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INHIBITIVE PROPERTIES OF *Garcinia kola (GK)* IN ALKALINE MEDIUM OF ALUMINUM ALLOY (AA4007)

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Abstract

The application of corrosion inhibitors is a more effective strategy tomitigate the impacts of aluminum corrosion. Phytochemical analysis, gravimetric technique, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used to investigate the inhibitory potentials of Garcinia kola aqueous leave extract for the corrosion of aluminum alloy (AA4007) in 1 M NAOH. The highest inhibition efficiency obtained was 98.5%. The result from the analyses collaborated that the leaf extract is a good inhibitor. The Langmuir, Freundlich and Temkin isotherm is in agreement that the inhibitor is physisorption. Garcinia kola showed high corrosion inhibition efficiency on aluminum alloy.

1.0 INTRODUCTION

Industries can reap significant benefits from the use of aluminum (Al) and its alloys due to a number of unique properties of the metal. However, it is known that corrosion is a common problem for many companies who employ the metal [1]. Using cathodic/anodic protection procedures, coating, encasing the metal in thin film oxide to increase passivity, and other methods are a few of the causes [2]. Applying corrosion inhibitors is a more effective strategy to postpone the impacts of aluminum corrosion, according to findings from a variety of literature types [3]. This is especially important in an aggressive media environment. Many documented cases wherein some corrosion inhibitors have been certified to be extremely effective for the protection of aluminum against corrosion have been connected to the persistent challenge of the environmental toxicity of most corrosion inhibitors, such as inorganic compounds [4]. Corrosion inhibitors must therefore be carefully selected to satisfy the following requirements: Easily accessible [5], reasonably priced [6], non-toxic or environmentally friendly [7], sustainable in the long run [8], and enhanced efficiency.

Given the aforementioned factors, corrosion researchers have designated certain chemicals that satisfy the specified parameters as "green corrosion inhibitors" [9]. Research has revealed that the majority of the key chemical classes that satisfy the criteria for green corrosion inhibition originate from natural sources, including plant and animal extracts

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[10]. Nevertheless, some of them have poor efficiency and make it difficult to identify the mechanism of inhibition since they are often variables with inhibition efficiency that come from a synergistic combination of multiple extract components[7]. As a result, a plan for advancing toward the objective of discovering or producing green corrosion inhibitors with remarkable effectiveness requires continual study and record-keeping. Determining the degree to which Gk leaf extract reduces corrosion is the aim of this investigation.

As stated in [11]. The extract of *Gk* leaf showed an increase in inhibitory efficacy from 67.21 to 88.19% with a temperature increase in the HCl acidic medium. [12] states that when *Gk* leaf extract is present, the rate at which aluminum alloy corrodes in 1 MHCl increases with temperature. The greatest rates of corrosion for the blank specimen were 67.76 mm/yr at 303 K and 127.09 mm/yr at 318 K. Furthermore, [12] found that the concentration of organic inhibitor increases the efficacy of inhibition. The lowest inhibition efficacy was found at 88.35% at the lowest concentration and 318 K, whilst the highest inhibition efficiency of 99.09% was attained. The ability of *Irvingia gabonensis* leaf extract to inhibit growth rises with plant extract concentration [1]. Thus, because the inhibitor's surface covering increases with concentration, [6] states that the leaf extract of *irvingia gabonensis* inhibits the adsorption of aluminum in HCl media. At concentrations of 0.2 and 1.0 g/L, the extraction efficiencies were 78% and 91%, respectively.

2.0 METHODOLOGY

2.1 Aqueous Extraction

Cold maceration was used to extract a known quantity (50g) of Gk leaves together with 450ml of ethanol. After that, it was filtered using Whatmann No. 4 filter paper after first passing through muslin cloth. After the ethanol was evaporated in a water bath maintained at 45 degrees, it was put into a sterile sample bottle.

2.2 Phytochemical Testing

The organic extracts underwent phytochemical analysis in accordance with the basic protocol of [13]. To find out if the sample included secondary plant components such alkaloids, tannins, flavonoids, saponins, phenols, and reducing sugar, basic phytochemical screening was performed using straightforward chemical tests. Unless otherwise noted, the research methodology employed in this study was that described in [13].

