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Synergistic Inhibition Effect of Rare Earth in the Corrosion of the AA2024-T3 and CFRP in Galvanic Couple

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Inhibition effect of $LaN_3O_9.6H_2O$, 3-amino-1,2,4-triazole (ATA) and 5-chlorobenzotriazole (5-Cl-BTA) at various concentrations (0.5, 2, 4 and 6) was analyzed to observe the corrosion behavior of the AA2024 in galvanic couple with CFRP using zero resistance ammeter and electrochemical impedance spectroscopy (EIS). A solution of 0.05 M NaCl was used as electrolyte. Results have shown that the addition of $LaN_3O_9.6H_2O$ at different concentration decreased the current density up to 21 h of exposition at the aggressive media, with a trend of decrease trough the time. Moreover, modulus of impedance showed that the electron flow decreased in the presence of La3+, rising its maximum efficiency at 6mM with a value of 92%. Furthermore, 5-Cl-BTA presented its highest efficiency at 6mM with a value of 72%.

1. Introduction

Aluminium alloy AA2024-T3 is one of the longest used in the aerospace industry due to its low weight and corrosion resistance (Rodič and Milošev, 2016). However, when is used in contact with other materials as carbon fibre reinforced plastic (CFRP) the resistance against corrosion is affected in a negative way (Palani et al., 2014). On this sense, the chloride contained in the environment can accelerate the corrosion processes due to the galvanic corrosion. In fact, the AA2024-T3 alloy is rich in Cu particles that are more active against the aluminium matrix (Qafsaoui and Takenouti, 2010). A lot of efforts has been focused on the use of environmentally-friendly corrosion inhibitors as an alternative to reduce the toxicity and the negative effect over the environment which is generated by the use of some aggressive chemical compounds. such as chromates, (Bethencourt et al., 1998). On this way, rare earths such as lanthanide compounds have been proposed as a good alternative to increase the service life of different materials such as aluminium alloys. Some authors such as Aballe et al., found that a binary solution of $CeCl_3$ and $LaCl_3$ gave the highest protection against corrosion of one aluminium alloy (Aballe et al., 2001). Moreover, some lanthanide salts were tested to evaluated their protection degree in neutral solution (Bernal et al., 1995) founding that they offered a good resistance to corrosion processes. However, other organic compounds such as 1,2,4-triazole groups are used with various materials in diverse environments to evaluate their efficiency as corrosion inhibitors (Finšgar, 2013). As various studies have demonstrated, the AA2024-T3 has intermetallic particles that contain copper in their structure where some 1,2,4 triazole groups have shown a good efficiency due that its molecules are strongly adsorbed in sites with Cu contain, suppressing the anodic dissolution of the aluminium matrix (Sherif et al., 2007). In the present research, the lanthanide compound $LaN_3O_9.6H_2O$ has been used as corrosion inhibitor for the aluminium alloy 2024-T3 immersed in 0.05 of NaCl in galvanic couple with CFRP (carbon fiber reinforced plastic). However, with the aim to find the best compound to reduce the degree of metallic surface degradation some organic corrosion inhibitors were tested at different concentrations (mM). Also, some combinations of ATA, 5-Cl-BTA and $LaN_3O_9.6H_2O$ shown a positive synergistic effect against corrosion processes.

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2. Experimental

2.1 Materials

The composition of the AA2024-T3 is shown on the table 1. Samples of AA2024 were cut with an area of 2x2 cm with a thickness of 0.2 cm, before the test they were ground with emery paper 300, 600 and 1000 grit size and degreased with ethanol, washed with distilled water and finally dried with dry air. Samples of carbon fiber reinforces plastic (CFRP) were used for simulating the galvanic couple with the AA2024-T3 which were cut with an area of 2x2 cm, slightly ground with emery paper 600 with the aim to remove the coating over the exposed surface, for improving the conductivity of the CFRP in the electrochemical analysis silver paint color was applied.

Table 1: Nominal composition AA2024-T3 (%).

