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# **An ABS Recycled Coating for Corrosion Protection and Conservation of Copper and Alloys of Cultural or Historic Value**

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Additional information is available at the end of the chapter

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## **1. Introduction**

During the 19<sup>th</sup> century, interest to establish chronologies to explain human past developments appeared. Such efforts were based on socio-cultural aspects, sustaining the argument of consecutive social phases such as: savagery, barbarian and civilization stages [1]. In 1836, Christian Jurgensen Thomsen [1] proposed an alternative conception based on industrial and technological development aspects [2]. The new created system proposed three stages to understand Prehistory: Stone, Bronze and Iron ages, which although no longer unanimously accepted, still illustrate the close relationship between the development of metallurgy and human culture. Therefore the history of metal technologies is considered a fundamental part of human history [3].

Cultural heritage conservation constitutes a relevant field of research, which frequently relies on material science to solve the challenges posed by the degradation of artifacts, architectural structures and ornaments [4-10]. Historic, artistic and archaeological items are frequently built of metals (Figure 1). Through the ages, copper and its alloys (bronze) constitute a particular set of metals widespread used in such manufactures [11-15]. Even when these materials tend to form protective patinas due to their interactions with the environment [16-20], such natural protective layers may fail, especially in highly polluted atmospheres [21-23].

The first step in the care of collections is to understand and minimize or eliminate conditions that can cause damage. The second step is to follow basic guidelines for care, handling and cleaning. Collections of un-conserved or ill-conserved archaeological artifacts might be unstable if they do not receive appropriate conservation treatment. It is not within the scope of this chapter to address in detail the problems associated with outdoor bronze sculptures [24].

Two or more metals are combined to form an alloy. Brass and bronze are copper alloys obtained by mainly adding zinc and tin respectively. Alloys generally have a different appearance or working properties compared to their component metals. Other alloys of copper include "gunmetal", bell metal, and German silver, also called nickel silver or "paktong" [24]. Brass is an alloy of about 70% copper with about 30% zinc. It may be cast into solid shapes, rolled into thin sheets, spun into vessel shapes or drawn wire. Brass is often found in scientific instruments, scale models and historical apparatus of all kinds. In its natural state it is typically light yellow-gold in appearance [25, 26].

Historic cast bronze has been widely used since antiquity to create weapons, sculptures and decorative objects. Bronzes are traditionally patinated and in such state they appear anywhere from light green to dark brown in color. Patinas are sometimes described as any controlled corrosion that imparts an aesthetically pleasing color and/or texture to the artifact. Patinas may be applied using chemicals or may have accumulated over time naturally [24]. Ancient cast bronze is usually composed of 90% copper, 6% tin and 4% zinc. However, different percentages of tin content have been reported between 11% [27] up to 25% [6].

Another category of artifacts that should be included in any discussion of brass and bronze is "bronzed" and plated finishes. Sometimes called "French Bronze", in the nineteenth century, paint or varnish containing bronze pigments were applied to cast iron or soft white metal [28]. These painted finishes may develop copper oxidation, but should not be polished. Another method of bronzing involved applying very thin copper plating to a metal surface; this kind of finish does not hold up to polishing either. Colored lacquers were sometimes applied to scientific instruments, and should be carefully considered as an original patina on a bronze artifact [25].

### **1.1. Causes of damage**

Corrosion, poor handling and inappropriate storage are the major causes of damage to metal artifacts. Copper alloys are relatively stable, corrosion-resistant materials if they are properly cared for. Active corrosion causes a loss of metal from the object, and is most closely associated, with an environment which is heavily polluted, or subjected to salt water evaporation. Salts, oils and moisture can cause corrosion development staining copper alloys [24]. Highly polluted urban or industrial atmospheres are prone to produce acidic rainfall. Under such low pH conditions crystallized copper sulfates dissolve from the corrosion crust initiating complex corrosion processes [29, 30]. Long term corrosion of bronze archaeological artifacts in soil has been related to acidification and salt pollution [31, 32]. Other alloys as nickel-aluminum bronzes have shown increased corrosion rates in sulfide polluted seawaters [33].

## 1.2. Corrosion

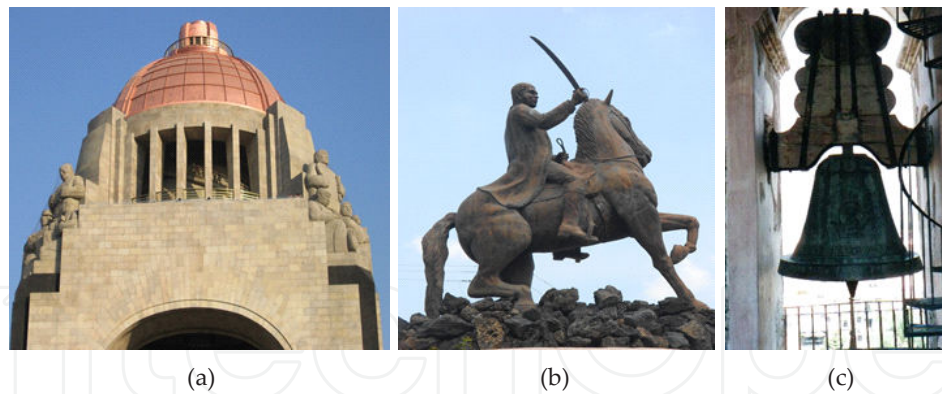
Uncoated copper and alloys artifacts that have been kept clean and dry will usually develop stable surfaces. Stable surfaces may appear reddish, black to brown, or green to blue. The brownish and black colors may result from natural, non-destructive oxidation of the copper, which is sometimes named "tarnish". Thick crusts may accumulate, but dense corrosion that does not progress may actually protect the object if it is left intact. Purposely applied, "patinas", which may be any variety of colors, usually act as a protection to the metal [24, 25].

The development of small spots of light green powder that grow rapidly, is indicative that the artifact is suffering from what is commonly called "bronze disease" and indicates active corrosion [34, 35]. As mentioned above, green surfaces are often seen but may not be cause for alarm, if the corrosion layer is continuous and does not flake off easily. Bright or 'waxy' whitish-green powder forming in small areas on the surface, or in cavities on the metal surface, indicates advanced active corrosion. If left in its current state, this type of corrosion can cause a significant amount of damage to historic copper alloys, as it causes pitting of the surface and a continuous loss of metal [36]. This condition is sometimes noticed when green powder falls from an undisturbed object. It is caused by the presence of salts in the air, or by deposits left behind from inappropriate cleaning or handling and progresses when the air is humid. High levels of ammonia pollution in the air will cause bluish deposits of corrosion. In rare cases, patinas contain corrosive ingredients that may contribute to corrosion [25].

