were also assessed. The best alternatives to the conventional Incralac exhibited were: (i) fluoroacrylate blended with methacryloxy-propyl-trimethoxy-silane (FA-MS) applied on patinated Cu-Sn-Zn-Pb bronze and (ii) 3-mercapto-propyl-trimethoxysilane (PropS-SH) applied on patinated Cu-Si-Mn bronze.

1. Introduction

The application of protective coatings is one of the most used conservation strategies in the field of Cultural Heritage for bronze artworks exposed outdoors. The choice of the best coating is imposed by the metal surface at the moment of coating application, the environment in which the coating must be



effective and the characteristics of the different coatings available. In addition, in conservation practice, protective coatings need to fulfil strict requirements, such as ease of application, minimal aesthetical impact, predictive performance, long-term durability and removability or at least re-applicability [1]. To fulfil these needs, a 2-year M.ERA-NET project B-IMPACT (Bronze-IMproved non-hazardous PATina CoaTing, www.b-impact.cloud) aimed at developing innovative, eco-friendly and non-hazardous protective coatings tailored for improving the protection of outdoor bronze artworks [2]. The B-IMPACT project has taken into account two different sand-cast bronzes, traditional Cu-Sn-Zn-Pb and modern Cu-Si-Mn alloys, with two different typical patinas (representative of natural patina for traditional alloy and aesthetical patina for the modern bronze) [3]. Several protective treatments (silane-based polymers, fluoropolymers and sol-gels) were tested by electrochemical methods and the most promising treatments were selected for the complete assessment of protectiveness, as well as the aesthetical impact of coating application and the occupational hazard tests [4–7]. The behaviour of the developed protective treatments was compared with the uncoated samples and with samples coated by an acrylic polymer containing BTA corrosion inhibitors (Incralac) usually applied for the restoration of bronze artworks. At last, some measurements concerning the long-term durability of the selected coating for traditional bronzes were carried out and are still ongoing [8]. This paper discussed the performance of the most promising protective treatments for patinated traditional and modern bronze alloys. In detail, a fluoropolymer (FA-MS) and a silane-based (PropS-SH) were selected and their performance in terms of aesthetical impact, protectiveness and long-term durability are reported.

2. Materials and Methods

Figure 1 reports the global procedure applied during B-IMPACT project. It is composed of 4 specific steps: (i) substrate preparation, (ii) coating development, followed by (iii) coating assessment and finally (iv) end-users tests and real environment exposure for long-term durability tests.

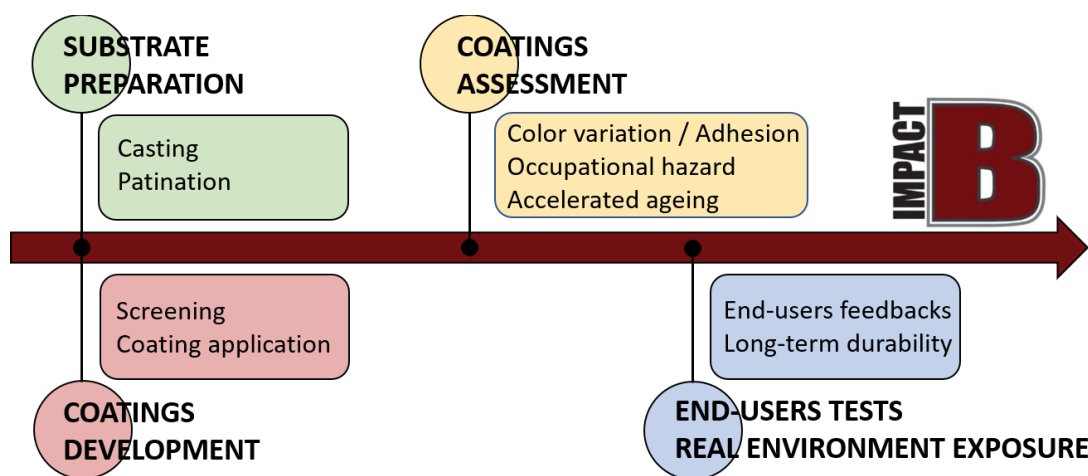


Figure 1: Methodology applied in the B-IMPACT project.