Element	Cu	Cr	Fe	Mg	Si	Ti	Zn	Other	Al
Concentration	3.8-4.9	0.1	0.5	0.3-0.9	0.5	0.15	0.25	0.15	Balance

2.2 Chemical compounds

A 0.05 M NaCl solution was used as blank test. Different inorganic and organic compounds (3-amino-1,2,4-triazole (ATA), 5-Chlorobenzotriazole (5-Cl-BTA), Lanthanum nitrate hexahydrate ($LaN_3O_9.6H_2O$)) were used as corrosion inhibitors and were added to the electrolyte at concentrations of 0.5, 1, 2, 4 and 6 mM before each electrochemical test.

2.3 Electrochemical technique

A four-electrode electrochemical cell was used for the electrochemical analysis. A Ag/AgCl electrode was used as the reference electrode, a platinum wire was used as the auxiliary electrode. A sample of AA2024-T3 with an exposed area of 0.5 cm^2 was used as working electrode 1 and a plate of CFRP with 0.5 cm^2 of exposed area as working electrode 2. Different arrangements were carried out in the electrochemical cell according to the technique to be used as follows.

ZRA technique was carried out during 21 h in a single cell. Two Ag/AgCl electrodes were used as reference electrode to measure the OCP parameters before the galvanic couple was closed by switcher and after switch off. The AA2024-T3 was used as WE1 and the CFRP as WE2, with an exposed area of 0.5 cm^2 the positive values of the current suggest that the AA2024-T3 is corroded. Electrochemical Impedance Spectroscopy was conducted in a conventional cell, which consists in the following arrangement: Ag/AgCl electrode was used as reference electrode (RE); a platinum wire like Auxiliary Electrode (AE); AA2024 alloy and CFRP plates with an exposed area of 0.5 cm^2 as working electrodes, W1 and W2, respectively. EIS was done in couple after zero resistance ammeter technique, by applying a sinusoidal perturbation of 10 mV RMS amplitude and a frequency sweep from 0.01 Hz to 30 kHz, current and potential versus time were recorded during 21 h.

3. Results and discussions

3.1 Zero resistance ammeter

Figure 1 showed the galvanic current and potential evolution for the AA2024 and CFRP up to 21 h, immersed in 0.05 M. One test was done in 0.05 M NaCl solution in the absence of inhibitors as a reference test of its behavior in the absence of protection conditions. Different concentrations of ATA, 5-Cl-BTA and $LaN_3O_9.6H_2O$ were used to find the optimal volume of inhibitor to be added at the solution without compromising the protection. Figure 1 a) shows that, when the corrosion inhibitor ATA was added, the galvanic current decreased from 0.032 mA/cm^2 for the blank to 0.025, 0.021, 0,028 and 0,024 mA/cm^2 for ATA at the concentration of 0,05, 2, 4 and 6 mM, respectively. This behavior could be attributed to the formation of a complex with the metallic surface via adsorption. However, a slightly increase in the current was observed at the end of the test. Moreover, the galvanic potential is more active due that present a trend to be more negative through the time, forming a barrier that slowdown the reaction rate of the cathodic processes. This is due to the formation of a protective layer over the metal surface as well as by the adsorption of the ATA molecules. These conditions implied a stable potential over the time. Similar effect was observed for 5-Cl-BTA (Figure 1 b) where, the galvanic current decreased from 0.032 mA/cm^2 for the blank to 0.01, 0.009, 0.006 and 0.007 mA/cm^2 when 5-Cl-BTA concentrations were 0.5, 2, 4 and 6 mM, respectively. In comparison with ATA, 5-Cl-BTA showed lower galvanic current values getting the best behavior at the concentration of 4 and 6 mM. Furthermore, the potential presented a more active trend due to the formation of a protective oxide layer over the metal surface and by the adsorption of the BTA on the intermetallic sites of the AA204-T3 that blocks the flow electrons between the AA2024-T3 and CFRP. As for the lanthanum nitrate hexahydrates, Figure 1 c), they showed the lowest values of galvanic current, under corrosion conditions, with respect to ATA and 5-Cl-BTA. This was due to the formation of a diffusion barrier of complex with the intermetallic particles of the AA2024 that slowed down the corrosion processes in the active zones, decreased the flow electrons in the metal surface, as well as, its interaction in galvanic couple with CFRP.