Corrosion will progress on copper alloys in the presence of high relative humidity (RH), normally above 70%. However, an upper safe limit of 46% is considered to avoid bronze disease [34, 37]. As for most metals, the critical RH may be lower in polluted atmospheres. Dust and grime left to accumulate on metal artifacts will actually hold moisture to the surface, and may induce corrosion even where the humidity is not that high. Varnished or lacquer brass and bronze can usually withstand corrosion as long as the coating is not broken. Where there are losses in the coating, corrosion will progress, usually seen as dark streaking where unprotected areas have oxidized [26, 38].

Polishing exposes fresh, reactive metal to the atmosphere and, therefore, to further oxidation. It might be desirable to coat objects that will be displayed at a museum exhibition. A lacquer coating to valuable silver and brass generally is applied, for their protection [39]. This also mitigates the need for frequent polishing, which inevitably wears away the metal surface if done frequently. A spray applied lacquer or wax coating are used commonly on large areas of metal as the best coatings. Wax provides a relatively flexible coating that is easily applied and that can be renewed. It can be used on top of original patinas and lacquers that are not meant to be disturbed, as long as they are cleaned first [40, 41].

On the other hand, acrylonitrile-butadiene-styrene (ABS) waste and residues represent a well-known discarded by-product from the automotive industry [42, 43]. Since law usually forbids the recycling of this material because all pieces must be brand new, considerable amounts of ABS become unused waste and a nuisance to dispose due to environmental restrictions. Therefore, research has been done trying to find usable recycling applications with added value, for this and other polymer discards. Due to the finite reserve of hydrocarbon in the



**Figure 1.** Copper and bronze historical and cultural artifacts. (a) Monument to the Revolution, Mexico City. (b) Morelos Monument, Universidad Autónoma del Estado de Morelos, Cuernavaca, Mexico. (c) 19th Bronze Bell, Cathedral of Cuernavaca, Mexico.

world, a proposal has been to obtain degradation oils from plastics, potentially useful as fuel [44]. However, such processes cannot avoid the presence of heteroatoms such as chlorine from poly(vinylchloride) (PVC) or nitrogen from ABS. These heteroatoms relate to corrosion of metallic parts and participate in the formation of dangerous compounds such as cyanic products, SO<sub>x</sub> or NO<sub>x</sub>, in the combustion process [45, 46].

The mechanical and chemical properties of ABS have been studied demonstrating its durability, elongation to break and impact resistance. However, thermo-oxidation processes can degrade this polymer due to hydrogen subtracted by oxygen [46]. Two models explain the ABS degradation: heat aging or physical aging [47-50]. It is well known that this polymer can be dissolved in organic solvents; also, thin layers become practically transparent. The application of coatings to both, clean or patina covered metallic surfaces has proved to be useful to preserve cultural heritage [51]. Two highly desirable conditions of conservation 'oriented' coatings are: transparency in order not to affect the aesthetical traits of the artifacts, as well as reversibility, which refer to an easy removal process [52]. Therefore, an ABS coating potentially fulfills some of the major requirements for coatings used in cultural heritage conservation. Hence, a combination of adequate properties and ecological values due to waste recycling and added value might be implied in the utilization of this coating for the stated purpose.

## 2. ABS coating

A coating development has been proposed recurring to the dissolution properties of ABS in acetone, applied by immersion of coupons. Characterization and evaluation of the protective properties of recycled ABS thin films on copper and bronze surfaces were performed. This was done simulating the degradation of the coatings exposed to a highly corrosive ambient. A comparison was made with the behavior of aliphatic polyurethane, a commonly used commercial coating for conservation purposes, as reported [51].

The ABS waste solution preparation consisted on cutting the polymer into small pieces and afterwards, dissolving them in acetone under constant stirring at room temperature. In this

way, the obtained solution was ready for the metal samples to be dip coated and then removed, allowing the acetone solvent to evaporate, at various cycles and times of immersion. The metallic coupons were immersed in consecutive: one (ABS-1), two (ABS-2) and three (ABS-3) thirty seconds per immersion cycles in the ABS solution. So the best preparation conditions were attained [51].

## 2.1. Characterization and evaluation

The recycled ABS coating was characterized in two different states: in raw form and in solution. Thermal analysis and Fourier Transformed Infrared Spectroscopy (FTIR) with Attenuated Total Reflectance (ATR) were used, being extremely reliable and recognized fingerprint characterization methods [53].

## 2.2. Polymer characterization

Figure 2a shows the TGA/DTA measurement results for recycling ABS, as it is discarded. The TG curve shows one stage weight decrease between 300 and 500°C, due to thermal decomposition with the onset in 400°C, remaining just 10% at 500°C, which corresponds to additives, fillers and other aggregates present in the copolymer because of the application for which it was tailored for. At the same time, the DTA curve shows two main peaks, a small one around 220°C due to melting of the elastic butadiene, and a bigger one that initiates at 420°C corresponding to the ABS copolymer decomposition [54].

The IR spectra of ABS in raw and in solution are shown in Figure 2b. Both present characteristic peaks of the three main components, but in solution they are clearly seen: the nitrile band of acrylonitrile at 2237 cm<sup>-1</sup>, the aromatic ring of styrene at 1602, 1494, 761, and 699 cm<sup>-1</sup>, and the double bond of butadiene at 967 cm<sup>-1</sup> trans and 911 cm<sup>-1</sup> vinyl. The rest of non-identified peaks in the spectra correspond to acetone major absorptions [55].

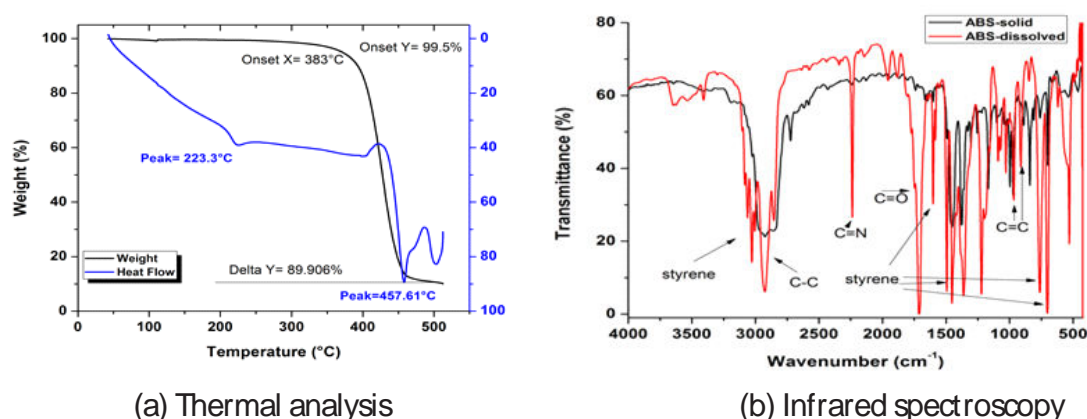


Figure 2. ABS characterization.

