Molina *et al. Heritage Science (2023) 11:94*
https://doi.org/10.1186/s40494-023-00937-0

Heritage Science

RESEARCH

Open Access

Testing protective coatings for metal conservation: the influence of the application method

María Teresa Molina[1*], Emilio Cano[1] and Blanca Ramírez-Barat[1]

Abstract

The lack of a standardised methodology for the application of coatings on heritage metals can lead to non-comparable results. A careful and meaningful study requires considering the different application variables involved, especially in the preparation of the coupons. In this work, the effect that these application variables can have on the protective capacity of the coatings used has been studied. The influence of the thickness, number of layers and drying time (between layers and final) of Paraloid B-72, C80 microcrystalline wax and Incralac has been evaluated. Coatings have been applied on bare steel coupons, thickness measured with an induction probe, and subject to artificial ageing on UV light/water condensation cycles. The performance of the coatings has been studied by visual inspection and electrochemical impedance spectroscopy (EIS). Morphology of the layers has been characterised by optical microscopy and the composition of the corrosion products by Raman spectroscopy. Results show that the number of layers is not always proportional to the final thickness of the coating, and that drying time is a critical factor affecting the thickness and the protective properties of the coatings. After accelerated ageing, some coatings that had been left to dry for 14 days have a much better protective capacity than those that were left to dry for less time. Without taking into account these factors, performance measured can be wrong and comparison between materials misleading.

Keywords Coatings, Application methodology, Metallic heritage, Drying time, Thickness, Number of layers, Accelerated ageing, Dewetting

Introduction

Design and application of protective coatings for metals in the field of heritage conservation is a challenge. Not only for the need to comply with conservation and restoration criteria, but also for the problem of the lack of a standardised methodology to test and compare them as has already been highlighted [1-3]. This methodology usually involves several aspects such as: the selection and preparation of samples, the weathering methods to test the resistance of the coating and the evaluation techniques to assess their performance. This methodological variability can lead to misleading results and/or make it difficult to compare different studies [4, 5].

The selection of the weathering procedures may vary depending on the intended application (indoor/outdoor protection, urban or marine climate, etc.) and other variables including duration. Methodologies defined in existing standards such as ISO or ASTM are usually not adapted to heritage studies, although they can be a guide to develop tailored test methods for this field. The selection of evaluation techniques is often conditioned by the availability of equipment and expertise. Electrochemical techniques are among the most commonly analytical method for evaluation of coatings performance. Electrochemical impedance measurements can

*Correspondence:
María Teresa Molina
mt.molina@cenim.csic.es
[1] Centro Nacional de Investigaciones Metalúrgicas (CENIM), Consejo Superior de Investigaciones Científicas (CSIC), Avenida Gregorio del Amo, 8, 28040 Madrid, Spain

Springer Open

© The Author(s) 2023. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/. The Creative Commons Public Domain Dedication waiver (http://creativecommons.org/publicdomain/zero/1.0/) applies to the data made available in this article, unless otherwise stated in a credit line to the data.

be used to study the efficiency and protective capacity of the coatings [6, 7, 8, 9, 10, 11, 12], but a multi-analytical examination is required to characterise the visual appearance, chemical and physical changes and other more complex studies for the development of the most innovative coatings [13, 14].

Probably the most critical aspect of achieving comparative results is the preparation of the coupons at the beginning of the test "starting point". In most of the cases, the focus is only on deciding the most suitable application method (brush, spray, dipping, etc.) but hardly ever on the thickness and number of layers. The number of layers determines, in theory, the thickness of the coating which in turn is associated with the ability to protect the metal through a barrier effect. Nevertheless, the concentration of the solution, dissolving capacity and volatility of the solvent, and the degree of dryness of the underlying coatings, might affect the thickness obtained by the application of further layers. Thus, the final layer´s thickness should be measured and considered when evaluating or comparing coatings.

Other parameter that is frequently overlooked is the final drying time of the coating. After its application, it takes some time for the solvent to evaporate [15] and the coating film to develop completely. This parameter is critical as it defines the starting point or time zero for assessing the ageing effect. Furthermore, in the case of artificial ageing, the degree of curing of the coating when it enters the climatic chamber can determine the final result.This has been observed in a preliminary study by the authors on the protective properties of different traditional coatings applied on steel and brass [16]. In this work, it was found that allowing the coatings to dry for 48 h before accelerated ageing was not enough to form a stable, defect-free coating, so the possibility of extending the drying time was raised. To the best knowledge of the authors, no systematic study has been published regarding the effect of drying time on the performance of coatings for metal conservation.

Therefore, the aim of this study is to investigate the influence of the coating preparation methodology on the performance of protective coatings in weathering tests, with special focus on the drying time and thickness. For this purpose, three representative coatings commonly used in metal conservation which have shown different behaviour in the previous work [16] (Paraloid B-72, Incralac, and C80 microcrystalline wax) have been tested on bare steel. Although this clean surface does not replicate the actual surface of artistic heritage, which usually include remains of corrosion products or patinas [4, 9], it is representative of scientific-technical objects of bare metal [16, 17]. Moreover, this substrate has been selected for this study as a simple model to avoid uncertainties introduced in the study by irregularities caused by the pre-corrosion of the metal.

Materials and methods

Sample preparation

Steel coupons (0.15% Mn, 0.026% C, <0.03 Si and between 0.038–0.014% of other minority elements; according to GDOES and combustion-IR absorption analysis for carbon) were cut in 5×5×0.2 cm, sanded with P320 and P600 grit emery paper and cleaned with ethanol.