2.3 Gravimetric Method

Aluminum coupons were fully submerged in 100 milliliters of the alkaline environment test solution (1M NaOH) at 303 K and 318 K with and without the inhibitor (Gk) for the mass loss measurements. The metal samples were taken out of the test solution every two hours for a duration of ten hours. After rinsing the coupons with distilled water to get rid of the inhibitor solution, ethanol and acetone were used to dry them and quench the reaction. The mass loss was calculated as the difference between the specimens' pre- and post-immersion weights, as measured with an electronic analytical balance (Metlar Terado) that had a 0.001g sensitivity.

To ensure the accuracy of the findings, the tests were conducted again, and the mass loss's mean value was given. Corrosion rate was obtained using the mass loss information. The formulae below were used to obtain the inhibitory efficiency (%) based on weight loss:

$$\Delta w = (w_1 - w_2) X\, 1000 \ (mg) \quad (1)$$

$$C.R. = \frac{K\Delta w}{APT} \quad (2)$$

Where, C. R. = corrosion rate, Δw = change in weight (mg), A = cross sectional area of aluminum (cm^2), P = density of aluminum, (g/cm^3), K = 87.6 (corrosion constant), T = time of study (hrs), w_A and w_B are the initial and final weights of aluminum coupon.

$$\text{Inhibition efficiency \%} = \frac{W_B - W_A}{W_B} X \frac{100}{1} \quad (3)$$

Where w_B and w_A are weight loss in the absence and presence of the inhibitor.

The degree of surface coverage (θ) was calculated from the weight loss measurements using Equation (4):

Surface coverage,

$$\theta = \frac{W_B - W_A}{W_B} \quad (4)$$

Where w_B and w_A are the weight loss in the absence and presence of the inhibitor.

In order to obtain weight loss at 303 K and 318 K, the effects of temperature on the inhibitor's ability to inhibit was investigated.

The Langmuir adsorption isotherm was determined by using Equation 5:

$$C/\theta = 1/Kads + C \quad (5)$$

Where, *C* represents *Gk* concentration, is the surface coverage, and *K*ads is the equilibrium absorptive constant [14].

The Langmuir adsorption equilibrium constant (kads) can be applied to evaluate the free energy associated with the adsorption process, based on the Gibb-Helmholtz equation (Equation 6) [15]

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$$\Delta Gads = -RT\ ln(Kads \times 55.5) \quad (6)$$

Where T represents absolute temperature and R the gas constant (8.314 kJ/mol). The quantity of water in solution, expressed in mol/L, is 55.5. At two distinct concentrations of *Gk* extracts, 303 K and 318 K, the adsorption parameter (*K*ads) will be computed from Langmuir isotherms.

2.4 Thermodynamic Studies

Knowing the thermodynamic factors that control the adsorption process allows one to predict the manner of adsorption of inhibitors, which can be either physio- or chemisorption. A variant of the Arrhenius Equation (7) was used to determine the activation energies Ea for the corrosion process in the presence and absence of *Gk* leaf extract.

$$\ln W = \ln A + \frac{-E_a}{2.303RT} \quad (7)$$

Where, W represents corrosion rate, A is the frequency, factor R is the gas constant and Ea is the activation energy which can be obtained when lnW is plotted against the inverse of absolute temperature 1/T. The activation energy becomes;

$$E_{a=} -\text{slope} X\ 2.303 X R \quad (8)$$

Where, R = 8.314; the real gas constant.

The Fruendlich and Temkin isotherm are consistent with the expression shown by Equations 9 and 10 [16]

$$\ln(\theta) = \ln K_{ads} + n\ln(C) \quad (9)$$

$$\theta = \frac{-lnK_{ads}}{2a} - \frac{lnC}{2a} \quad (10)$$

Where, a is the attractive parameter.

2.5 Electrochemical Impedance Spectroscopy

Impedance analysis is critical to electrochemical systems [17]. Nyquist plots were created for an Al electrode immersed in 1 M HCl in the protected medium at 1000 mg/L and 100 mg/L, respectively, and the unprotected medium. This study considers the following factors: (IE%), double layer capacitance (cdl), and Rct. The resistance of charge transfer (Rct) and the double layer capacitance (cdl), which are both characterized as follows [17], are the primary factors obtained from the analysis of the Nyquist spectra.

$$Cdl = 1/(2\pi fmax\ Rct) \quad (11)$$

Where, fmax is the rate at which the imaginary part of the impedance is elevated-Zim (max).