ABS shows accelerated thermal degradation due to aging at elevated temperatures above 80 °C. The impact resistance decreases dramatically beyond a critical aging time at 120 °C and

this reduction depends on surface property modifications during aging. Visual examination of specimen cross-sections after aging, verifies that discoloration is limited to a surface layer, which is characteristic of degradation where oxygen diffusion into the bulk is limited [55]. Also, degradation causes an increase in Young's modulus at the specimen surface, which in turn promotes brittle failure. Absorbance bands from Fourier transform infrared spectroscopy indicate that surface degradation proceeds by chain scission and cross-linking in the polybutadiene (PB) phase of aged ABS specimens [54]. Dynamic mechanical thermal analysis also supports the occurrence of cross-linking, as shown by an increase in the glass transition temperature of the PB phase after aging. Although degradation in the styrene-acrylonitrile (SAN) phase is less significant to the reduction in overall mechanical properties of ABS compared to the PB phase, an assessment of SAN copolymer indicates that heat aging decreases impact resistance [55]. As temperature and aging time influence degradation, it is proposed that at ambient service temperatures (40 °C or less), the degradation mechanism differs to that at elevated temperatures, and comprises both surface and bulk polymer degradation effects. These characteristics support the idea of the application of ABS as a coating for ambient temperature, as obtained and reported [54-56].

To evaluate the corrosion performance, electrochemical methods were performed in commercial copper and bronze (73% Cu, 25% Sn and, 2% Zn by wt.) coupons. All electrochemical evaluations (Figure 2) performed include: corrosion potential, electrochemical noise measurement, impedance spectroscopy, and potentiodynamic polarization, the details being reported elsewhere [57-61].

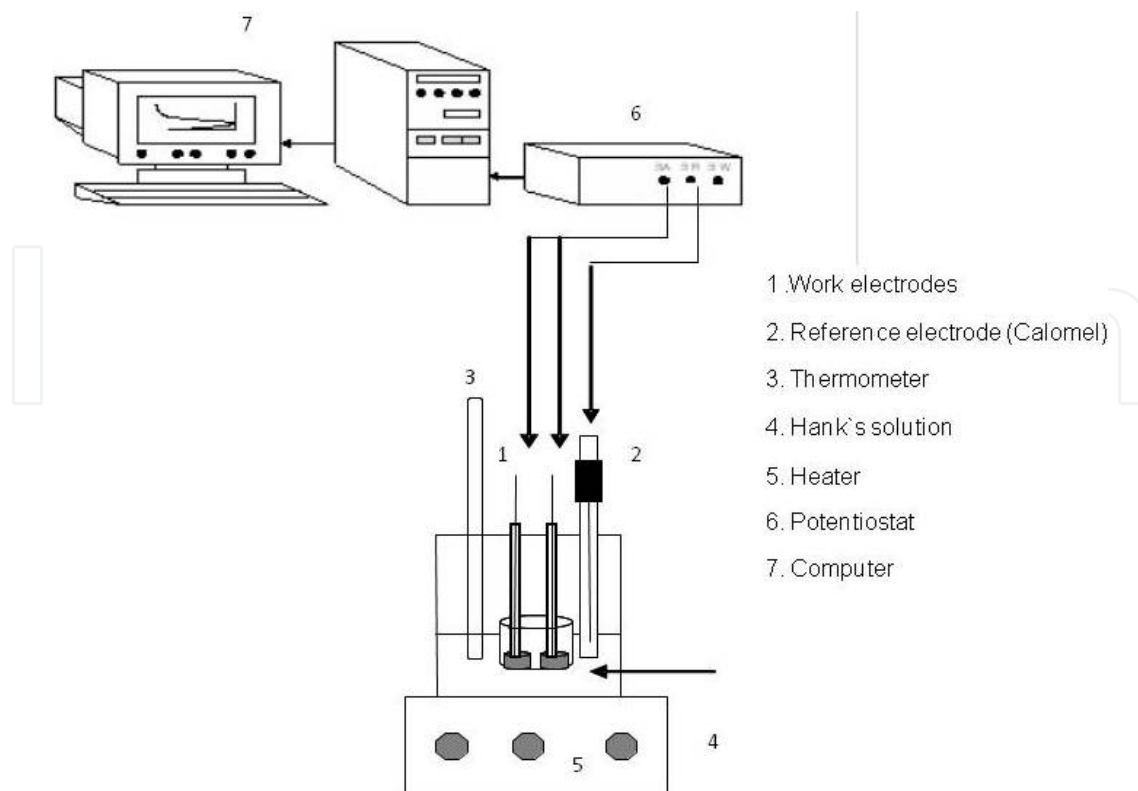
A first group of samples were used as blank to evaluate the electrochemical properties of the base materials in two different solutions. As a reference, a second group of coupons were coated with commercial aliphatic polyurethane (varnish). The application consisted of a single layer using a small brush, simulating the manual procedure, frequent in conservation.

A third group of samples were coated by three successive dip coating immersions in the ABS solution. Coupons with different immersion cycles (ABS-1, ABS-2, and ABS-3) were evaluated electrochemically as a function of time for two weeks in the test solutions. The first solution,  $\text{Na}_2\text{SO}_4$  0.1M, is mildly aggressive while the second one,  $\text{Na}_2\text{SO}_4$  0.1M + 3% wt. NaCl, presents highly corrosive properties, simulating an aggressive urban-marine atmosphere. Also, ABS coated copper and bronze samples were scribed with a cutter to evaluate the coating adherence, using the "pull-up" test, after 2 weeks of immersion.

### 2.3. Coating thickness measurements

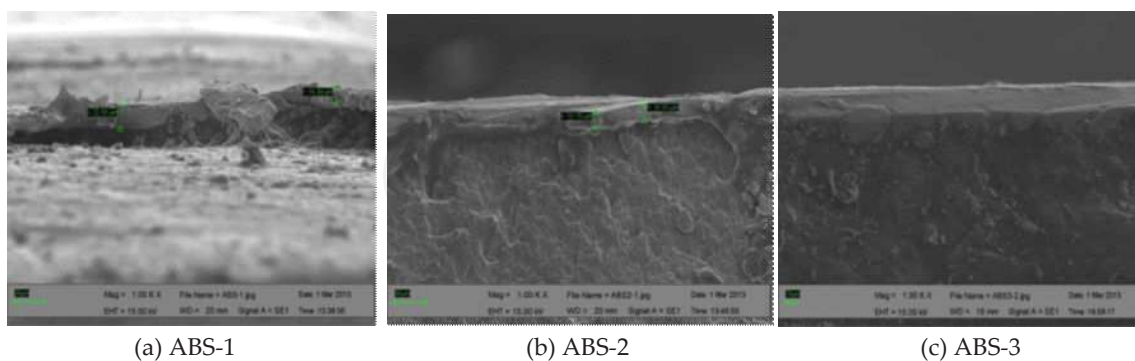
Scanning electron microscope (SEM) was used to determine the thickness of the coatings for each case. Alternatively, five measurements over the coated coupons surface were made using a coating thickness gauge, obtaining an average coating thickness over the metal sample.