Selected conservation coatings were (Table 1): Paraloid B-72 and Incralac (supplied by Kremer Pigmente GmbH & Co.) as acrylic resins and C80 microcrystalline wax (supplied by C.T.S España S.L.). Wax was warm dissolved at 10% by mass in white spirit (~17% aromatics basis; REF.: 86460, Sigma-Aldrich), according to the technical data sheet of the supplier. Incralac was used as received and Paraloid B-72 was dissolved at 10% by mass in acetone (ACS reagent, ≥99.5%; REF.: 179124, Sigma-Aldrich) and in xylene (mixture of isomers, pure; REF.: 141769, Panreac AppliChem).

Paraloid B-72 was initially prepared in acetone, which is along with xylene, one of the most commonly used solvents for the preparation of coatings for iron objects. Acetone was chosen because of its lower toxicity. However, the result was not satisfactory because waves started to develop in the coating after applying the second layer onwards, leaving a heterogeneous appearance. The high volatility of acetone excessively reduces the coating formation time [17] and tends to redissolve the layers previously applied. Therefore, it was decided to use a less volatile solvent such as xylene for the Paraloid B-72 coatings.

The three coatings were applied by brushing (Brush Premium Synthetic series 631, 50 mm (supplied by MILAN; FACTIS, S.A.)) in one or two criss-cross layers. For this study, brushing has been used because it is the application method most commonly used by restorers. Each layer was left to dry in a ventilated environment (inside the laboratory at 24.6±3 °C and 38.2±5% RH, conditions averaged over the drying time period) for 24 h, 72 h and 1 week before applying the second

Table 1 Composition of the coatings used and their assigned identification code in the text

Product	Composition	Code
Paraloid B-72	Ethyl methacrylate and methyl-acrylate copolymer	B72
Incralac	Methyl-methacrylate and ethyl-acrylate copolymer + BTA	INC
Microcristalina C80	Microcrystalline wax	C80

one. This drying environment was also used for the final coatings.

Thickness measurements

Thickness measurements were taken during the application of layers and after final drying with an Elcometer 456, using a probe for ferrous materials based on electromagnetic induction. The manufacturer reports a ± 2.5 µm precision in measurement for this probe. A 12.3-micron gauge (Ser. Nº KC8913) was used for calibration and a thicker 23.9-micron gauge (Ser. Nº KC8888) was used to interpose between the probe and the C80 wax coating to avoid pressure marks. For each coupon, 16 measurements were taken and then averaged.

Ageing tests

This artificial ageing was carried out on a UV/CON chamber (Q-Lab Corporation) alternating UV-A light of 340 nm and condensation, according to ISO 4892:3 standard [18]. Alternating cycles of 4 h UV-A light (0.63 W/(m^2·nm) at 60 ± 2.5 °C and 4 h of condensation (dark period) at 50 ± 2.5 °C were performed during 336 h. At 168 h, the test was paused for several days to evaluate the different coatings.

Characterisation techniques

Coatings were evaluated by electrochemical impedance spectroscopy (EIS) using the G-PE cell developed for electrochemical analysis in metallic heritage [19, 20]. An AISI 316 stainless steel wire (1.5 mm thick) and AISI 316 stainless steel mesh were used as pseudo reference and counter electrode respectively. Distilled water with 10 ppm acetic acid [16] gelled with 2% w/v agarose as electrolyte [21] was used. EIS spectra have been acquired with a Gamry Reference 600 potentiostat, with 20 mV RMS amplitude (at the open circuit potential, OCP) and 10 points/decade from 100 kHz to 10 mHz. The system was left to stabilise at OCP for 30 min before measurements. The area exposed to the electrolyte was 3.14 cm^2. The experimental data were represented as Bode diagrams.

An Olympus BX41M LED Reflected Light Metallurgical Microscope with a 5x objective was used to observe the homogeneity and appearance of the coatings at microscopic scale before and after accelerated ageing. The images were obtained from Olympus Stream Basic software. For a more visual and general analysis, a macroscale photographic monitoring was carried out with a Canon EOS 700D camera and a Canon 18–55 mm macro lens.

Corrosion products were characterised with a custom-made Raman (MicroBeam), using an Exemplar Pro CCD spectrometer configured with a 532 nm green laser model DPSS, both from B&W Tek. Sampling was performed by a video-microscope from the same company (ref.: BAC151C) with a 50X objective. Images of the general sampling areas were taken with a 20X objective at working distance of 8.8 mm. Raman measurements were taken in a range from 150 cm^{-1} to 2000 cm^{-1}, for 100 s with 3 accumulations and the laser power did not exceed 10% of its maximum power (100 mW) due to the sensitivity of the iron oxides. Spectra were acquired and smoothed with the BWSpec®4 software and plotted and deconvoluted with Origin 2022 software.

Results and discussion

Coating thickness

Applying a coating in two crossed layers is very effective to reduce the presence of defects and to achieve a homogeneous film, at least to the naked eye. However, it is important to consider the interval between applications to ensure an effective addition of the layers. Table 2 summarises the thickness results of a separate preliminary test carried out to estimate when to apply the second layer to the coupons. The second layer was applied to different set of coupons at 24 h, 72 h or 1 week after the first layer was applied. With one layer of Incralac, a thickness of about 8 µm is obtained. Regardless of the drying time before applying the second layer, the thickness increases considerably. However, the end result is a heterogeneous coating with a too glossy appearance. B72 and C80 had a lower thickness after the first layer, which did not increase significantly when a second layer was applied after 24 or 72 h. For these short drying times, solvent of the new layer redissolves the previous one. Allowing 1

Table 2 Thickness measurements of the first layer and the second one applied after 24 h, 72 h or 1 w of drying at different coupons