3.0 RESULTS AND DISCUSSION

Table 1: Qualitative phytochemical screening of *Gk* extract

Phytochemical	*Gk*
Saponin	++
Alkaloids	+++
Tannins	++
Flavonoid	+++
Phenol	++
Reducing Sugar	+++

-Absent, +Mild, ++Moderate, +++Abundance

3.1 Phytochemical Analysis

Table 1 shows that the extracts had moderate levels of tannins (++), phenolics (++), and saponins (++), and high levels of alkaloids (++), flavonoids (++), and reducing sugar (++). The leaf extract's presence of heteroatoms with numerous bonds or those with high electron densities such as phosphorus, sulphur, nitrogen, or oxygen justifies the Gk extracts' ability to prevent corrosion. This is in line with Kumar [18], who found that dried leaves are the primary source of polyphenolic compounds like flavonoids and phenolic acids in considerable quantities.

3.2 Mass Loss

Figure 1 showed how quickly the aluminum alloy lost weight when Gk extract was not present (blank). Nevertheless, the rise in mass loss for different inhibitor concentrations was slowed down when Gk extract was introduced. The corrosion rate also decreases due to reduction in mass loss, suggesting that Gk is a potent inhibitor.

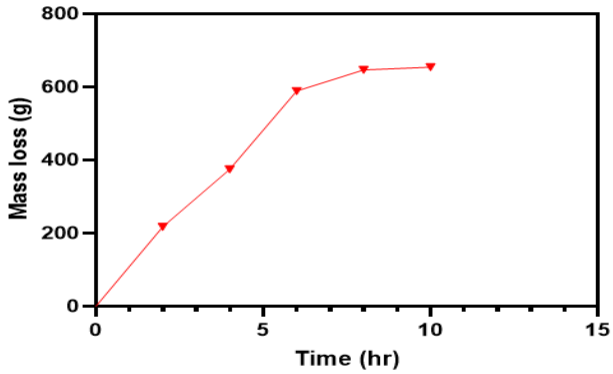

Figure 1: Mass loss values of Aluminum in 1.0 M NaOH without *Gk* against time (hr)

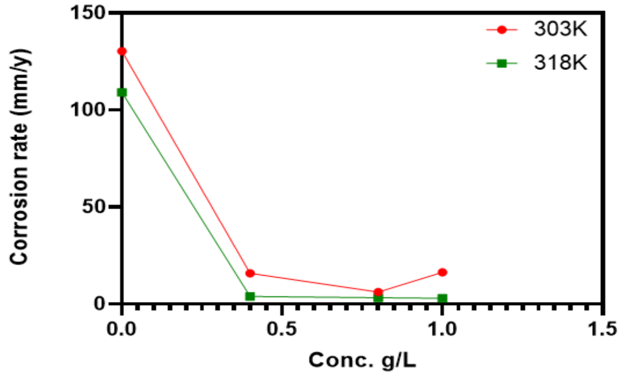

Figure 2: Corrosion rate variation of aluminum alloy in 1.0M NaOH at different temperatures

3.3 Corrosion Rate

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The data presented in Figure 2 indicates that, on average, the corrosion rate decreases with exposure duration, indicating the potency of Gk as an inhibitor. It is also noted that, in most cases, the corrosion rate increases; however, after the second hour, the corrosion rate gradually decreased, showing that the inhibitor becomes active as a result of adsorption between the inhibitor's molecules and the aluminum alloy's molecules. These findings are in line with the findings reported by [19]. The plot indicates that the rate of corrosion decreases as both inhibitor concentrations and temperature rise.