Figure 3a presents the coating thickness after one immersion with an interval between 14 to 22  $\mu\text{m}$ , looking not very compact and disbonded. After the first immersion, the procedure was repeated once (ABS-2) (Figure 3b) and twice (ABS-3) for 30 s (Figure 3c). The coating looks compact but maintaining a thickness around 13 to 16  $\mu\text{m}$ . These results suggest that immersion



**Figure 3.** Electrochemical setup.

cycles did not increase the coating thickness, but rather, pores present after the first immersion were sealed and the compactness was improved (see below). Also during the second and third immersions, the ABS solution promotes partial removal of the top of the coating due to the action of acetone.



**Figure 4.** Coating thickness measurement by SEM.

For varnish brush painted metal surfaces, the average thickness was 144 and 297  $\mu\text{m}$  for copper and bronze samples, respectively. For ABS-3 deposited coatings the average thickness after three immersion cycles, was 36.8 and 41.2  $\mu\text{m}$ , for copper and bronze respectively (table 1). The varnish coatings were an order of magnitude thicker as compared to the ABS-3 ones.



Sample	Coating Thickness					Average ( $\mu\text{m}$ )
	( $\mu\text{m}$ )					
Cu-ABS-3	40	34	35	34	41	36.8
Cu-varnish	134	133	144	112	142	133
Bronze-ABS-3	44	37	28	56	41	41.2
Bronze-varnish	290	329	134.7	422	311	297

**Table 1.** Coating thickness

### 3. Results and discussion

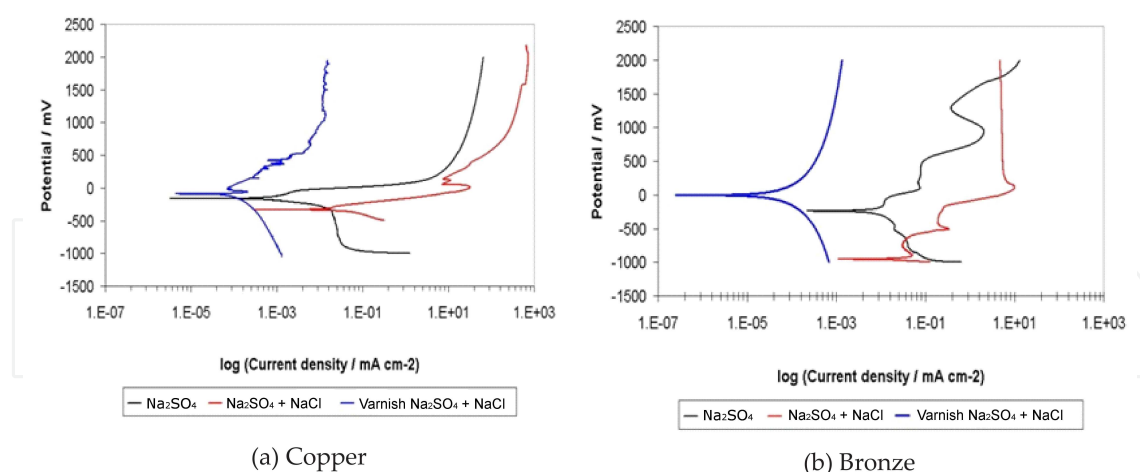
#### 3.1. Electrochemical evaluation

Table 2 presents free corrosion potentials as a function of time of immersion for the metal coating schemes tested. The potential evolution reflects the degradation process of the coating, starting with noble potential values becoming more active as time elapses. ABS-3 coated metal samples presented more negative values than varnish coatings, especially for bronze coated coupons. Values are similar to the ones registered for bare (blanks) copper and bronze samples [6, 60, 61].

Time (h) / Coating System	Copper-Varnish	Copper-ABS-3	Bronze-Varnish	Bronze-ABS-3
	$E_{\text{corr}}$ (mV)			
0	-49	-98	-3.3	-108
24	-108	-127	-3.2	-134
48	-111	-133	-3.1	-211
168	-114	-241	-16	-382
360	-324	-246	-336	-557
Rest Potential. Polished surface in $\text{Na}_2\text{SO}_4 + \text{NaCl}$		-254		-299

**Table 2.** Rest potentials of copper and bronze coupons in time.

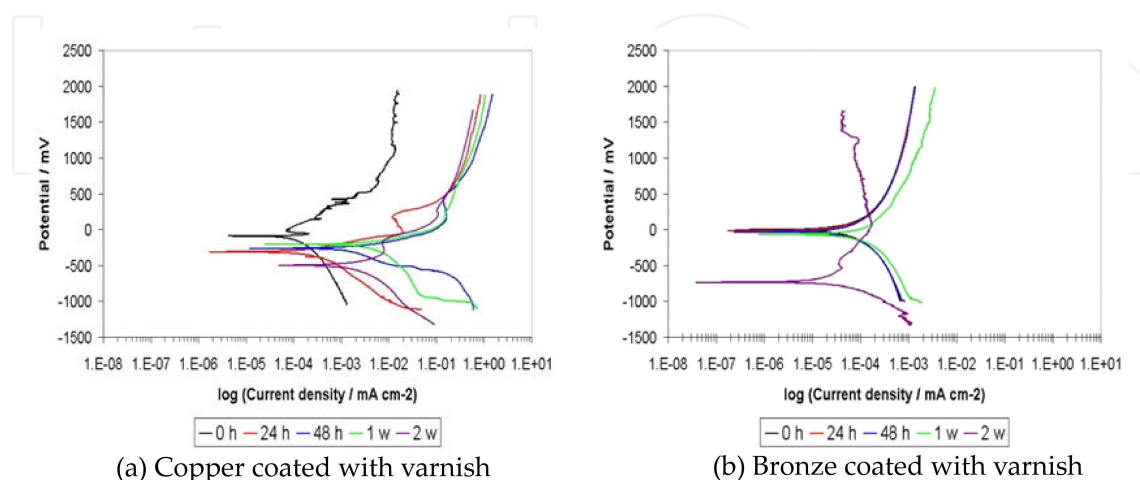
Figure 4 shows the polarization curves of the copper and bronze coupons used as blank obtained in  $\text{Na}_2\text{SO}_4$  0.1M and  $\text{Na}_2\text{SO}_4$  0.1M + 3% wt. NaCl solutions. It also includes the curve corresponding to the varnish coated coupons in the aggressive solution. The corrosion rates of copper increase two orders of magnitude in comparison to the mild solution. In contrast, the copper coated with varnish decreases the corrosion rates as much as three orders of magnitude compared to the uncoated copper in the aggressive solution, demonstrating the protectiveness of the coating. The performance of the varnish is considered as reference to compare the protectiveness of the polymer coating under evaluation.