	Average (µm) and ± SD					
	24 h between layers		72 h between layers		1 w between layers	
	1st layer	2nd layer	1st layer	2nd layer	1st layer	2nd layer
B72	2 ± 1	2.4 ± 0.7	2.5 ± 0.3	2.4 ± 0.9	2 ± 0.3	4.4 ± 0.9
INC	9 ± 2	14 ± 3	8 ± 2	16 ± 5	8 ± 1	15 ± 4
C80	3.0 ± 0.7	2.1 ± 0.6	1.9 ± 0.5	2.1 ± 0.5	1.5 ± 0.6	2 ± 0.5

week between applications, the thickness increases as the first layer is dry enough and is not redissolved by the solvent of the second one. These results show that the thickness is not always proportional to the number of layers and that it will depend on the composition and concentration of the solvent/polymer and whether it is completely dry or not.

Based on these results, a total of 27 coupons were prepared for the ageing test, allowing one week of drying between layers, for better control of thickness and appearance. After applying the second layer (or not in the case of Incralac), the coupons were left to dry for different times: 3, 7 and 14 days. Their thicknesses can be seen in table 3. In general, thin coatings of the range of 1–6 µm are observed which are close to the detection limit given by the manufacturer. If the precision of the equipment (±2.5 µm) and the fact that they are hand-applied layers are also considered, the uncertainty rises, so that making coupons in triplicate as a minimum is indispensable. Standard deviations only exceed 1 µm in cases where some waves have formed due to accumulation of material on application.

In terms of the relation between thickness and protective ability, coatings before ageing have been compared by electrochemical impedance spectroscopy. The |Z| of Bode diagrams (from medium frequencies up to 10 mHz) of coupons with the same coating, show an ascendant tendency as the thickness increases. This is evident for the B72 and INC coupons (Fig. 1). Results are irregular in C80, but this can be attributed to imprecisions in thickness measurement because the probe may be deforming the coating, as it is so soft.

As expected, thicker coatings have better protective properties, but a compromise has to be found between good protection and the visual appearance of the finish. Thicker coatings can lead to an increase in gloss and a more uneven distribution of the product, resulting in waves, brush marks, etc.

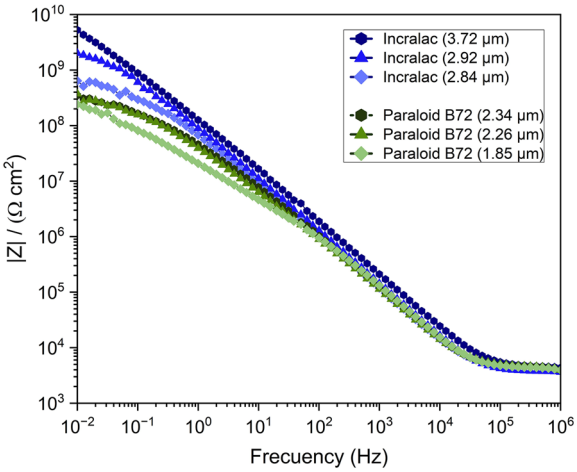

Fig. 1 Bode plot comparing the different thicknesses of a set of INC and B72 coupons before accelerated ageing. INC yields the highest impedance of the tested coatings

In any case, variability of samples has to be considered in a statistical approach when comparing. If measurements are made in an area reasonably above or below the mean thickness of the whole coupon, there is a risk to compare values in different extremes of the range (i.e. the best possible result of a coating with the worst for another). As in coupons preparation, several measurements should also be taken to lead to more accurate results.

Once the thickness is similar for different coatings, it is possible to compare other factors such as the nature of the coating or the adhesion and the possible existence/absence of defects that would affect the penetration of the electrolyte.

Table 3 Thickness data of coupons carried out in triplicate for B72, INC and C80 and for each final drying time: 3, 7 and 14 days

Average (µm) and ± SD				
	Dried 3 d	**Dried 7 d**	**Dried 14 d**	**Nº samples**
B72 coupons (2 layers)	2.3 ± 0.8	2.4 ± 0.5	2.1 ± 0.8	9
	2 ± 1	2.4 ± 0.6	2.5 ± 0.7	
	1.9 ± 0.6	2.6 ± 0.9	3.3 ± 0.9	
INC coupons (1 layer)	3 ± 2	2.9 ± 0.8	4 ± 2	9
	3 ± 1	3.0 ± 0.8	5 ± 2	
	3.3 ± 0.8	3.7 ± 0.9	3 ± 1	
C80 coupons (2 layers)	2.4 ± 0.7	2.2 ± 0.6	2.2 ± 0.4	9
	1.6 ± 0.4	2.2 ± 0.4	2.0 ± 0.6	
	2.0 ± 0.6	2.4 ± 0.6	2.2 ± 0.7	

Performance vs. drying time of the coatings

Visual changes

All coupons were visually monitored at the middle of the test (t = 168 h) and after the end at t = 336 h. At 168 h, the corrosion products were already covering a large part of the surface of the C80 coupons, while only localised pitting was visible on the B72 ones. As can be seen in Fig. 2 after 336 h, the coupons start to corrode at the edges and then spread to the centre.