In particular:

- i. Substrate preparation: suitable bronze alloys were supplied by a Slovenian artistic foundry (Livartis d.o.o). An artificial patination was carried out on traditional bronze by Dropping test in order to simulate real patinas in unsheltered exposure conditions, while on the modern alloy, the patina was applied by the artistic foundry with specific aesthetical aim.
- ii. Coatings development: Several polymeric coatings were tested by electrochemical methods, as promising protective candidates, such as silane-based coatings with and without corrosion inhibitors, sol-gels, fluoropolymers and multilayer polyelectrolyte coatings. All the tested coatings were applied by brushing or spraying in order to fulfil the requirement of ease of coating application in the real practice.

- iii. Coating assessment: the aesthetical impact of coating application and the eco-toxicity of the selected products were evaluated, in order to investigate the suitability of the selected coatings. Adhesion of the selected coatings was also assessed. In addition, the protectiveness assessment of the selected coatings was carried out after accelerated ageing, by analysing the coated surface and the weathering solutions.
- iv. End-users test and field exposure: as final action of the B-IMPACT project, two real bronze artefacts (made of the two tested alloys) were exposed outdoors after the application of the selected coatings. First data on durability are available. Finally, removability was also tested by applying mechanical methods (brushing), so as to avoid the use of toxic solvents usually used in cleaning procedures. The removability of the selected coating was evaluated by morphological observation of the surfaces and by chemical composition.

2.1 Materials

Traditional bronze is a quaternary alloy with an elemental composition of: 6.9 ± 0.6 Sn, 3.1 ± 0.4 Zn, 2.0 ± 0.9 Pb (wt%), with Al, P, Mn and Si in traces (Cu to balance), while modern alloy is a Si-bronze with a composition of: 3.1 ± 0.4 Si, 0.9 ± 0.1 Mn and Sn, Zn and P as trace elements. Both the as-cast alloys showed the typical dendritic structure, as shown in the optical micrographs reported in Figure 2a and 2e, respectively. Shrinkage cavities were observed, as well as micro-segregation of Sn for traditional bronze [3] and Si and Mn for the modern alloy in the interdendritic spaces.

Within several promising candidates tested in the framework of the B-IMPACT project, a fluoroacrylate copolymer (FA) blended with methacryloxy-propyl-trimethoxy-silane (MS) as an adhesion promoter was selected for the protection of the traditional patinated bronze, while 3- mercapto-propyl-trimethoxy-silane (PropS-SH) was applied on the modern bronze substrate. The FA-MS solution was prepared by mixing 5 wt% of FA and 10 wt% of MS in a solvent mixture solution and was applied by brushing, as detailed in [4,8]. 3-mercapto-propyl-trimethoxy-silane (PropS-SH, purity 95%, Sigma Aldrich) was dissolved in a hydroalcoholic solution (90/5/5 v/v ethanol/water/PropS-SH), acidified to pH=4 by the addition of few drops of diluted sulphuric acid solution. After 24 h of hydrolysis, the solution was applied by spraying on the traditional bronze samples [7,9]. Lastly, Incralac was used as a commercial reference product. It was applied on both the patinated bronze samples by spraying using a 3 wt% solution in ethyl acetate solvent up to a final specific weight of 5.6 g cm^{-2} .

2.2 Patination

Patination step was applied on both the bronze substrates prior to coating application.

The traditional quaternary bronze was patinated by Dropping test, simulating unsheltered exposure of outdoor monuments [10]. Patination procedure consisted of the dropping of artificial rain, falling down in 4 drops over the samples inclined by 45° . The average dropping rate was $270 \text{ cm}^3/\text{h}$ per sample and 12 h of dropping was continuously alternated with 12 h of dry until a total time of wetness (ToW) of 37 days. More details are reported in [3]. The synthetic acid rain solution (AR, pH 4.30) was prepared according the natural rainfalls collected in winter months in a monitoring station in Bologna, Italy. Its chemical composition is reported in [11]. The modern alloy was patinated according the good practice of the artistic foundries. In particular, the as-cast bronze surfaces were initially sand-blasted, then pre-heated using a torch up to $50 - 60^\circ\text{C}$. An aqueous solution of potassium sulphide (3 wt% K_2S) was then applied by brushing until a black-coloured patina appeared. Further details are reported in [7].