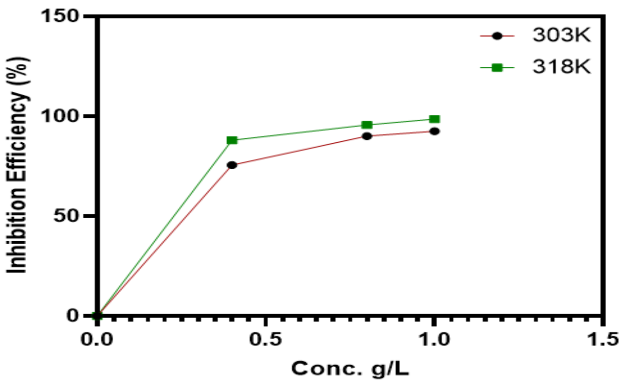

Figure 3: Inhibition Efficiency of aluminum alloy in 1.0M NaOH at different temperatures

3.4 Inhibition Efficiency

Figure 3 makes it evident that the inhibitory efficacy increases with exposure duration. Moreover, the inhibitory efficacy rises with increasing Gk leaf extract concentrations. [20] came to a similar conclusion. The greatest measured inhibition efficiencies were 98.5% in 318K and 92.5% in 303K, according to plotting, which shows that inhibition efficiency increases with temperature. These outcomes agree with those reported in [12]. This could imply that molecules of Gk leaf are adsorbed at the aluminum/NaOH interface [20].

3.5 Thermodynamic Isotherm

3.5.1 Langmuir isotherm

Plotting c/θ against C for Gk yields a straight line, as seen in Figure 4, and all regression coefficients (R2) for 303k and 318k are extremely near to unity (one), indicating that the adsorption of Gk's organic molecules on the aluminum surface is governed by Langmuir adsorption. Table 2 further demonstrates that all values of the slopes derived from 303k and 318k are extremely near to unity; the slopes' divergence from unity is frequently taken to mean that the adsorption species occupy, roughly speaking, a typical adsorption site at the metal [21]. As revealed in Table 2, the adsorption constant (Kads) is derived from the plots by taking the reciprocal of the intercept values. This number can be related to Gibb's free energy of adsorption, or ΔGads, by equation (6). Table 2 presents the ΔGads values for 303k and 318k of Gk in 1M NaOH, as determined by the Langmuir parameters. Positive Gibb's free energy values imply that Gk is not adsorbed on the aluminum surface naturally; rather, the adsorption reaction requires the supply of external energy. Less than 20 kJ/mol can be found in Table 2's Gibb's free energy estimates at temperature of 303 K and 318 K, suggesting that Gk adsorption in an alkaline solution is essentially physical in nature. The electrostatic interactions between charged molecules and molecules near metallic surfaces cause the inhibition [22].

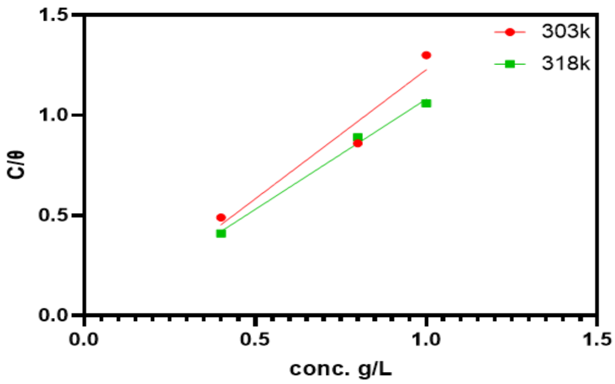

Figure 4: Langmuir isotherm for adsorption of Gk on aluminum alloy in 1.0M NaOH

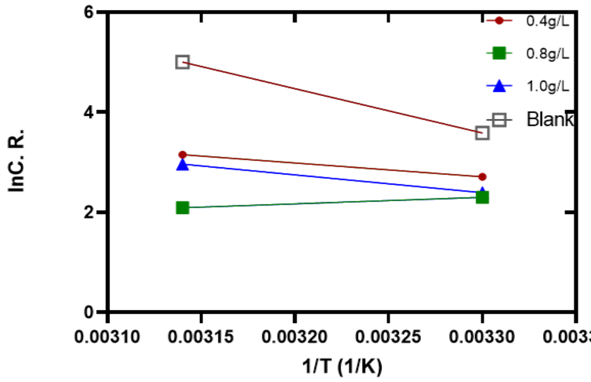

Figure 5: Plot of ln C.R. against 1/T for Aluminum alloy corrosion in 1.0M NaOH (Blank) and inhibited solutions at various concentrations of *Gk*

3.6 Activation Energy Ea

Table 3 lists the estimated activation energy values for Gk. The graphs in Figure 5 were used to determine the values. The activation energy was obtained from the plot slopes using equation (7). It was observed that the activation energy values of the sample containing the organic inhibitor (Gk) were lower than those of the blank sample. This suggests that the inhibitor lowers activation energy.