At t = 336 h each of the coatings shows different results. In C80, the extent of corrosion products tends to decrease with increasing drying time (see Fig. 2A) while in B72 (Fig. 2B) this tendency is not entirely clear. INC is not affected by drying time, and no corrosion is visible except for a few stains in the borders (Fig. 2C). These coupons have the same appearance independently

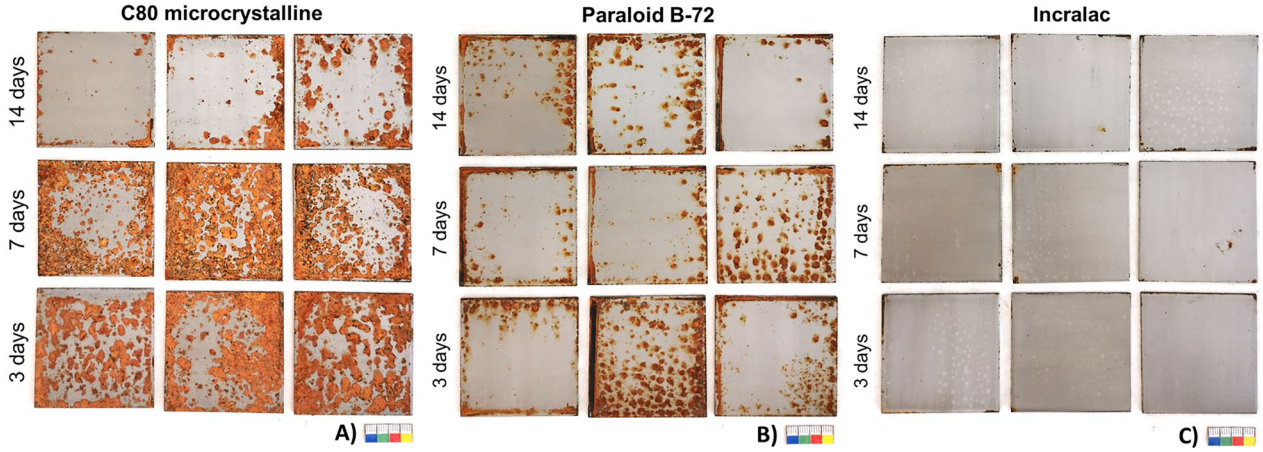

Fig. 2 Visual appearance of the 27 coupons after 336 h of accelerated ageing. Triplicates for each coating left to dry for 3 d, 7 d or 14 d are shown

of whether they have dried for 3 days or 14 days. Whitish spots can be observed due to the condensation and the fogging of the coating as it happened in the previous paper [16].

Aesthetically, it can be said that only INC has performed well. This could be due to the presence of BTA UV-absorbing inhibitor in its composition [22].

Coating defects

Several studies have shown that exceeding the glass transition temperature of a polymer leads to the mobility of its chains and therefore affects the coating performance [23]. Exposing these coating to 60 °C during UV cycles would lead to exceeding the Tg in most of them, andthis can result in a homogenization of the coating, correcting even pores and application defects, or have the opposite effect. In this experiment, continuous exposure to accelerated ageing cycles results in large-scale deformation of the polymer and thus minimisation of the contact area with the substrate, producing a phenomenon described as dewetting [24, 25]. This process of coating retraction can be observed with the clumping of the polymeric material, forming a kind of bubbles/craters that leave areas of the metal with a lower coverage (Fig. 3). However, as the drying time increases, it can be observed how the film is more homogeneous (Fig. 3A–C at 14 d). Some craters and pores are visible but do not leave gaps between them, with a few isolated exceptions, where corrosion of the metal starts to develop.

As observed in the previous work [16], this phenomenon is more evident in B72, because it has a Tg of 40 °C, which has clearly been exceeded with accelerated ageing. However, the evidence that the coating had fewer defects as the drying time increased (Fig. 3A), confirms that the presence of solvent inside the film keeps it flexible and with a lower Tg, similar to the ambient temperature [15]. Therefore, as the solvent evaporates over time, we obtain a more rigid and stable coating with a higher Tg, which leads to an improvement in the protective capacity.

Aspect of INC is different, with smaller and more separated pores (Fig. 3B) in a film that is not as deteriorated as B72. This difference may be related to INC starting from a higher Tg (similar to the temperatures in the UV cycle). In this case no differences are observed between coatings with different drying times. INC is a coating that dries to the touch within a few hours and, as we observed in the preliminary test (Table 2), its thickness increases almost proportionally with the number of coats even at short drying times. All these results could be related to the presence of some additives in its composition, such as plasticisers, which can accelerate the film formation process [22].

In the coupons coated with C80 dewetting phenomenon is not so clearly visible and practically after t = 336 h, there is hardly any coating left on coupons dried for 3 days and 7 days (Fig. 3C). It can be seen how the wax layer deforms and allows water to enter very early in the ageing process. Recent studies have shown that in humid environments waxes retain water trapped at the steel-coating interface, contributing to the formation of corrosion products [26, 27].

So far, no references have been found that consider dewetting when evaluating the performance of protective coatings in heritage. However, this phenomenon is being studied in relation to cleaning processes and reversibility of polymeric resins [28, 29]. Although temperatures used in our accelerated test might seem too high, metals exposed to the sun outdoors can reach temperatures of this order, so this phenomenon might play a significant

