SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF ESSENTIAL OILS BASED PROTECTIVE COATINGS FOR SILVER CULTURAL HERITAGE OBJECTS

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The necessity of replacing hazardous chemicals with natural compounds with similar activity is urgent, in different fields, from environmental protection to cultural heritage protection. In this respect, the aim of this paper is to demonstrate that natural compounds from two plants of the Lamiaceae family, namely mint and lavender, can be proposed as corrosion inhibitors for polymeric coatings for silver objects. The obtained results have demonstrated that the incorporation of the essential oils increases the corrosion protection, without affecting the properties of the base copolymeric materials.

Keywords: silver objects; anticorrosion; inhibitors; protective coatings; essential oils.

1. Introduction

Protective coatings for silver objects are crucial for preserving their appearance and preventing tarnish, corrosion, and scratches. The use of coatings is an effective practice in protection of metals against corrosion, especially heritage objects when they are threatened by potential reactions between metals and water, oxygen and different pollutants, some of the main factors in corrosion process [1]. The disadvantage of this protective effect is limited both in terms of effectiveness and time, and interactions between the coating and substrate material. Also, in order

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to use the protective coating for cultural heritage objects, the layer must preserve the esthetic and historical aspect of the object, to ensure reversibility, present low toxicity and ease application [2].

Traditionally, coatings based on waxes [3], organosilanes or polymers [4] were used, but their applicability must be considered for each material, substrates, modes of application, type of aging or deterioration.

Among different compounds available on market, Paraloid compounds are most often used. Paraloid B-72® is the most popular polymer used in conservation as consolidant, adhesive and coating, being soluble in different organic solvents [4]. Its properties were enhanced by the addition of different compounds, such as nanopigments or cysteine, in order to protect silver or bronze objects [5,6]. For Paraloid B-44®, different inhibitors can be used, such as benzotriazole [7] or imidazole and mercaptoimidazole type, to protect against the degradation of archaeological bronze covered with patina [8].

Despite the popularity and efficiency of these synthetic compounds, there is an urgent need to replace these hazardous chemical compounds for environment, with other ones, similar in properties, obtained from natural resources, which are not harmful for health. Essential oils from *Juniperus oxycedrus* L. or plant extracts, such as *Sida acuta* Burm. f can be used as corrosion inhibitors, as literature studies demonstrate [9, 10].

In the present study, the effect of coating with Paraloid 72® and Paraloid 44® mixed with mint and lavender essential oil, on the corrosion process of silver object was studied. Also, characterization methods before and after the coating treatment were performed. All the tests were performed on silver objects, designed for these experiments, in order to use the results for further studies on ancient objects.

2. Experimental

2.1. Materials and methods

The solvent used were analytical-grade reagents (max. 0,005% H_2O), supplied by Merck KGaA (Darmstadt, Germany), Paraloid B44**®** and Paraloid B72**®** from CTS (Italy, Originale Rohm and Haas), NaCl (Chimreactiv, Romania), and essential oils of mint and lavender (Fares, Romania), respectively.

2.2. Obtaining coating solutions and samples characterization

Solutions of Paraloid B72 and Paraloid B44 were obtained as a strong glue, solving 5 g of each resin in 25 ml toluene. In each solution were added 2 ml of mint essential oil, respectively 3 ml of lavender essential oil, at continuous stirring on a magnetic stirrer (600rpm).

Silver discs (diameter of 22 mm, height of 2 mm) were washed with distilled water end ethanol, in order to remove residual contamination from handling. After air-drying, they were covered with 150 µL of each solution and dried at room temperature until a glossy surface was obtained, and any trace of solvent was totally evaporated.

The table below shows the abbreviations used for the tested samples:

Table 1

Abbreviations for the synthesized materials

Synthesized material	Abbreviation
Paraloid B72	R1 (blank sample)
Paraloid B44	R2 (blank sample)
Paraloid B72; 2 ml Mentha Oil	R1M
Paraloid B72; 2 ml Mentha Oil, 3 ml Lavandula oil	R1ML
Paraloid B44; 2 ml Mentha Oil	R2M
Paraloid B44; 2 ml Mentha Oil, 3 ml Lavandula oil	R2ML

The characterization of the silver substrates was performed by X-ray fluorescence (XRF) and scanning electron microscopy with EDX accessory (SEM-EDX) in order to confirm the purity of silver discs used in the tests. Also, gloss studies were performed (using a glossmeter PCE-GM80-ICA), while Fourier transform infrared spectroscopy (FTIR) analyses were performed in order to evaluate the composition of the developed coatings.