2.3 Coating and protectiveness assessment

Electrochemical measurements consisted in ohmic drop-compensated polarization curves that were collected after 30 days of immersion in tenfold concentrated synthetic acid rain ($\text{AR} \times 10$, pH 3.30) using a conventional three-electrode cell. Separate anodic and cathodic potential scans, always starting from E_{cor} , were carried out at a rate of 0.1667 mV s^{-1} . The corrosion current densities, i_{cor} , were obtained by the Tafel method from the polarization curves.

The coated samples were characterized by the measurement of the colour coordinates in the CIELab colour space, using a Datacolor D400 spectrophotometer with a D65 illuminant, a 10° observer, a measured area of \varnothing 6.6 mm and specular component excluded (SCE), operating with a d/0 SCE measuring geometry. In the CIELab space, each colour is defined by three coordinates: L^* , lightness, a^* and b^* , chromatic coordinates and total colour change (ΔE^*) was calculated through Equation (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

At least, three measurements were carried out for each sample. In general, ΔE^* values lower than 3 can be assumed as not significantly appreciable and, in the field of Cultural Heritage, ΔE^* in the range between 3 and 5 are considered still acceptable [12,13]. Practical adherence measurements of the selected coatings were also carried out in accordance with the international standard ISO 14679-1997 by applying a three-point bending test on coated patinated substrates, as detailed in [5,14,15]. After three-point bending, samples were optically observed to define the type of failure (adhesive or cohesive). Lastly, the potential toxicity of the developed coatings was tested by the determination of the Exposure Limit (EL), by sampling the VOCs release during the application of 500 mL of coating by brushing on 700x700 mm glass plates for 1 h, as detailed in [16].

To assess the protectiveness of the developed coatings, accelerated ageing was performed by Dropping test. It consisted of two weekly cycles of 3 days of dropping / 1 day of dry and 2 days of dropping / 1 day of dry, for a total time of wetness (ToW) of 10 days. The concentration of the Cu cations in the weathering solutions was analysed by Atomic Absorption Spectrometer (AAS) Perkin-Elmer AAnalyst 400 reaching a Limit of Detection (LoD) of 0.3 $\mu\text{g/L}$ for Cu. In addition, SEM observations of the uncoated and coated bronze after ageing were carried out using a FEG-SEM FEI Helios NanoLab 600i coupled to EDS system (Aztec Oxford apparatus). After surface examination, *in situ* cross-sections of specific representative locations were obtained by Focused Ion Beam (FIB) milling (Ga^+ ions) as detailed in [3].

2.4 Long-term durability analysis

Long-term durability of the developed coatings was tested on two real bronze objects made of the two representative alloys considered within the project. The two artworks are the depiction of the Slovenian poet France Prešeren (1800 – 1849), representative of a replica of the sculpture by Ivan Zajec and are exposed in the park of ZAG Institute in Ljubljana, Slovenia. PropS-SH was applied on Cu-Si-Mn bronze alloy with black patina, while FA-MS was used as coating for Cu-Sn-Zn-Pb alloy after natural patina development (11 months prior to coating application). XRF measurements were carried out after coating application and during the natural outdoor exposure by using Portable XRF Niton (USA).

3. Results and discussion

3.1 Patinated substrates

Patination by Dropping test on traditional quaternarybronze produced a corroded surface linked to decuprification process, inducing internal oxidation and preferential release of Cu and Zn, as demonstrated in previous studies [10,17]. Figure 2b and 2c highlight a non-uniform corrosion attack, in which Cu-rich dendrite cores are the most affected. Moreover, the patination process produced a thin corrosion layer, up to 2 μm in the anodic parts, characterised by nano-porosities within the patina (Figure 2d). Only few nm-thick corrosion layers are observable close to the eutectoid in the dendrite borders. Therefore, the patina obtained by Dropping test is representative of the aged surfaces of outdoor bronze monuments [17]. On the other hand, the application of black patina (K_2S aqueous solution) by torch method produced a very rough surface, characterised by the typical dark grey / black colour, as highlighted in Figure 2f and 2g. In addition, it displays a variable thickness, from 500 nm up to 3 μm (as shown in FIB cross-section observation in Figure 2h), as reported in [7]. In conclusion, the two patinated substrates representative of traditional and modern bronze showed very different morphological and structural properties, making the selection of protective coatings very specific.