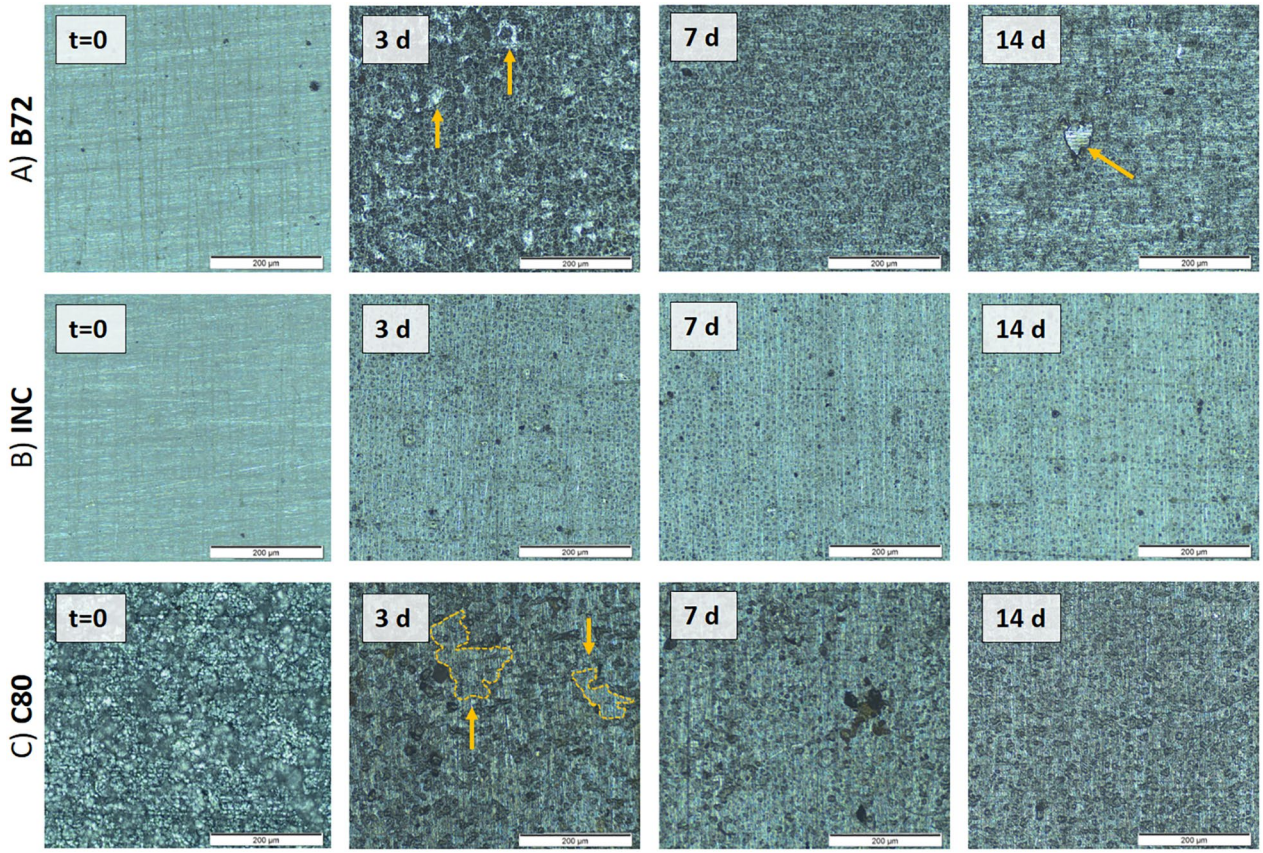

Fig. 3 Comparison of the defects produced in coatings with different drying times at t = 336 h with the initial surface before ageing (t = 0). A higher number of defects is observed in B72 **A** and C80 **C** when they have been left to dry for a shorter time. In INC **B** the drying time is not related to the defects. Some areas where the metal is exposed are marked in yellow. Scales corresponds to 200 µm

role in the protective properties of coatings for metal conservation.

Protective capacity

The interpretation of EIS results was performed in a simplified way, obtaining the impedance modulus (|Z|) value at the lowest frequency (10 mHz). At low frequencies, a global indication of the protective capacity of the coating is obtained, as has been proven in some studies on coatings for metallic heritage [6, 30]. For each condition (drying time and ageing time), the average values of |Z| of the three coupons are represented, with error bars showing the maximum and minimum measured values. The results are in accordance to the visual analysis and observed defects described in previous sections. For the coupons of B72 and C80, two orders of magnitude higher impedance modulus at low frequencies is obtained when the coating has been left to dry for two weeks at t = 336 h (Fig. 4A–B), so EIS confirms that as the drying time increases, so does the protective capacity upon ageing. The effect of drying time on B72 was not obvious in the visual aspect (Fig. 2), due to the irregularity of the corrosion distribution, but is clearer in the EIS results. For INC, increase of drying time does not influence the results (Fig. 4C). |Z| decreases by about one order of magnitude at t = 168 h and remains stable until the end of ageing regardless of the drying time.

This decrease also occurs in respect to t = 0 for all coupons to a greater or lesser extent. This is caused by the degradation of the coating and the defects formed what allow the electrolyte to penetrate more easily. This therefore result in a lower impedance of the system (Fig. 5, t = 168 h). When this happens, corrosion products start to form in the interface. Some of these corrosion products are protective (as show by Raman in next paragraphs) and build up over time, and can hinder the access of the electrolyte to the base metal, hence increasing the measured impedance (Fig. 5, t = 336 h). This effect can be observed in Fig. 4 for all coatings except C80 dried 3 days and C80 dried 7 days, where the degradation of the coating is evident and formed corrosion products are not protective (see Raman results below).