To assess the metal content of the tested silver substrates and identify potential impurities in their structure, X-ray fluorescence analysis was employed, namely Vanta C Series Handheld XRF, equipped with a 40 kV X-ray tube, rhodium anode and Silicon Drift Detector. Each beam had a 60-second acquisition time during the analysis process.

For scanning electron microscopy (SEM) was used an instrument Hitachi TM4000plus II (Hitachi HiTech), coupled with an energy dispersive X-ray spectrometry accessory (EDX - Oxford Instruments). In order to obtain the widest possible characterization, the following technical characteristics were taken into account: BSE detector, acceleration voltages of 5 kV, 10 kV or 15 kV and the magnification range between x100÷x100000.

The aesthetic effects of the treatment on the silver discs were performed through gloss tests in several points. For tests was used a glossmeter (PCE-GM80-ICA), equipped with an external gloss sensor, and the measurements were made on a 4.5 mm surface at an angle of 60°.

The FTIR spectra were obtained using a Jasco FTIR 6300 spectrometer (Jasco Corporation, Tokyo, Japan) coupled with a diamond crystal attenuated total reflection accessory (KRS5 lens). The measurements were conducted within the 400–4000 cm^{-1} range, involving 30 scans, with 4 cm^{-1} resolution.

2.3. Electrochemical behavior

The samples electrochemical behavior was carried out by the polarization resistance technique (Tafel technique) [11,12]. This technique consists in plotting linear polarization curves involving the following steps:

- measurement of the open circuit potential (E_{OC}), for a duration of 1 hour;
- plotting the potentiodynamic polarization curves from -0.2 V (vs E_{OC}) to +0.2 V (vs E_{OC}) - Tafel plots, with a scan rate of 0.167 mV/s.

The tests were performed with a Potentiostat/ Galvanostat (model PARSTAT 4000, manufactured by Princeton Applied Research, USA) to which a low current module (LCI, manufactured by Princeton Applied Research, USA) was connected, and the potentiodynamic curves were acquired using VersaStudio v.2.62 software.

The tests were performed at room temperature (25±1°C) using saline solution (NaCl 3.5%) as electrolyte.

The tested materials consisted of discs (uncoated and coated) with a diameter of 22 mm (samples codifications presented in table 1) that were inserted into a special Teflon support so that only one of the surfaces was in contact with the electrolyte and subjected to electrochemical tests.

To perform the corrosion tests, an electrochemical corrosion cell was used consisting in a saturated calomel electrode (SCE) - reference electrode, a platinum electrode - auxiliary electrode and the working electrode consisted of the investigated samples (Ag and Ag coated with different resins).

3. Results and discussions

From the characterization performed by XRF analysis (as an average of five determinations), was observed that silver is the major element (approx. 94.5±2.3%) with impurities due to the manufacture process (Cu- approx. 5.3%, Ni-0.05%, Zn-0.01%, Sb-0.01%, Pb-0.05%) (Fig. 1). SEM analysis revealed that surface support does not present major scratches or other types of imperfections (Fig. 2).