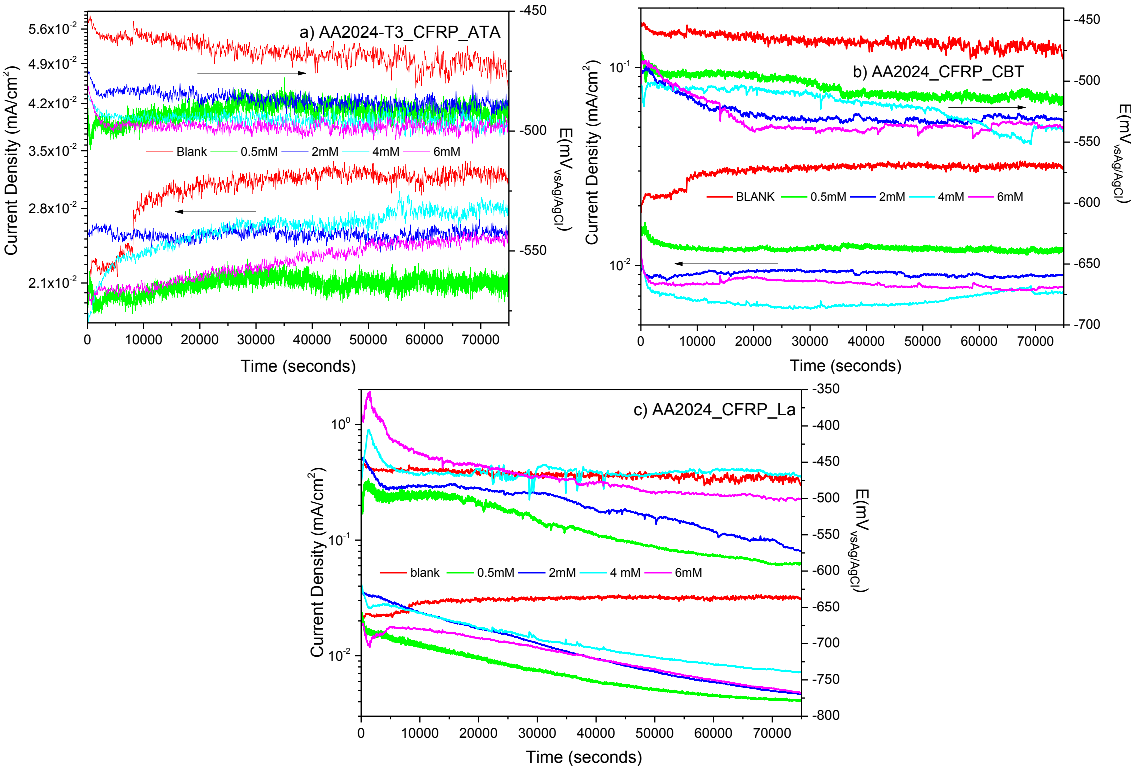

Figure 1: ZRA measurements evolution for the AA2024 and CFRP in galvanic couple immersed up to 21 h., in 0,05 M NaCl in absence and presence of: a) ATA, b) 5-Cl-BTA and $LaN_3O_9.6H_2O$.

3.2 EIS Measurements

Figure 2 shows the performance of ATA, 5-Cl-BTA and $LaN_3O_9.6H_2O$ when these compounds were added into the electrolyte (0.05 M NaCl) for improving the corrosion resistance against the galvanic couple. This effect took place on the metal surface of AA2024-T3 when it was in electrical contact with CFRP. Figure 2 a) shows the modules of impedance that was measured with EIS technique. It is evident that it does not exist an important advantage in the impedance values when ATA was present in the electrolyte. However, when 5-Cl-BTA was added in the aggressive media the impedance values increased in comparison with the inhibitor-free test. This is due to the fact that these compounds form complex with the intermetallic compounds thus blocking the active areas on the metallic part and thus avoiding the electrons flow with CFRP. As is known, the benzotriazole derivate could be adsorbed on the copper surface, on this sense the reduction of the galvanic effect that take place in the intermetallic areas against the matrix could be contribute to reduce the galvanic effect of the AA2024-T3 in couple with the CFRP, since was demonstrated with the ZRA test the current presented a trend to decrease in function with inhibitor concentration, generating a slower flow of electrons between intermetallic, aluminium matrix and CFRP (Sentence too long and not clear. Please revise). When $LaN_3O_9.6H_2O$ was evaluated (Figure 2 c)), the impedance values achieved an 89% efficiency in almost all the concentrations, due to the La3+ works to form hydroxide precipitates on the intermetallic particles, thus delaying the galvanic effect in the active areas over the metal surface.