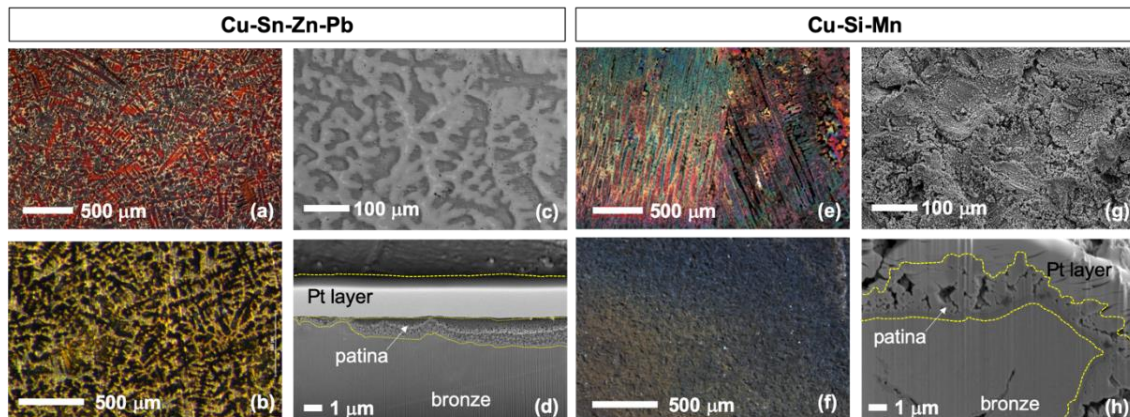


Figure 2: Microstructural observation of patinated bronze substrates before coating application (Cu-Sn-Zn-Pb and Cu-Si-Mn, respectively): (a, e) dendritic structure of bronze alloys; (b, f) patinated surfaces by optical microscope; (c, g) patinated surface morphologies observed by SEM; (d, h) representative FIB cross-sections of the patinated bronze substrates.

3.2 Performance of applied coatings

All the requirements for coating application in Conservation practice were analysed and discussed in this study. Firstly, the aesthetical impact induced by coating application was evaluated by colour variation (ΔE^*) measurements reported in Table 1. Both FA-MS and PropS-SH coating induced a colour variation lower than the acceptable threshold in Cultural Heritage applications, while Incralac showed higher ΔE^* values when is applied on traditional Cu-Sn-Zn-Pb. Furthermore, the adhesion strength of the selected coatings was investigated by three-point bending test and reported in Table 1. PropS-SH and FA-MS coatings underwent adhesive failure at bronze / coating interface, while Incralac exhibited cohesive failure within coating itself. The best adhesion performance was found when silane-based coating (PropS-SH) was applied. Finally, occupational hazard results showed that the selected coatings have lower EL value, compared to Incralac that exhibited $EL > 1$, so to be considered hazardous for operators, as reported in [18,19].

Table 1: Coating performances in terms of practical adherence by three-point bending test and type of failure, of occupational hazard results (Exposure Limit, EL) and of colour variation (ΔE^*) induced by coating application.

Coatings	ΔE^*	SD	F_{max} (N)	SD	Failure type	EL
Incralac	5.18 ^a / 2.85 ^b	1.02 ^a / 1.18 ^b	23.3	2.2	Cohesive	1.108
PropS-SH	3.75	0.31	36.9	4.2	Adhesive	0.019
FA-MS	3.23	0.67	10.1	1.5	Adhesive	0.301

^a Applied on traditional Cu-Sn-Zn-Pb. ^b Applied on modern Cu-Si-Mn.

3.3 Protectiveness efficiency

Several aspects were investigated to assess the protectiveness of the selected coatings. The main results regarding FA-MS for patinated traditional substrate and PropS-SH for patinated modern bronze are reported in Figure 3 and compared to the performance of uncoated sample and Incralac layer. Based on results from electrochemical tests, FA-MS and PropS-SH offer a good protection to patinated bronze, showing a significant decrease of corrosion current density (i_{cor}) compared to uncoated samples and similar i_{cor} values of Incralac. The assessment of the protectiveness of the selected coatings was performed applying the accelerated ageing by Dropping test (ToW=10d). Mass variation, cumulative Cu release and colour variation of the uncoated and coated samples induced by ageing are reported in

Figure 3b-d and 3g-h for patinated Cu-Sn-Zn-Pb and Cu-Si-Mn, respectively. An improvement of all these parameters was detected for coated samples compared to uncoated ones, while no strong differences are highlighted if the selected coatings are compared to Incralac. It is possible to conclude that FA-MS and PropS-SH showed comparable protective performance to Incralac, the commercial product typically used in Conservation practice.