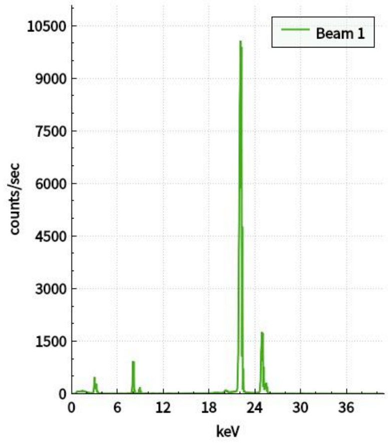


Fig. 1. XRF spectrum for uncoated silver disc

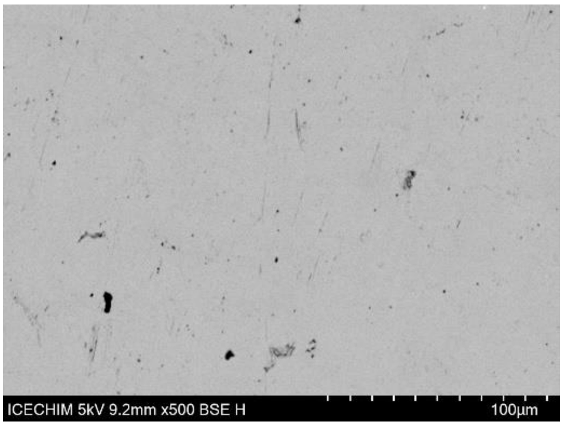
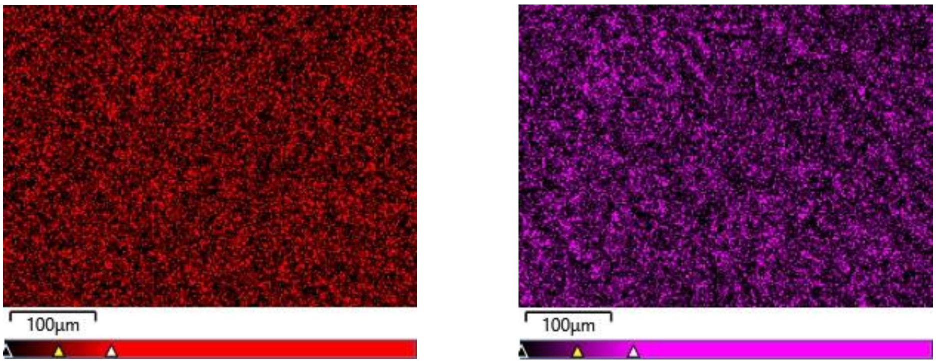
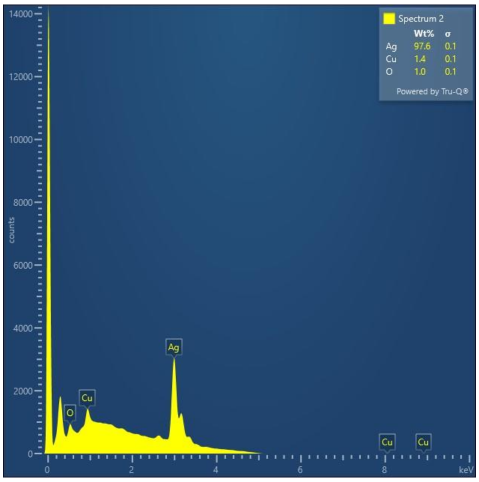


Fig.2. SEM Image of the uncoated silver disc

Fig. 3 presents the distribution map of Ag (Fig. 3a), and Cu (Fig. 3b), while the EDX spectra recorded is shown in Fig. 3c.



(a) (b)



(c)

Fig. 3: Elemental distribution map of silver (a), copper (b) and EDX spectra (c).

The results presented in Fig. 3 confirms the findings of XRF analyses; the differences recorded between the two methods can be explained by the characteristics of each method: while the XRF method characterizes the entire sample (in our case), the EDX analysis is only performed on a small area of the sample.

The FTIR spectra presented in Figs. 4 and 5, reveals a minor influence of the essential oils on the final composition of the coating, with no specific peaks being recorded.

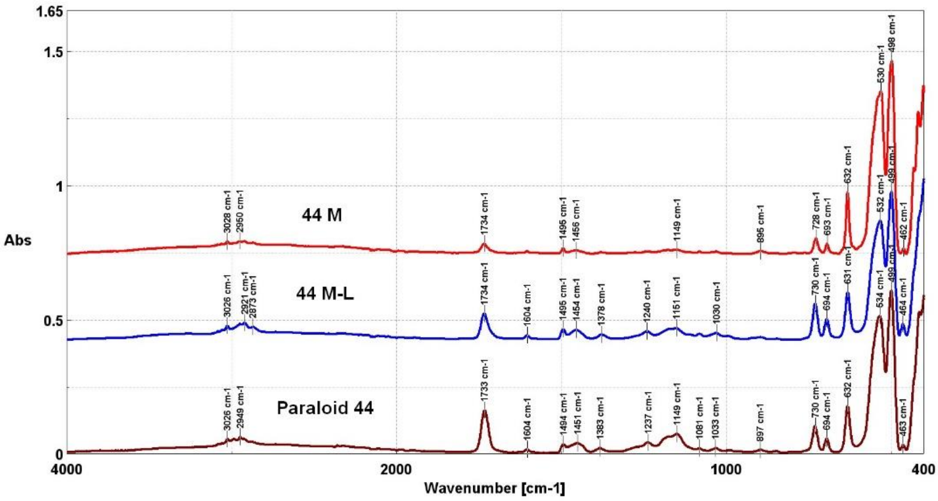


Fig. 4. FTIR spectra of Paraloid B44 with Mentha, respectively Lavandula essential oil compared to the blank solution