**Figure 5.** Polarization curves of blanks and coated with varnish samples in  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 + 3 \text{ wt. } \% \text{ NaCl}$  solution.

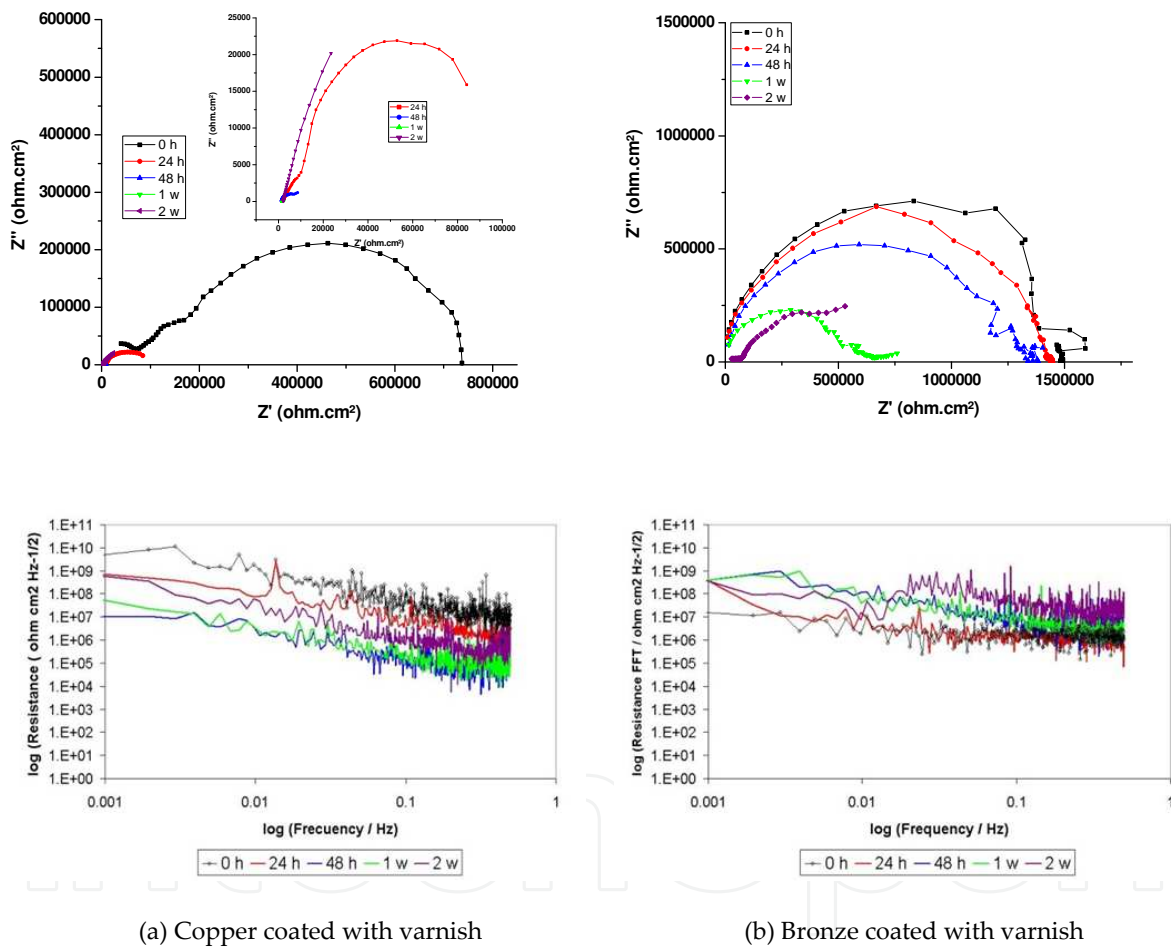
In Figure 5 it is shown the polarization curves of the varnish coated copper (Figure 5a) and bronze (Figure 5b) coupons in aggressive solution for different times of immersion up to two weeks. As time elapses, the corrosion rates increases suggesting the degradation of the coating, in the case of copper samples. For bronze is the other way around. It is coherent with the presence of passivation regions after 24 to 48 hours probably due to the oxidation of the base material and corrosion products are formed, as the solution reaches it through the coating pores or cracks. Nevertheless, the current densities observed are in the same order of magnitude as expected [6].

A high tin content in a bronze tends to inhibit corrosion, a fact which is suggested to be connected with the precipitation of insoluble  $\text{SnO}_2 \cdot x\text{H}_2\text{O}$  on anodic sites. On the other hand, an alloy with high zinc and low lead content tends to exhibit the highest corrosion rate in some corrosive environments [6, 62-64].



**Figure 6.** Polarization curves for samples in  $\text{Na}_2\text{SO}_4 + \text{NaCl}$  solution, as a function of time.

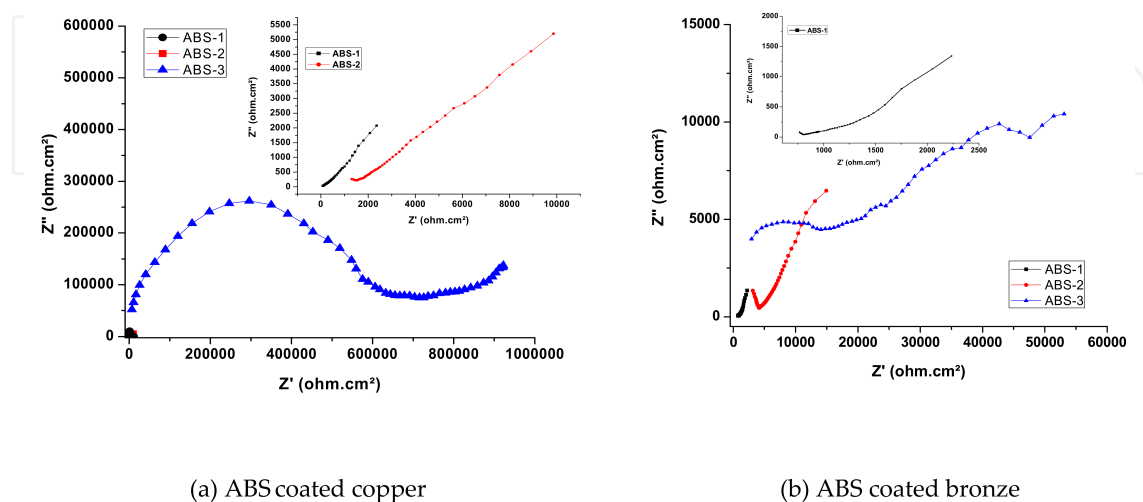
Figure 6 presents the electrochemical noise and impedance measurements for the varnish coated copper and bronze coupons. The Nyquist impedance diagrams show that the total impedance values decrease in time although there is an increment after two weeks, which once again is related to the corrosion products formed as the coating deteriorates. This behavior was registered for both metals. Such oxidation can start as early as 24 to 48 hours according to the polarization curves. The electrochemical noise resistance values show similar behavior as the impedance measurements, although an increase can be seen from week one. For the bronze sample (Figure 6b) the noise impedance at the time of immersion presents the lowest value in contrast with the copper electrode (Figure 6a). Therefore, the results of all the electrochemical techniques are coherent to each other since they show similar trends (see below Figure 10).