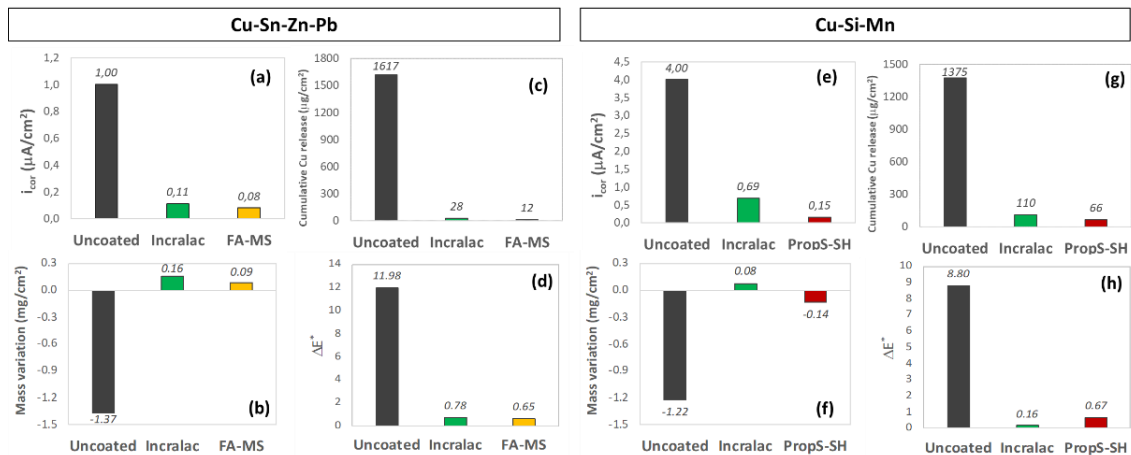


Figure 3: Assessment of the protectiveness of the selected coatings FA-MS (traditional bronze) and PropS-SH (modern bronze) compared to uncoated samples and Incralac coated samples: (a, e) Corrosion current density (i_{cor}); (b, f) Mass variation induced by 10 days of ToW of Dropping test; (c, g) Cumulative Cu release in the weathering solutions during at the end of the artificial ageing; (d, h) Colour variation (ΔE^*) due to ageing.

Figure 4 reports FIB cross-sections of uncoated and coated samples after 10 days of ageing. Cross-sections observation gave information about the physical features of the polymeric coatings applied and the protectiveness ability of FA-MS and PropS-SH.