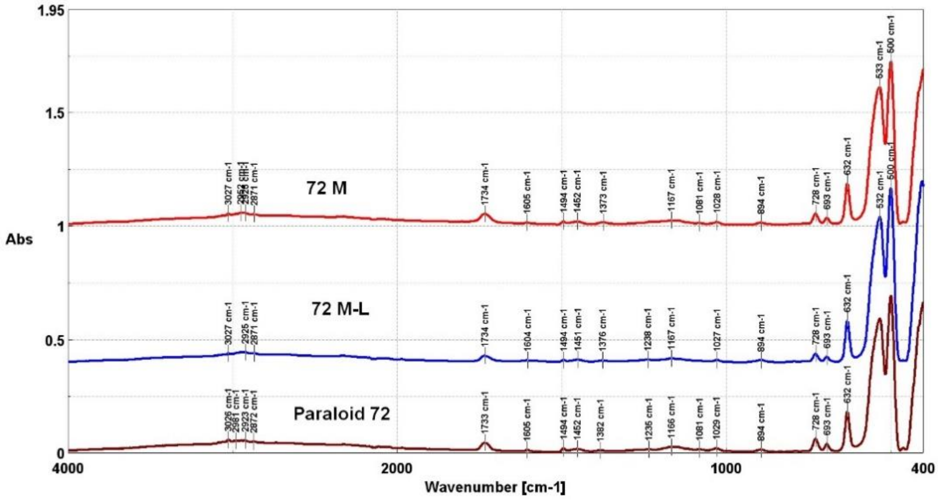


Fig. 5. FTIR spectra of Paraloid B72 with Mentha, respectively Lavandula essential oil compared to the blank solution

In order to evaluate the FTIR results, the composition of the two base-materials must be considered: both Paraloid samples are copolymers, B44 representing an (ethyl acrylate/methyl methacrylate copolymer), while B72 represents a poly ethylmethacrylate/methylacrylate. The recorded maxima in all six samples can be attribute to the polymer mixtures: for both samples, the peaks appearing at 1733 cm^{-1} can be attributed to the characteristic stretching vibration of the ester carbonyl group, the ones at approx. 2981 and 2950 cm^{-1} can be attributed to the C−H stretching, 1494 and 1452 cm^{-1} to the asymmetric CH_3 bending, the ones around 1380 cm^{-1} to the symmetric CH_3 bending, the peaks around 1150 and 1030cm^{-1} to the C−C(=O)−O stretching, while the peaks around 894 and 728 cm^{-1} can be attributed to the C−H rocking vibrations [13]. One major conclusion which can be drawn from FTIR analysis is that the addition of the essential oils do not negatively influence (degrade) the polymeric base, thus maintain of the Paraloid samples.

The gloss tests measurements were performed in triplicate and the result was the average of the measurements. The tests were carried out before and after treatment at 24 and 48 hours, using as blank sample an uncoated disc. Colorimetric studies and gloss tests revealed no major alteration after the addition of the essential oils to the coating treatment in the aesthetic of the silver discs (table 2).

Table 2

Results for gloss test (before and after the treatment, at 24 and 48 hours)

Gloss and color tests		
	24H	48H
M (uncoated disc)	375.7	375.7
R1M	345.1	344.9
R1ML	336.7	332.4
R2M	329.9	328.3
R2ML	348.5	337.1
R1	367.3	366.2
R2	354.1	352.3

The influence of the coating material is expressed by a minor reduction of the gloss parameter, further reduced by the addition of the essential oils.

For corrosion tests, the Tafel curves corresponding to the tested samples are presented in Figs. 6-12 and in Fig. 13 they are overlapped.