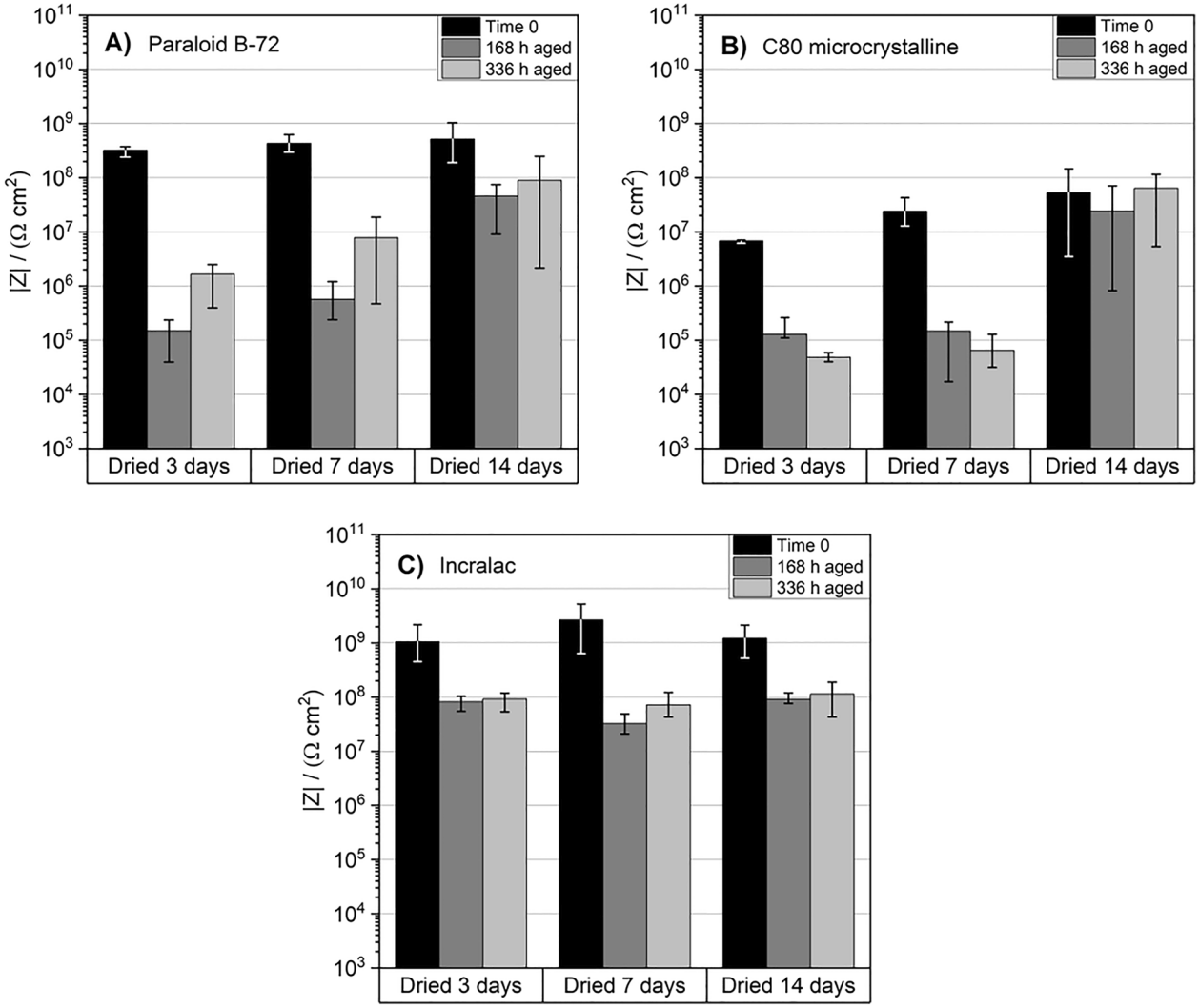

Fig. 4 Bar plot of the average |Z| at 10 mHz of triplicate coupons for B72, C80 and INC coatings left to dry at different times. Error bars represent the maximum and minimum measured values. Drying times are compared for different ageing times of the coupons

The surface of the coupons was also analysed by Raman to try to extract more information about the corrosion suffered by the samples with the different coatings. In all B72 coupons, regardless of the drying time, lepidocrocite (γ-FeOOH) with characteristic peak at 250 cm^{-1} and occasionally hematite (α-Fe_2O_3) were identified in the upper layers according to the peak assignments at 223 cm^{-1}, 289 cm^{-1} and 404 cm^{-1} (Fig. 6; Red spectrum). Magnetite (Fe_3O_4) was identified in the lower layers with characteristic peak at 670 cm^{-1} (Fig. 6; Blue spectrum) [31]. The latter is one of the most stable phases of the iron corrosion along with goethite (α-FeOOH), which could not be identified after deconvolution of the lepidocrocite spectrum as the peaks may overlap.

In the case of the C80 coupons, only lepidocrocite is found in all corrosion layers. The large amount of these corrosion product all over the surface, makes it difficult to analyse the areas closest to the metal where magnetite could hardly be identified. With this characterisation, it is also confirmed that hardly any coating remains on the substrate, so it is understood that the protective capacity observed by visual inspection and EIS decreases with ageing time. As mentioned in the previous section, the wax retains a lot of moisture [26, 27], so it may also have hindered the formation of non-hydrated and therefore more stable corrosion products as in the case of the B72 coupons. INC coupons presented only a few localised corrosion spots, and although small lepidocrocite peaks

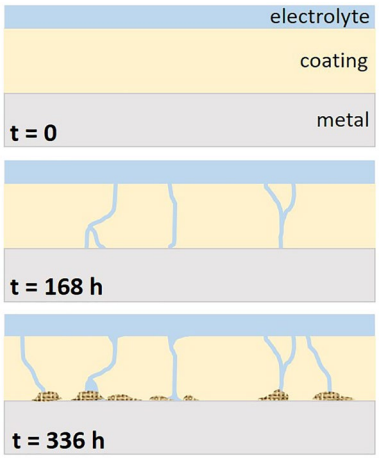

Fig. 5 Schematic representation of the evolution of a coated metal upon ageing. At t = 0 the coating is intact. At t = 168 h the electrolyte reaches the metal through small pores or defects developed upon ageing. At t = 336 h corrosion spots formed at the contact points block some pores and hinder the electrolyte penetration