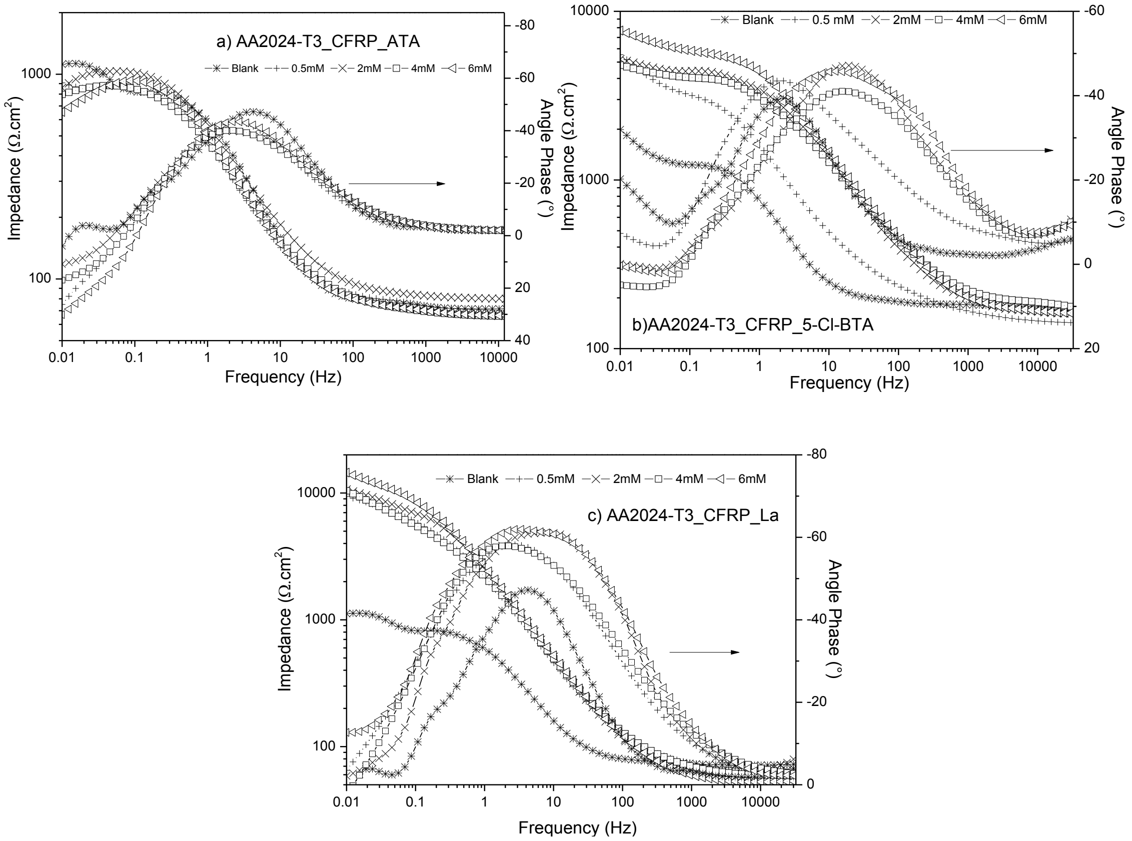

Figure 2: Modules impedance and angle phase plots for the AA2024 and CFRP in galvanic couple immersed in 0.05 M NaCl in absence and presence of: a) ATA, b) 5-Cl-BTA and $LaN_3O_9.6H_2O$.