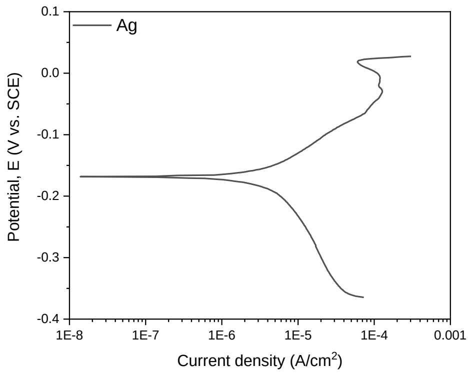


Fig. 6. Tafel plot for silver sample

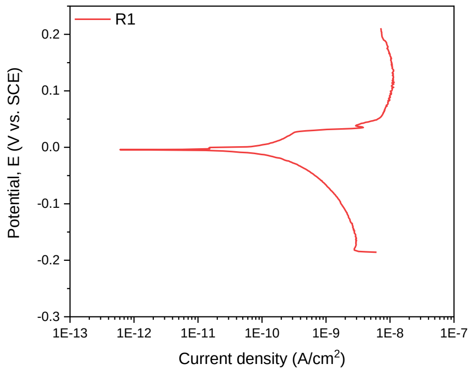


Fig. 7. Tafel plot for sample R1

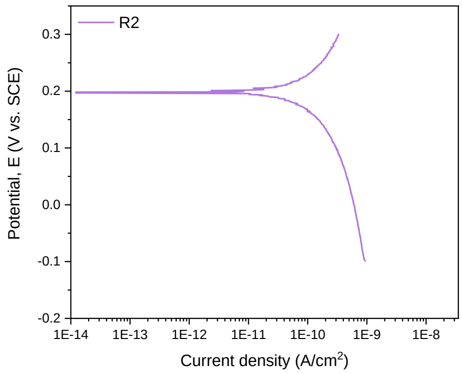


Fig. 8. Tafel plot for sample R2

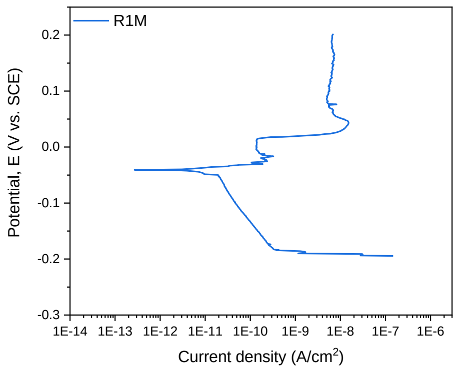


Fig. 9. Tafel plot for sample R1M

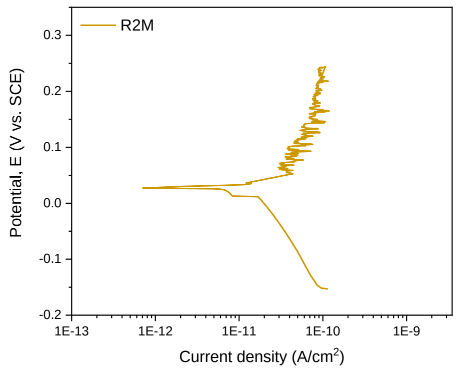


Fig. 10. Tafel plot for sample R2M

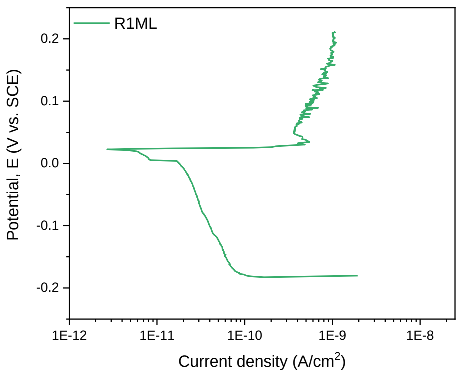


Fig. 11. Tafel plot for R1ML sample

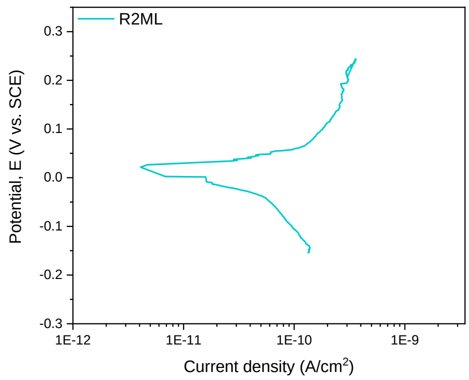


Fig. 12. Tafel plot for sample R2ML

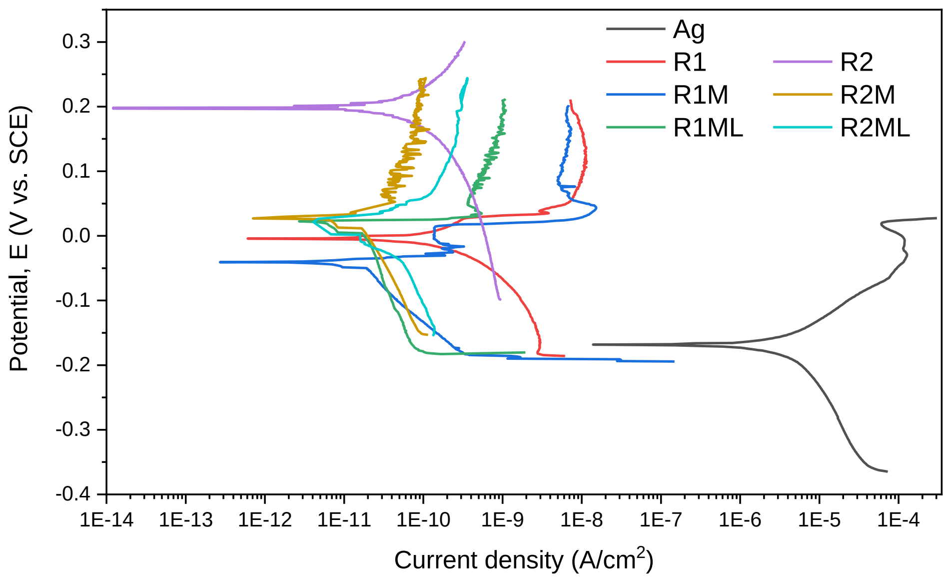


Fig. 13. Tafel plots of the investigated materials

Table 3

The main electrochemical parameters of the investigated samples

#	Sample	E_{corr} (mV)	i_{corr} (A/cm^2)
1	Ag	-167	4.98×10^{-6}
2	R1	-42	3.36×10^{-10}
3	R1M	-40	3.83×10^{-11}
4	R1ML	20	5.03×10^{-11}
5	R2	198	5.88×10^{-11}
6	R2M	27	2.20×10^{-11}
7	R2ML	22	4.83×10^{-11}

The electrochemical behavior can be evaluated on the basis of several characteristics, of which the most important ones are the corrosion potential (E_{corr}) and the current density of the corrosion (i_{corr}).

If we consider the corrosion potentials (E_{corr}), it is known that a more electropositive values, indicate a better electrochemical behavior, and thus an enhanced corrosion resistance. Comparing the values obtained in Tabel 3. of the experimental coated samples with silver samples, it can be observed that all the coatings have registered a more electropositive potential value, underlining that all the coatings improve the resistance of the substrate to corrosion. The most electropositive potentials were registered for the type 2 resins.