**Figure 7.** Nyquist and electrochemical noise impedance diagrams for samples in  $\text{Na}_2\text{SO}_4 + 3 \text{ wt. } \% \text{ NaCl}$  solution, as a function of time.

Figure 7 shows the Nyquist diagrams for each of the three coating cycles: ABS-1, ABS-2, and ABS-3. For ABS coated copper electrodes (Figure 7a), even when no significant increase of thickness was achieved with the consecutive immersions, the total impedance increased as a function of the number of immersion. This can be related to the fact that each immersion sealed the pores of the polymer layer. The total impedance values of the ABS-3 coupons reached

similar values compared to the varnish coated coupons. In the case of bronze samples (Figure 7b), total impedance values are lower than the copper samples, but with a similar trend. Nevertheless, the impedance behavior observed for the first two immersions suggest a highly capacitive response, therefore a good protective coating film.

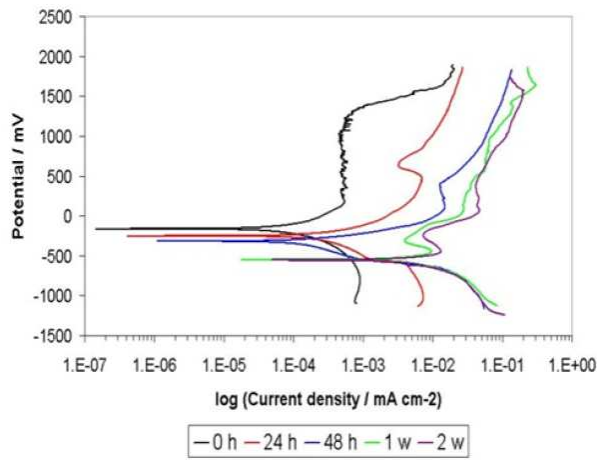


**Figure 8.** Nyquist impedance diagrams for samples in  $\text{Na}_2\text{SO}_4 + 3 \text{ wt. } \%$   $\text{NaCl}$  solution.

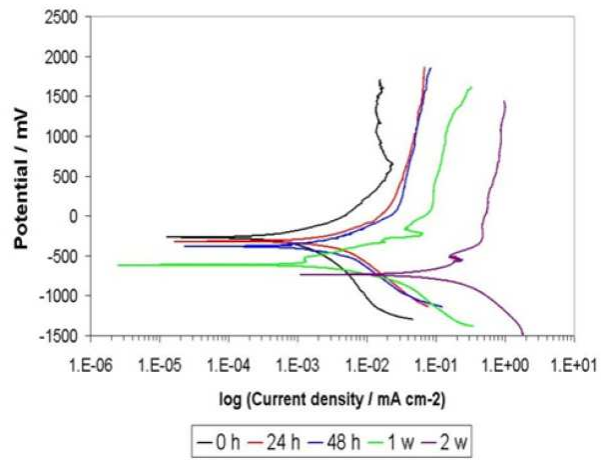
Figure 8 shows the polarization curves of the ABS-3 copper and bronze coupons. In the initial immersion time of the ABS-3 copper sample (Figure 8a), there is a well-defined passivation region suggesting corrosion and film formation process in the surface of the base material. As time elapses, the passivation region tend to diminish and the corrosion rates increase as the coating deteriorates. Corrosion potentials become more negative in time indicating surface activation of the metal. For coated bronze samples (Figure 8b), the corrosion potential becomes active and the passive current increases as a function of time, so the corrosion rate indicating a deterioration of the coating film.

Figure 9 presents the impedance and electrochemical noise measurements as a function of time for the ABS-3 coated copper and bronze coupons. The Bode and noise impedance diagrams (Figure 9a) show that the total impedance values decrease in time without any increment as observed in the case of the varnish sample. The electrochemical noise impedance values also show a general decrease, compared with the initial time of immersion. However, there is an increase in impedance values after one week. The same trend was observed for the impedance values of the ABS-3 coated bronze electrodes (Figure 9b). This behavior is similar to the one observed for the varnish coated samples and suggest that after coatings deteriorate, a protective film over the metal samples is developed blocking the pores formed over the coating.

Figure 10 compares the total impedance ( $Z_t$ ) and noise resistance ( $R_n$ ) values in time for both, the varnish and ABS-3 copper coupon. In both cases, the behaviors decrease as time goes by and the coatings deteriorate. The resulting values are similar in magnitude and trend comparing each other and hence, it is possible to suggest that the protective performance of the coatings is comparable. In the case of  $Z_t$ , the ABS coating stays with higher protective values

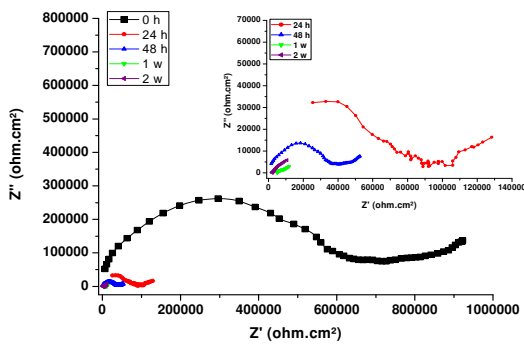


(a) ABS-3 coated copper

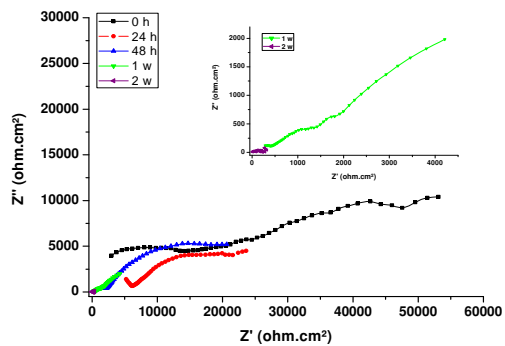


(b) ABS-3 coated bronze

Figure 9. Polarization curves of ABS-3 samples in  $\text{Na}_2\text{SO}_4 + 3 \text{ wt. \% NaCl}$  solution, as a function of time.