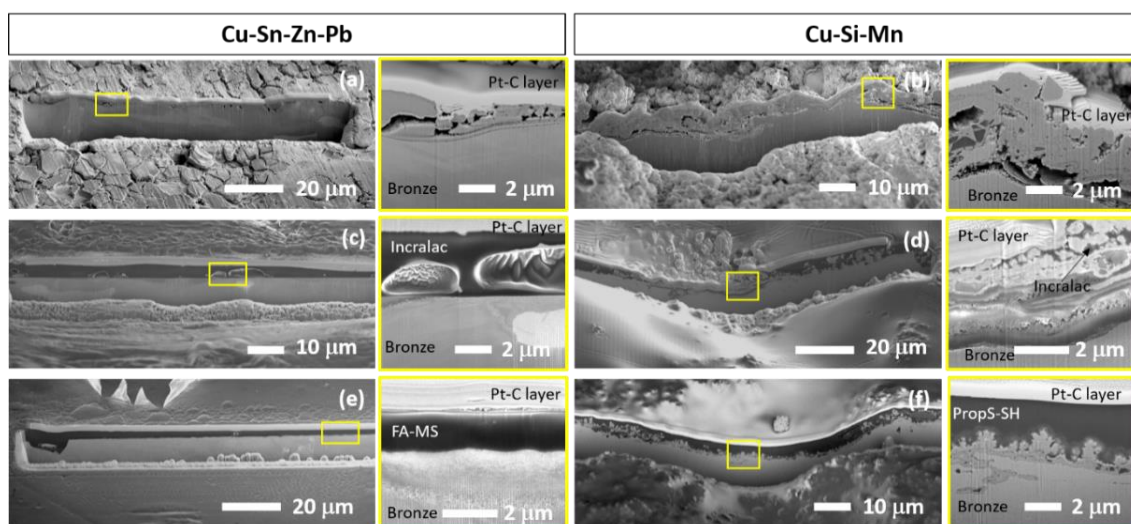


Figure 4: Observation of FIB cross-sections of uncoated and coated patinated Cu-Sn-Zn-Pb (left) and Cu-Si-Mn (right) after accelerated ageing by Dropping test: (a, b) uncoated patinated substrates; (c, d) Incralac; (e) FA-MS; (f) PropS-SH. Inlays of the FIB cross-sections at higher magnification are reported in yellow boxes.

The impact of accelerated ageing is highlighted by cross-sections of uncoated samples, as reported in Figure 4a and 4b. FA-MS coating applied on traditional patinated bronze produced a continuous layer

of about 2 μm (Figure 4e), while the application of Incralac (Figure 4c) produced some uncovered areas, as well as micro-porosities embedded within the protective layer. Regarding the protectiveness of the selected polymer on patinated Cu-Si-Mn, both Incralac and PropS-SH produced continuous layer (Figure 4 d and f, respectively). However, Incralac was not able to penetrate within all the cavities characteristic of the rough patina, while PropS-SH covered more homogeneously the patinated substrate. Finally, in correspondence of very thin Incralac layer, precipitation of corrosion products in the bronze / patina interface was observed in FIB cross-sections reported in Figure 4d (inlay).

3.4 Long-term durability and end-users testing

On real naturally patinated bronze (Cu-Sn-Zn-Pb) coated by FA-MS, the comparison of the XRF data recorded after 9 months of natural exposure with the ones measured after coating application showed that no changes in compositions were detected, as detailed in [8]. This indicates that FA-MS coating well protects the bronze surface. Long-term durability tests are still ongoing for longer exposure time for FA-MS coating, as well as XRF data for PropS-SH applied on black patina.

At the final stage of B-IMPACT project, a test-kit was sent to end-users (*e.g.* restorers and artistic foundries,). It was composed of a small bronze object (tree shaped- Cu-Si-Mn bronze alloy with black patina), the selected coating (PropS-SH), guidelines for coating application (in English, French, Italian and Slovenian). End-users were requested to fill-up an online questionnaire after the trial application of the coating on the small object. The aim was to collect feedbacks from trained operators, in order to evaluate some aspects such as ease of application, the appearance after the application of the coating and the overall quality on the basis of their expertise. The end-users reported very positive feedbacks. End-users pointed out that PropS-SH is easy to apply and shows good wettability. The only drawback was the strong odour during application. This end-user test, however, did not give any information about long-term durability and coating reversibility.

4. Conclusions

The following conclusions can be drawn by this study:

- the application feasibility, protectiveness and durability of innovative and non-hazardous coatings was assessed for the conservation of outdoor bronzes in the field of Cultural Heritage;
- the developed coatings for two different patinated bronze substrates representative of traditional and modern art (FA-MS applied on Cu-Sn-Zn-Pb and PropS-SH on patinated Cu-Si-Mn) showed outstanding performance in terms of low aesthetical impact due to coating application and protectiveness compared to uncoated samples under accelerated ageing by Dropping test;
- compared to the commercial reference product Incralac, the developed coatings (FA-MS and PropS-SH) showed comparable protective performance but lower occupational hazard, defined by a lower Exposure Limit (EL) compared to Incralac;
- long-term durability tests are currently ongoing on real bronze monument coated with FA-MS and exposed outdoor. First results after 9 months of natural outdoor exposure showed no variation of the chemical composition of the bronze surfaces (in-situ XRF measurements).

Finally, further research on removability and re-applicability is in progress to complete the assessment of the selected coatings. A first study about removability of FA-MS applied on traditional quaternary alloys was performed using only simple mechanical cleaning methods (brushing and blasting), so as to avoid the use of chemicals that can be hazardous for the health of operators. First results are reported in [8].

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