Three equivalent circuits are proposed to describe the metal-electrolyte surface (Figure 3). Where R_s is the solution resistance, W_s is a finite diffusion process, R_{ct} the resistance of charge transfer, R_{ox} the resistance of the oxide products, CPE_{dl}, and CPE_{ox} their admittances, respectively. The parameters used to fit EIS data for each inhibitor are given in Table 3, 4 and 5. It is evident, based on the efficiency of each inhibitor, that $LaN_3O_9.6H_2O$ gave the best protection for the AA2024-T3 in galvanic couple with CFRP. A concentration of 6mM resulted in a 92% efficiency for $LaN_3O_9.6H_2O$, followed by 5-Cl-BTA whose maximum efficiency was 76% at 6mM. In contrast, when ATA was added into the aggressive media, the current density has trend to increase after up 21 h accelerating the corrosion on the metallic surface, meaning that the protective layer that was formed over the metal surface is missed, accelerating the corrosion processes. The efficiency was calculated by using the following expression:

$$IE\%=\left(1-\frac{R_p^0}{Rp_p^{inh}}\right) \qquad 1)$$

Where R_p^0 is the polarization resistance in the absence of inhibitor and R_p^{inh} corresponds to the polarization resistance in the presence of inhibitor.

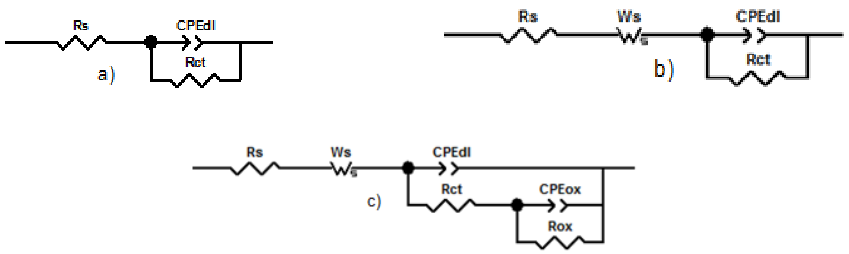

Figure 3: Equivalent circuits for fitting the EIS data of the AA2024-T3 and CFRP in galvanic couple immersed in 0,05 M NaCl in absence and presence of: a) ATA, b) 5-Cl-BTA and c) $LaN_3O_9.6H_2O$.

Based on the results, a combination of La, ATA and 5-Cl-BTA was tested. Figure 4 shows that the combination of $LaN_3O_9.6H_2O$ +ATA at 2mM gave an increase on the impedance value rising a resistance of 6.12e3 $\Omega.cm^2$. Moreover, the combination of $LaN_3O_9.6H_2O$+5-Cl-BTA increased the impedance values at 1.93 e^4 $\Omega.cm^2$. This indicates that a combination between organic and inorganic compounds generates a positive synergistic effect over the metal surface, phenomenal that could be attribute at the formation of new complexes over the metallic surface.

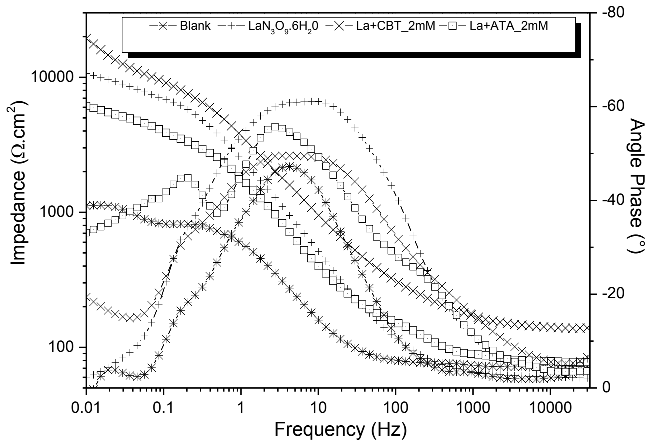

Figure 4: Modules impedance and angle phase plots for the AA2024 and CFRP in galvanic couple with CFRP immersed in 0,05 M NaCl in absence and presence of combination of $LaN_3O_9.6H_2O$, ATA and 5-Cl-BTA at a concentration of 2mM.

Table 2: Impedance parameter for AA2024-T3/CFRP in galvanic couple immersed in 0.05 M NaCl solution with and without BTA. ATA.