The electrochemical measurements showed that the most electropositive potential, and therefore the best electrochemical behavior, was obtained for the sample R2 (198 mV).

It is known that a smaller corrosion current density (i_{corr}) indicates a better resistance to corrosion. According to these criteria, it can be noted that the smallest corrosion current density value is the one obtained for the R2M sample (2.20×10^{-11} A/cm^2), followed by the value registered for the R1M sample (3.83×10^{-11} A/cm^2).

Nonetheless, it can be observed that all the coatings regardless of their nature lead to a considerable improvement of electrochemical behavior, as highlighted by the i_{corr} values, which have decrease by several orders of magnitudes. The addition of the mint extracts has led to a decrease of i_{corr} irrespective of the resin type, while the addition of the lavender extracts contributed to a smaller increase in the i_{corr} values, without exceeding the values registered in the case of bare resin-based coatings.

Analyzing the electrochemical parameters from the table presented above, it can be observed that all the coatings, regardless of their nature, have enhanced corrosion resistance of silver, highlighting the efficiency of the proposed coatings.

4. Conclusions

The obtained results presented potential for further studies, in order to increase the anticorrosion efficiency of different natural compounds incorporated in resins used traditionally for coating or adhesive purposes (Paraloid B44 and B72).

More than that, it was demonstrated that the incorporation of the essential oils increases the corrosion protection, without affecting the properties of the base copolymeric materials.

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