(a) ABS-3 coated copper



(b) ABS-3 coated bronze

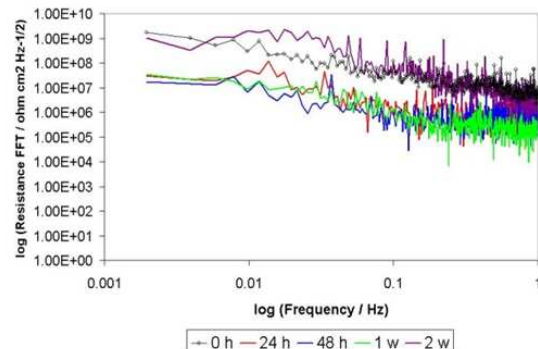
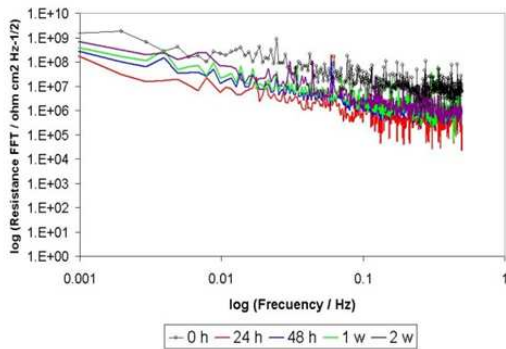
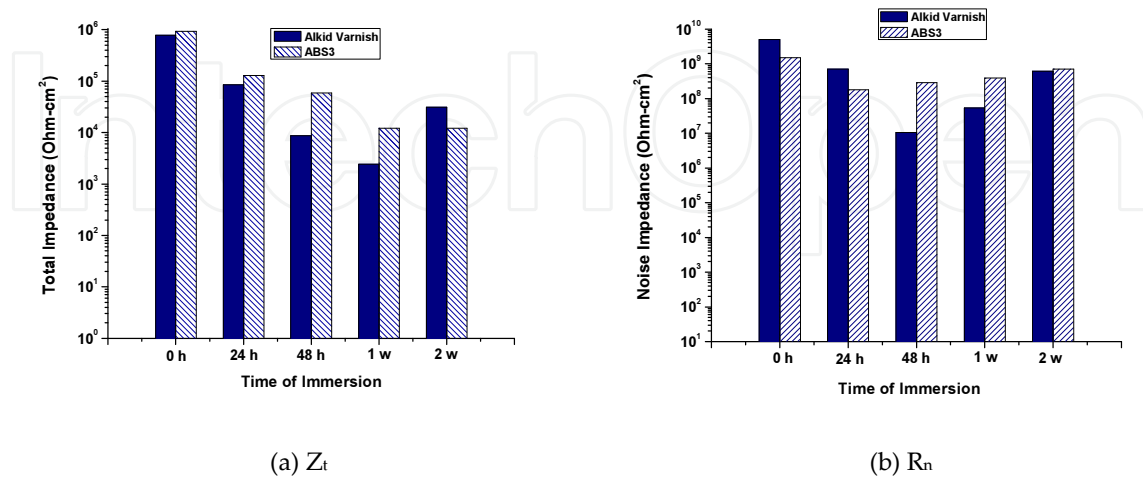


Figure 10. Nyquist and noise impedance spectra for ABS-3 samples in  $\text{Na}_2\text{SO}_4 + 3 \text{ wt. \% NaCl}$  solution, as a function of time.

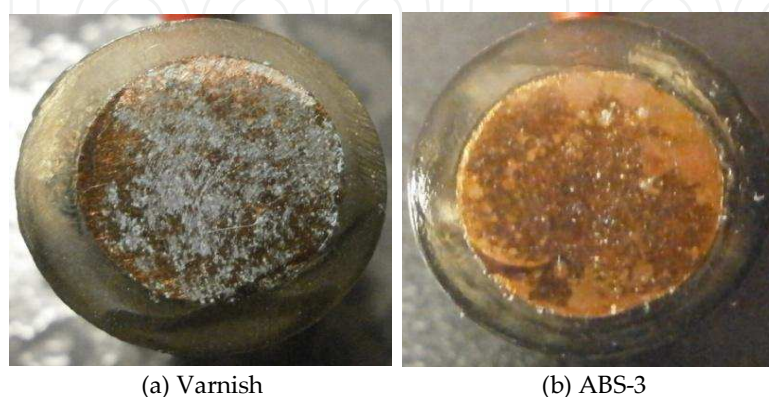
during a considerable time.  $R_n$  values indicate that even when initially the protection of the ABS coating is slightly below in relation to the varnish, at some point in time, the parameter

values are inverted and both coatings reach very similar values. Being the noise resistance independent of the frequency, the values obtained and presented in the noise impedance spectra are related totally to the coating performance [47, 48].



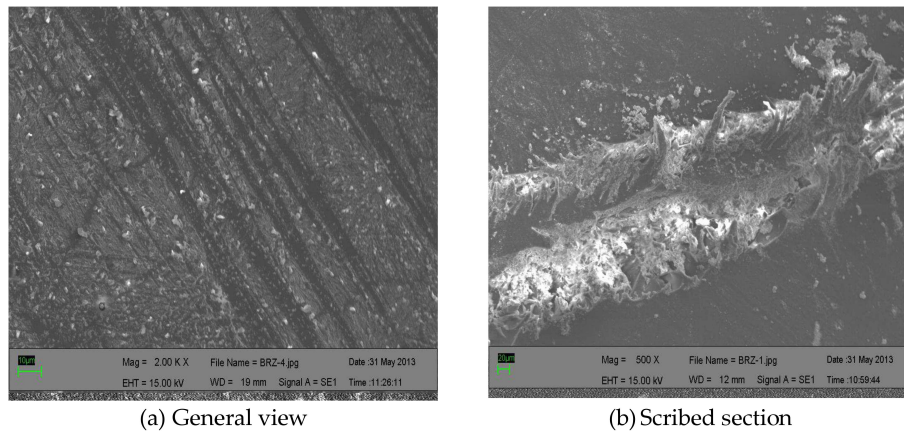
**Figure 11.** Comparative values of total and noise impedance for varnish and ABS-3 coated copper as a function of time.

Figure 11 compares the macroscopic aspect of coupons coated with varnish and ABS-3 after two weeks in the aggressive solution. The coupon protected with varnish shows blue-green corrosion products while the one coated with ABS-3 stayed in the copper color range. This suggests that the pores and/or failures in the varnish allow diffusion of bigger ions in solution such as sulfates reaching the metallic surface, which combined with chloride and oxygen may form  $\text{CuSO}_4$ , as compared to those in the ABS coating. In the latter, probably smaller pores allow diffusion only of oxygen, generating a highly adherent and protective copper oxide ( $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ) patina whose properties combine with those of the ABS-3 coating. Also, the difference observed in both samples corroborates the suggestion made as to the immersion cycles and pore sealing presented and discussed in Figure 2 above.