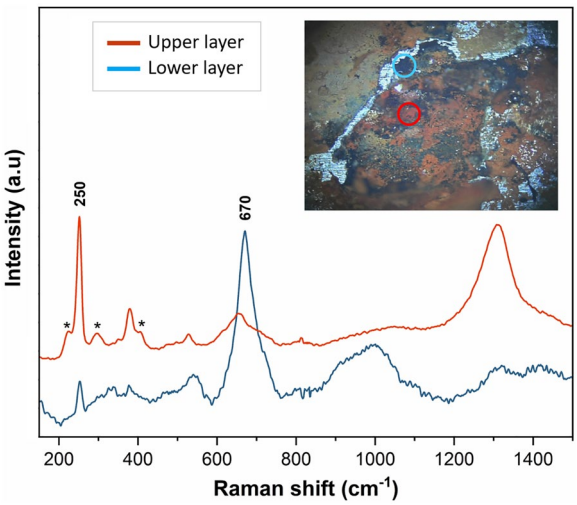

Fig. 6 Raman spectra of the corrosion products (marked with red and blue circles) found in a B72 coupon left to dry for 1 week, after accelerated ageing (t = 336 h). The phases are usually mixed but the presence of lepidocrocite is higher in the upper layers and magnetite in the lower ones. Peaks assigned to haematite in the lepidocrocite spectrum are marked with *

were detected, signal and the fluorescence of the coating predominates in the spectra, so not much information can be extracted.

Conclusions

In this paper, we have studied the effect of the thickness of the coating and drying time, both between layers and final, in the protective properties of coatings commonly used for heritage metals protection. It has been shown that the different application procedures of a coating can dramatically influence the results obtained.

Results presented here demonstrate that drying time is a critical variable that can define the behaviour of the coating exposed to aggressive conditions. Lack of proper drying can favour degradation processes such as dewetting and increased water permeability. On bare steel surface considered in the present study, some coatings such as C80 and B72 should be allowed to dry for 14 days after application to ensure that as stable a film as possible is formed prior to any ageing test, while INC achieves good protective properties after just 3 days. In any case, the optimum drying time needs to be established on different heritage metal surfaces in further studies.

It is important to prepare coatings with similar thickness to compare the performance of different materials. It has been shown that the number of layers does not directly correlate with the final thickness of the coating, so a direct measurement of this variable should be made in any study comparing the behaviour of coatings. Induction-based thickness meters, such as the one used here, have the advantage of speed, low cost and accessibility for any real case; however, in further studies, the results obtained will be compared with other thickness measurement techniques to check their accuracy.

The importance of the application methodology has become clear. Variables such as thickness and drying time have to be considered to compare the results between different protection systems, ageing methods and any type of study related to the evaluation of the protective capacity of both traditional and innovative coatings for metallic heritage. Not taking them into account or not making clear the methodology used in the work may lead to non-reproducible results and even wrong conclusions.

Acknowledgements

The authors acknowledge the support of the Plataforma Temática Interdisciplinar "Patrimonio Abierto: Investigación y Sociedad" (PTI-PAIS) of CSIC. We are also grateful for the support for the publication fee from the CSIC Open Access Publishing Support Initiative through its Research Information Resources Unit (URICI) and for the suggestions of Marc Gener, PhD.

Author contributions

EC and MTM conceptualised the study and designed the methodology. MTM performed the experiments and analysed the data with BRM, MTM carried out the investigation and wrote the original draft, which was reviewed and edited by EC and BRM. All authors read and approved the final manuscript.

Funding

This work has been funded by MCIN/AEI/10.13039/501100011033 and "ERDF A way of making Europe", under the project COMPACT (HAR2017-89911-R) and the predoctoral grant PRE2018-086667 additionally funded by "ESF Investing in your future". It is also been funded by the Community of Madrid and the European Social Fund, under the TOP Heritage-CM programme (P2018/NMT-4372).

Availability of data and materials
The datasets generated and analysed during the current study are available in the following institutional repository: https://digital.csic.es/ and can be consulted and cited through: https://doi.org/10.20350/digitalCSIC/15237.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare no competing interests.