C_{inh} (mM)	Rs ($\Omega.cm^2$)	CPE_{dl} $Y0(\Omega^{-1}s^n)$	n	R_{ct} ($\Omega.cm^2$)	Ws (mS $s^{1/2}/cm^2$)	R_p ($\Omega.cm^2$)	E%
Blank	72.07	2.06 e^{-4}	0.83	9.30 e^2	------------	1.00 e^3	---
0.5	69.97	5.57 e^{-4}	0.99	2.40 e^2	6.15 e^2	9.25 e^2	0
2	79.34	3.25 e^{-4}	0.74	7.09 e^2	3.07 e^2	1.09 e^3	9
4	64.94	6.03 e^{-4}	0.85	3.21 e^2	5.28 e^2	9.14 e^2	0
6	65.85	4.50e^{-4}	0.94	3.14 e^2	5.28 e^2	9.31 e^2	0

Table 3: Impedance parameter for AA2024-T3/CFRP in galvanic couple immersed in 0.05 M NaCl solution with and without 5-Cl-BTA.

Cinh (mM)	Rs ($\Omega.cm^2$)	CPEdl $Y0(\Omega^{-1}s^n)$	n	R_{ct} ($\Omega.cm^2$)	R_{ox} ($\Omega.cm^2$)	CPE_{ox} $Y0(\Omega^{-1}s^n)$	n	Ws (mS $s^{1/2}/cm^2$)	R_p ($\Omega.cm^2$)	E%
Blank	72.07	2.06 e^{-4}	0.83	9.30 e^2	---------	----------	------	----------	1.00 e^3	-------
0.5	66.93	2.11 e^{-4}	0.96	5.15 e^2	---------	----------	------	7.93 e^2	1.37 e^3	27
2	65.32	5.29 e^{-5}	0.82	1.05 e^3	8.10 e^2	3.40 e^{-5}	0.89	1.97 e^3	3.91 e^3	74
4	76.40	8.08 e^{-5}	0.84	2.06 e^3	---------	----------	------	1.19 e^3	3.32 e^3	70
6	71.28	1.34 e^{-5}	0.84	1.35 e^2	3.81 e^3	3.64 e^{-5}	0.77	1.39 e^2	4.16 e^3	76

Table 4: Impedance parameter for AA2024-T3/CFRP in galvanic couple immersed in 0.05 M NaCl solution with and without $LaN_3O_9.6H_2O$.

Cinh (mM)	Rs ($\Omega.cm^2$)	CPEdl $Y0(\Omega^{-1}s^n)$	n	R_{ct} ($\Omega.cm^2$)	R_{ox} ($\Omega.cm^2$)	CPE_{ox} $Y0(\Omega^{-1}s^n)$	n	Ws (mS $s^{1/2}/cm^2$)	R_p ($\Omega.cm^2$)	E%
Blank	72.07	2.06 e^{-4}	0.83	9.30 e^2	---------	----------	------	----------	1.00 e^3	-------
0.5	64.9	1.27 e^{-4}	0.72	9.39 e^3	---------	----------	------	6.47	9.46 e^3	89
2	60.02	7.63 e^{-5}	0.78	8.31 e^3	---------	----------	0.89	5.61 e^2	8.93 e^3	89
4	57.11	1.13 e^{-4}	0.68	6.17 e^3	---------	----------	------	1.63 e^3	7.86 e^3	87
6	51.26	9.00 e^{-5}	0.78	1.04 e^4	3.81 e^3	3.64 e^{-5}	0.77	1.48 e^3	1.19 e^4	92

4. Conclusions

Analysis of three different organic and inorganic compounds were evaluated using electrochemical techniques such as zero resistance ammeter and electrochemical impedance spectroscopy (EIS). Highest efficiency of inhibition was obtained with Lanthanum nitrate hexahydrate rising its maximum value at 6mM of inhibitor. Moreover, 5-Cl-BTA showed an efficiency around 70% at high concentration (2, 4 and 6 mM). However, when ATA was present in the electrolyte, the resistance decreased due to the loss of the protective layer that was formed over the metal part. (Sentence too long and not perfectly clear that should be rewritten).
Three equivalent circuits were proposed to analyze the EIS data, with the aim to determine the parameters obtained from each tested inhibitor of corrosion. A diffusion process was observed for all of them which could be attributed to the oxygen reduction processes. Since it was explained, some complexes could be formed over the metallic surface by the BTA derivate as well as for La3+ allowing improve the protection against corrosion processes. However, the possible mechanism that governs the corrosion process is the charge transfer at low frequencies. A positive effect was observed when the lanthanum nitrate hexahydrate was combined with ATA and 5-Cl-BTA at 2mM increasing the corrosion resistance of the metal surface.

Acknowledgements

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