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3.7 Temkin Isotherm

Equation (10) was used to generate the Temkin parameters and the temperature values for 303k and 318k, respectively, that are displayed in Table 2. The Gk plots of θ against logC were shown in Figures 4.18a–4.18e. The negative outcomes indicated that the adsorption is physisorption at both 303K and 318K temperatures, as shown by the Gibb's free energy values from Table 2. The attractive parameter (a) values at 303K and 318K temperatures are positive, suggesting that there is attraction between the adsorption layers.

Table 2: Fitted isotherms parameters for the adsorption of ethanol extract of *Gk* leaf in 1.0M NaOH

ISOTHERM	PARAMETER	303K VALUE	318K
Langmuir			
	Slope	1.289	1.100
	Intercept	-0.06214	-0.02000
	R^2	0.9435	0.9938
	Kads	16.093	-50.000
	ΔGads	-15.42	17.99
Freundlich			
	Slope	-0.1499	-0.1184
	Intercept	-0.2010	-0.1293
	R^2	0.8830	0.9992
	Kads	-4.975	-7.734
	ΔGads	12.76	13.759
	n	-6.671	-8.467
Temkin			
	Intercept		
	a	0.75	0.29
	ΔGads	-7.97	-8.99
	Kads	0.426	0.638
	R^2	0.2679	0.1339

Table 3: Activation energy value of *Gk* in 1.0M NaOH for aluminum alloy

BLANK	0.4g/L	0.8g/L	1.0g/L
169.57	53.13	-25.01	68.34

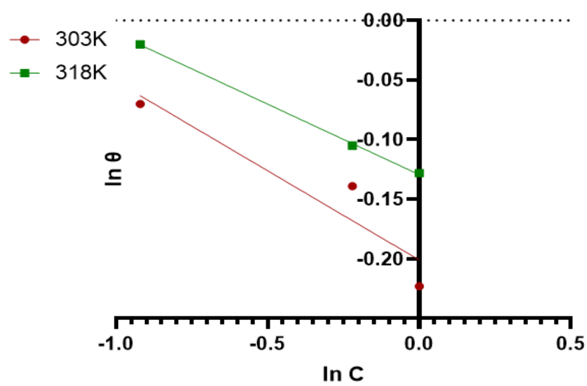

Figure 6: Freudlich isotherm for adsorption of *Gk* on aluminum alloy in 1.0M NaOH

3.8 Freundlich Isotherm

The experimental data was fitted into the Freunlich isotherm using Equation 9 and values obtained from the plot as observed in Figure 6 and recorded in Table 2. Since the regression coefficient of the plot for the temperatures of 303K and 318K was almost equal to unity, the result indicated that the experimental data fit into the Freunlich isotherm.