Received: 10 February 2023 Accepted: 23 April 2023
Published: 12 May 2023

References

1. Argyropoulos V, Boyatzis S, Giannoulaki M, Polikreti K. The role of standards in conservation methods for metals in cultural heritage. In: Dillmann P, Watkinson D, Adriaens A, editors. Corros Conserv Cult Herit Met Artefacts. Sawston: Woodhead Publishing; 2013. p. 478–517.
2. Watkinson D. Preservation of Metallic Cultural Heritage Shreir's Corros. Oxford: Elsevier; 2010. p. 3307–40.
3. Watkinson D, Emmerson N, Channell I. Towards quantitatively assessing the success of dodecanoic acid as an inhibitor for the treatment of archaeological iron nails. EUROCORR 2017 Annu Congr Eur Fed Corros. 2017.
4. Letardi P. Testing new coatings for outdoor bronze monuments: a methodological overview. Coatings. 2021;11:1–16.
5. Jáuregui-Gónzalez D, Rodríguez-Gómez F, Contreras-Vargas J, Roncagliolo-Barrera P, López-Arriaga M. Influence of the application and preparation of wax coatings on artificially patinated bronze surfaces. New Delhi, India: Met. 2016. Proc. Interim meet ICOM-CC MWG; 2016. p. 170–7.
6. Ellingson LA, Brostoff LB, Shedlosky TJ, Bierwagen GP, De la Rie ER. The use of electrochemical impedance spectroscopy in the evaluation of coatings for outdoor bronze. Stud Conserv. 2004;49:53–62.
7. Ramírez Barat B, Letardi P, Cano E. An overview of the use of EIS measurements for the assessment of patinas and coatings in the conservation of metallic cultural heritage. Neuchatel, Switzerland: Met 2019 Proc Interim Meet ICOM-CC MWG; 2019.
8. Hosbein KN, Swartz NA, Clare TL. Electrochemical identification and categorization of the protective quality of intact and damaged coatings. Electroanalysis. 2014;26:1935–44.
9. Cano E, Bastidas DM, Argyropoulos V, Fajardo S, Siatou A, Bastidas JM, et al. Electrochemical characterization of organic coatings for protection of historic steel artefacts. J Solid State Electrochem. 2010;14:453–63.
10. Salvadori B, Cagnini A, Galeotti M, Porcinai S, Goidanich S, Vicenzo A, et al. Traditional and innovative protective coatings for outdoor bronze: application and performance comparison. J Appl Polym Sci. 2018;135:1–12.
11. Cano E, Lafuente D, Bastidas DM. Use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage: a review. J Solid State Electrochem. 2010;14:381–91.
12. Ramírez Barat B, Crespo A, García E, Díaz S, Cano E. An EIS study of the conservation treatment of the bronze sphinxes at the Museo Arqueológico Nacional (Madrid). J Cult Herit. 2017;24:93–9.
13. Masi G, Balbo A, Esvan J, Monticelli C, Avila J, Robbiola L, et al. X-ray photoelectron spectroscopy as a tool to investigate silane-based coatings for the protection of outdoor bronze: the role of alloying elements. Appl Surf Sci. 2018;433:468–79.
14. Mirambet F, Reguer S, Rocca E, Hollner S, Testemale D. A complementary set of electrochemical and X-ray synchrotron techniques to determine the passivation mechanism of iron treated in a new corrosion inhibitor solution specifically developed for the preservation of metallic artefacts. Appl Phys A Mater Sci Process. 2010;99:341–9.
15. Vinçotte A, Beauvoit E, Boyard N, Guilminot E. Effect of solvent on PARALOID® B72 and B44 acrylic resins used as adhesives in conservation. Herit Sci. 2019;7:1–9.
16. Molina MT, Cano E, Leal J, Fort R, Álvarez de Buergo M, Ramírez-Barat B. Protective coatings for metals in scientific-technical heritage: the collection of the Spanish national museum of science and technology (MUNCYT). Heritage. 2023;6:2473–88.
17. Newey H. Conservation and the preservation of scientific and industrial collections. Stud Conserv. 2000;45:137–9.
18. British Standards Institute. ISO 4892-3: Plastics—Methods of exposure to laboratory light sources—Part 3: Fluorescent UV lamps. 2006.
19. Ramírez Barat B, Cano E, Letardi P. Advances in the design of a gel-cell electrochemical sensor for corrosion measurements on metallic cultural heritage. Sensors Actuators B Chem. 2018;261:572–80.
20. Cano E, Crespo A, Lafuente D, Ramirez BB. A novel gel polymer electrolyte cell for in-situ application of corrosion electrochemical techniques. Electrochem commun. 2014;41:16–9.
21. Ramírez Barat B, Cano E. Agar versus agarose gelled electrolyte for in situ corrosion studies on metallic cultural heritage. ChemElectroChem. 2019;6:2553–9.
22. Wolfe J, Grayburn R. A review of the development and testing of Incralac lacquer. J Am Inst Conserv. 2017;56:225–44.
23. Forrest JA, Dalnoki-Veress K. The glass transition in thin polymer films. Adv Coll Interface Sci. 2001;94:167–95.
24. Reiter G. Unstable thin polymer films: rupture and Dewetting processes. Langmuir. 1993;9:1344–51.
25. Mukherjee R, Sharma A. Instability, self-organization and pattern formation in thin soft films. Soft Matter. 2015;11:8717–40.
26. Thickett D, Stanley B. The Use and Mis-use of Renaissance Wax. Neuchatel, Switzerland: Met 2019 Proc Interim Meet ICOM-CC MWG; 2019.
27. Thickett D, Pretzel B. FTIR surface analysis for conservation. Herit Sci. 2020;8:1–10.
28. Baglioni M, Montis C, Chelazzi D, Giorgi R, Berti D, Baglioni P. Polymer film Dewetting by water/surfactant/good-solvent mixtures: a mechanistic insight and its implications for the conservation of cultural heritage. Angew Chemie. 2018;57:7355–9.
29. Castel A, Gutfreund P, Cabane B, Rharbi Y. Swelling, dewetting and breakup in thin polymer films for cultural heritage. Soft Matter. 2020;16:1485–97.
30. Letardi P. Laboratory and field tests on patinas and protective coating systems for outdoor bronze monuments. Neuchatel, Switzerland: Met 2004 Proc Interim Meet ICOM-CC MWG; 2004. p. 379–87.
31. Neff D, Bellot-Gurlet L, Dillmann P, Reguer S, Legrand L. Raman imaging of ancient rust scales on archaeological iron artefacts for long-term atmospheric corrosion mechanisms study. J Raman Spectrosc. 2006;37:1228–37.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Submit your manuscript to a SpringerOpen journal and benefit from:

- ► Convenient online submission
- ► Rigorous peer review
- ► Open access: articles freely available online
- ► High visibility within the field
- ► Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com