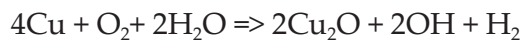
**Figure 12.** Macroscopic aspect of coupons coated after two weeks in the aggressive solution [51].

Figure 12(a) presents the general aspect of the ABS-3 coated metal immersed in the electrolyte for two weeks. A good surface condition can be observed through the transparent ABS-3 coating, suggesting good corrosion protection. In Figure 12(b) the scribed section shows good adhesion of the coating after the *pull up* test, presenting corrosion products only within it.



**Figure 13.** SEM micrographs of ABS-3 coating.

Atmospheric corrosion of copper reaction is [49, 50]:



Under polluted conditions:



Copper and alloys such as bronze, show moderate stability under atmospheric conditions, but due to increasing pollution and acid rain, in urban environments exposed bronze undergoes into accelerated corrosion, expressed by some impairment of appearance. Corrosion of copper and its alloys form complex patinas over the surface, being more or less protective depending upon the environmental conditions and the nature of the pollutants present. In the atmosphere, the range in corrosion rates is in the order of less than  $0.1\mu\text{m}/\text{year}$  for rural atmospheres, to approximately  $5.6\mu\text{m}/\text{year}$  for industrial-marine environment [49]. Electrochemical measurements immersed in neutral solution on samples with patinas formed after long exposures under different atmospheres, rendered polarization resistance values of  $5.4\text{ kohms}\cdot\text{cm}^2$  for rural atmospheres up to  $35.2\text{ kohms}\cdot\text{cm}^2$  for industrial-marine polluted atmospheres. For comparison bare copper, presents polarization resistance values in the range from  $1.5$  to  $6\text{ kohms}\cdot\text{cm}^2$  [50]. These results show low atmospheric corrosion rates for rural atmosphere being higher in polluted atmospheres. Nevertheless the patinas formed under contaminated conditions are more protective according to the electrochemical results.

In comparison under similar experimental conditions, for copper samples coated with a commercial varnish used for restoration and conservation of pieces of works of art of cultural and historic heritage, polarization resistance values obtained were in the range from  $10$  to  $100$

kohms-cm<sup>2</sup> [24]. Results obtained and presented in this work, compares favorably with the results previously reported for this type of coatings. When using a copper corrosion inhibitor such as benzotriazole a polymeric oxide is formed [53, 54], and the polarization resistance values obtained in chloride solution, were around 50 kohms-cm<sup>2</sup>. According to the results obtained in this work, the ABS-3 coating presents good performance when compared to other corrosion protection systems [48, 49].

Work Title	Types of studied coatings	Reference
An Analysis of Polyethylene Coating Corrosion in Oil and Gas Pipelines	Three Polyethylene layers (Epoxy primer plus Adhesive (polyglue) plus PE Top Coating)	65
Electrochemical evaluation of patinas formed on nineteenth century bronze bells	Patinas on bronze	6
Electrochemical assessment of the restoration and conservation of a heavily corroded archaeological iron artifact.	Rust converter	7
Corrosion resistance properties of electroless nickel composite coatings	Electroless nickel (EN) composite coatings incorporated with PTFE and/or SiC particles	66
Corrosion protection by multilayered conducting polymer coatings	Multilayered coatings consisting of combinations of conducting polymers polyaniline (Pani) and polypyrrole (Ppy),	67
Effect of Mg and Si on the microstructure and corrosion behavior of Zn-Al hot dip coatings on low carbon steel.	Zn and Zn-6Al Coatings with or without 0.5 %wt Mg and 0.1%wt Si	68
Electroactive conducting polymers for corrosion control	Electroactive conducting polymer coatings.	69
Studies of a new accelerated evaluation method for coating corrosion resistance—thermal cycling testing	Aerospace electrodeposition-coat primer plus plasma polymer pretreatment SrCrO <sub>4</sub> -pigmented epoxy-polyamide primer (PEPP)	70
Characterization of the corrosion behavior of Zn and Zn alloy electrodeposits: Atmospheric and accelerated tests.	Zn, Zn-Co (0.6%), Zn-Fe (0.4%) and Zn-Ni (12%) coatings	71
Effect of the amine functional group on corrosion rate of iron coated with films of organofunctionalsilanes	Coatings made with two silanes, one with a functional group ( $\gamma$ -aminopropyltriethoxysilane [ $\gamma$ -APS]) and one without a functional group (bis-triethoxysilyl ethane, BTSE),	72
Corrosion protection using polyaniline coating formulations	Polyaniline (PANI) coatings	73
Polyaniline/epoxy coatings with good anti-corrosion properties	Polyaniline/epoxy blend coatings	74



Work Title	Types of studied coatings	Reference
Use of electrochemical impedance spectroscopy for the study of corrosion protection by polymer coatings	Alkid coatings	75
Passivation of metals by coating with polyaniline: corrosion potential shift and morphological changes	Coatings with polyaniline dispersions	76
Evaluation of corrosion behavior of coated metals with AC impedance measurements	Polybutadiene coating of $8 \pm 2 \mu\text{m}$ thickness applied by spin coating	77

**Table 3.** Examples of surface treatments in order to improve protective characteristics.

## 4. Summary

Historically, copper and its alloys constitute a relevant group of metals used in the manufacture of cultural heritage. Even when these materials tend to be self-protective under atmospheric conditions, pollution, acid rain and other factors can disrupt their natural protective patinas. Therefore, several procedures have been designed from the materials science perspective in order to protect these and other metallic materials. Such treatments vary in efficiency and not all may fulfill the requirements for conservation purposes.

The ABS films fulfill two major requirements for cultural heritage conservation purposes that are transparency and reversibility. Transparency is usually required due to the need of not altering the visual properties of the artifacts. Reversibility has been considered an ideal goal because in reality, any intervention will leave some degree of impact or residues in the materials. However, a tendency towards reversibility is highly desirable. Both properties are achieved by dissolving ABS in organic solvents such as acetone, combined with a highly acceptable protective capacity of the material. Small, delicate artifacts might be more suitable to undergo the proposed process. Tests were done simulating aggressive ambient, hardly found within the security of museums or similarly protected surroundings.

The proposed application for conservation adds value to an industrial waste and contributes to find recycling alternatives for this discarded polymer, hence collaborating not only with the conservation science, but also with the ecological concerns and needs. In the present, all kind of residues contribute to the ambient degradation and therefore any recycling proposal has an intrinsic value. Indicated high performance of the coatings needs further studies to characterize and optimize the system, still the application becomes reasonable valid and its use in further conservation cases represents a viable option.

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