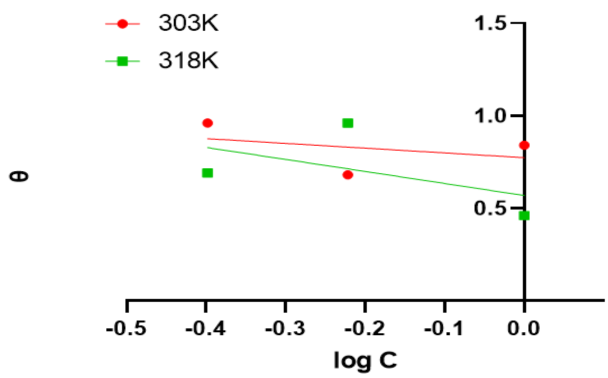

Figure 7: Temkin isotherm for adsorption of *Gk* on aluminum alloy in 1.0M NaOH

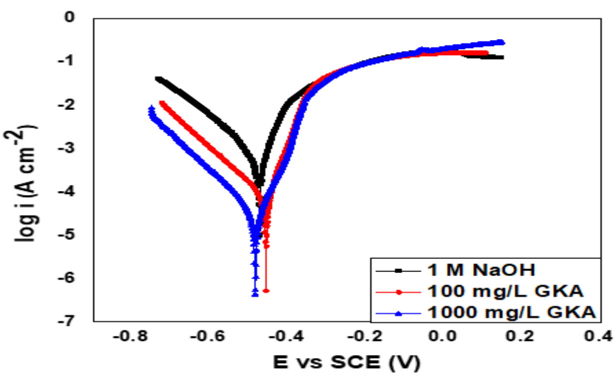

Figure 8: Potentiodynamic polarization (PDP) plots of Aluminum in the presence of *Gk* in 1 M NaOH environment

3.9 Potentiodynamic Polarization

When Gk was added to 1M NaOH, Figure 8 shows how the tafel polarization curves shifted toward greater negative potentials when compared with the blank system. This change implies that the cathodic inhibitory actions of the inhibitors are more pronounced [2]. The result presented in Figure 8 revealed that there are less than 85 mV in difference in Ecorr values between inhibited and uninhibited systems [1]. This difference for Gk is 21.7 mV, indicating that it is a mixed-type inhibitor with a predominant inhibitory effect on cathodic processes. The predicted inhibitory efficiency values and the gravimetric study results accord well, indicating that the Gk content enhanced ηPDP. It was observed that the greatest inhibitory efficacy was reached at 79.4%.As the concentration of inhibitor rises, the current density of corrosion or icorr (µA/cm2),

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decreases. The blank sample had the highest corrosion current density measurement, 147.2.

3.10 Electrochemical Impedance Spectroscopy (EIS) for *Gk* in 1M NaOH

The Nyquist plots from the EIS investigation, as revealed in Figure 9, indicated that the radius of the semicircle grew as the concentration of the Gk inhibitors increased. The roughness of the metallic surface and other defects cause the EIS spectra to be faulty semicircles with a diffusion tail that exhibit frequency scattering, according to [23]. The result that Rct (Ωcm2) values increase with inhibitor concentration could be explained by the inhibitors' molecules covering a larger surface area on aluminum metal [14]. The features of the Nyquist plots demonstrate that inhibition effectiveness improved as the inhibitor's concentration increased in comparison to the blank, with the maximum inhibition efficiency of 76.4% occurring at the greatest concentration.

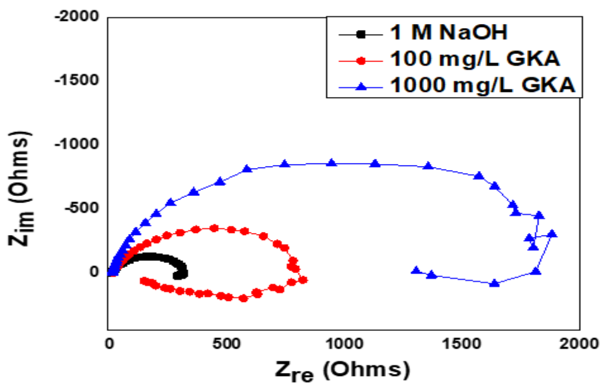

Figure 9: Electrochemical impedance spectra plots of Aluminum with *Gk* in 1 M NaOH environment

4.0 CONCLUSION

It was observed that the Gk leaf extract has the active ingredients (Phytochemicals), in various proportions, making it a potent green inhibitor. The gravimetric analysis indicates that the corrosion rate rises with exposure time; in contrast, the corrosion rate gradually falls with exposure time when the inhibitor is present. This means that the molecules of the Gk inhibitor adsorbed to the metal and attached to the aluminum surface, obstructing the corrosion sites.The greatest inhibitory efficacy of 98.5% was reached in 318K. Freundlich and Temkin noted that physisorption was responsible for the Gk adsorption on aluminum alloy, which followed the Langmuir adsorption isotherm. The findings of the EIS investigation clearly showed that the inhibition efficiency increases with increasing inhibitor concentrations.

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